NOVEL INTEGRATED DESIGN TECHNIQUES FOR BIOREFINERIES

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ABSTRACT

Utilisation of biomass is identified as one of the promising solutions to reduce society's dependence on fossil fuels and mitigate climate change caused by the exploitation of fossil fuels. By using the concept of biorefinery, biomass can be converted into value-added products such as biofuels, biochemical products and biomaterials in a greener and sustainable way. To enhance the efficiency of biorefinery, the concept of integrated biorefinery which focuses on the integration of various biomass conversion technologies is utilised. To date, various biomass conversion pathways are available to convert biomass into a wide range of products. Due to the substantial amount of potential products and conversion technologies, determining of chemical products and processing routes in an integrated biorefinery have become more challenging. Hence, there is a need for a methodology capable of evaluating the integrated process in order to identify the optimal products as well as the optimal conversion pathways that produce the identified products.

This thesis presents a novel approach which integrates process with product design techniques for integrated biorefineries. In the proposed approach, integration between synthesis of integrated biorefinery and computer-aided molecular design (CAMD) techniques is presented. By using CAMD techniques, optimal chemical product in terms of target properties which fulfils the required product needs is designed. On the other hand, in order to identify the conversion pathways that produce the identified optimal chemical product in an integrated biorefinery, chemical reaction pathway map (CRPM) and superstructural mathematical optimisation approach have been utilised. Furthermore, this thesis also presents various chemical product design approaches. In order to solve chemical design problems where multiple product needs are required to be considered and optimised, a novel multi-objective optimisation approach for chemical product design has been presented. By using fuzzy optimisation approach, the developed multi-objective optimisation approach identifies optimal chemical product based on multiple product properties. In addition, fuzzy optimisation approach has been further extended to address chemical product design problems where the accuracy of property prediction model is taken into account. A robust chemical product design approach is developed to design optimal chemical products with consideration of accuracy of property prediction model. Furthermore, together with CAMD techniques and superstructural mathematical optimisation approach, the developed multi-objective optimisation approach has been utilised for the design of mixtures in an integrated biorefinery. For this purpose, a systematic optimisation approach has been developed to identify optimal mixture based on multiple desired product needs as well as the optimal conversion pathways that convert biomass into the optimal mixture. Finally, possible extensions and future opportunities for the realm of the research work have been highlighted in the later part of this thesis.

LIST OF PUBLICATIONS

Refereed journals

Ng, L. Y., Chemmangattuvalappil, N. G., & Ng, D. K. S. (2014). A multiobjective optimization based approach for optimal chemical product design, *Industrial & Engineering Chemistry Research*, 53, 44, 17429 – 17444, DOI: 10.1021/ie502906a

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Ng, L. Y., Andiappan, V., Chemmangattuvalappil, N. G., & Ng, D. K. S. (2015). Novel methodology for the synthesis of optimal biochemicals in integrated biorefineries via inverse design techniques, *Industrial & Engineering Chemistry Research*, DOI: 10.1021/acs.iecr.5b00217 (in press)

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Abbreviations

AAE	Average Absolute Error
ARE	Average Relative Error
BB	Branch and Bound
CAFD	Computer-Aided Flow Sheet Design
CAMD	Computer-Aided Molecular Design
CAMPD	Computer-Aided Molecular and Process Design
CoMT	Continuous-Molecular Targeting
CRPM	Chemical Reaction Pathway Map
CPU	Central Processing Unit
CR	Certain Region
EFB	Empty Fruit Bunch
EGA	Efficient Genetic Algorithm
FT	Fischer-Tropsch
GA	Genetic Algorithm
GC	Group Contribution

GHG	Greenhouse Gas
GWP	Global Warming Potential
HEN	Heat Exchanger Network
HMF	Hydroxymethylfurfural
HSGA	Hammersley Stochastic Genetic Algorithm
HSTA	Hammersley Stochastic Annealing Algorithm
IL	Ionic Liquid
IS	Industrial Symbiosis
LP	Linear Programming
LUR	Lower Uncertain Region
MEN	Mass Exchange Network
MILP	Mixed-Integer Linear Programming
MINLP	Mixed-Integer Nonlinear Programing
MSA	Mass Separating Agent
NLP	Nonlinear Programming
NPV	Net Present Value
NREL	National Renewable Energy Laboratory
OA	Outer Approximation
ODP	Ozone Depletion Potential

ORC	Organic Rankine Cycle
PCP	Perturbed Chain Polar
PSE	Process System Engineering
POPC	Palm Oil Processing Complex
QSAR	Quantitative Structure-Activity Relationships
QSPR	Quantitative Structure-Property Relationships
SA	Simulated Annealing
SAFT	Statistical Associating Fluid Theory
SCP	Sustainable Consumption and Production
THFA	Tetrahydrofurfuryl alcohol
TI	Topological Index
TS	Tabu Search
UNIFAC	Universal Quasichemical Functional-Group Activity Coefficients
UR	Uncertain Region
UUR	Upper Uncertain Region
VR	Variable Range

Indexes

b	index for biomass feedstock

d	index for signature
i	index for first order molecular group for group contribution method
j	index for second order molecular group for group contribution method
k	index for third order molecular group for group contribution method
m	index for chemical component in mixture
p	index for target product property
q	index for conversion pathway for biomass in integrated biorefinery
q'	index for conversion pathway for intermediate in integrated biorefinery
s	index for intermediate in integrated biorefinery
s'	index for product in integrated biorefinery
y	index for individual objective function for weighted sum multi-objective optimisation approach

Parameters/Variables

$A^{\text{weighted sum}}$	overall objective function for weighted sum multi-objective optimisation approach
A	individual objective function for weighted sum multi-objective optimisation approach

a	weighting factor for A for weighted sum multi-objective optimisation approach
B_b^{Bio}	flow rate of biomass feedstock b
CRF	capital recovery factor
C_i	contribution of first order molecular group
C_j	contribution of second order molecular group
C_k	contribution of third order molecular group
E_b^{Bio}	cost of biomass feedstock b
$E_{s'}^{\mathrm{Prod}}$	cost of product s'
E_{bq}^{Cap}	capital cost for conversion of biomass feedstock b through pathway q
$E_{sq'}^{\mathrm{Cap}}$	capital cost for conversion of intermediate s through pathway q'
E_{bq}^{Opr}	operating cost for conversion of biomass feedstock b through pathway q
$E_{sq'}^{\mathrm{Opr}}$	operating cost for conversion of intermediate s through pathway q'
F_{bq}^{I}	flow rate of biomass feedstock b to pathway q
$F_{sq'}^{\mathrm{II}}$	flow rate of intermediate s to pathway q'
G	molecular graph
GP^{Total}	total annualised cost

h	height of signature
H_v	heat of vaporisation
HHV	higher heating value
K_{oc}	soil sorption coefficient
l	colouring sequence for molecular signature descriptor
L	TI values for each signature root
LC_{50}	lethal concentration/toxicity
LFL	lower flammability limit
MW	molecular weight
n_1	number of signatures of valency one
n_2	number of signatures of valency two
n_3	number of signatures of valency three
n_4	number of signatures of valency four
N_i	number of occurrence of first order molecular group
N_j	number of occurrence of second order molecular group
N_k	number of occurrence of third order molecular group
N_S	total number of signatures in a molecule
N_{DB}	number of signatures with one double bond in a molecule
N_{MB}	number of signatures with two double bonds in a molecule

N_{TB}	number of signatures with one triple bond in a molecule
O	number of circuits in a molecular graph
OC	oxygen content
R	retention
R^2	coefficient of determination
RON	research octane number
R_{bqs}^{I}	conversion rate of biomass feedstock *b* to intermediate *s*
$R_{sq's'}^{\mathrm{II}}$	conversion rate of intermediate *s* to product *s*’
TAC	total annualised cost
$TACC$	total annualised capital cost
$TAOC$	total annualised operating cost
TLC	toxic limit concentration
T_b	boiling point
T_{ig}	auto-ignition temperature
T_f	flash point
T_s^{Inter}	total production rate of intermediate *s*
$T_{s'}^{\mathrm{Prod}}$	total production rate of product *s*’
u	constant specific to TI

UFL	upper flammability limit
v_p^{L}	lower limit for target property p
$v_p^{\mathrm{MIX,\,L}}$	lower limit for target property p for mixture
v_p^{LL}	lower lower limit for target property p
v_p^{LU}	lower upper limit for target property p
v_p^{U}	upper limit for target property p
$v_p^{\mathrm{MIX,\,U}}$	upper limit for target property p for mixture
v_p^{UL}	upper lower limit for target property p
v_p^{UU}	upper upper limit for target property p
V_E	affinity
V_p	value for target property p
V_p^{MIX}	value for target property p for mixture
V_{p*}	value for target property p with unknown target property ranges
VP	vapour pressure
V_m	molar volume
$w^{\mathrm{I}}, w^{\mathrm{II}}, w^{\mathrm{III}}$, $w^{\mathrm{IV}}, w^{\mathrm{V}}, w^{\mathrm{VI}}$	correlation constants for group contribution models
x_m	fraction of chemical component m in mixture

z^{I}	binary coefficient of second order molecular group
z^{II}	binary coefficient of third order molecular group
α	occurrence number of each signature
χ	connectivity index
χ^{v}	valence connectivity index
$\Delta\chi$	delta connectivity index
χ_{np}	connectivity index of molecular non-polar structure
δ	Hildebrand solubility parameter
ε	edge adjacency index
λ_p	degree of satisfaction for target property *p*
λ_p^{r}	degree of satisfaction for property robustness for target property *p*
λ_p^{s}	degree of satisfaction for property superiority for target property *p*
λ_p^{*}	degree of satisfaction for target property *p* in two-phase approach
μ	mobility
η	viscosity
Ω_p	normalised property operator for target property *p*

Ω_{mp}	normalised property operator for target property p for chemical component m
Ω_p^{MIX}	normalised property operator for target property p for mixture
Ω_p^{L}	lower limit for normalised property operator Ω_p
$\Omega_p^{\mathrm{MIX,\,L}}$	lower limit for normalised property operator Ω_p^{MIX}
Ω_p^{U}	upper limit for normalised property operator Ω_p
$\Omega_p^{\mathrm{MIX,\,U}}$	upper limit for normalised property operator Ω_p^{MIX}
σ_p	standard deviation for property prediction model for target property p
θ_p	property function corresponding to target property p

CHAPTER 1

INTRODUCTION

1.1. Problem Background

Since the age of industrialisation, fossil fuels (petroleum, natural gas and coal) have been widely utilised as the main source of energy for heat and power production. Besides heat and power, fossil fuels have also been an important feedstock for the production of various commodities and specialty chemicals. Although the utilisation of fossil fuels has provided developments and conveniences to the society, the extensive consumption of fossil fuels has also contributed to a number of environmental issues (Panwar et al., 2011). One significant environmental issue is the increased level of greenhouse gases (GHGs) in the atmosphere. In addition, the vast consumption of fossil fuels has also led to the diminishing of fossil fuel reserves (Farhad et al., 2008). In order to simultaneously mitigate climate change and reduce the dependence on fossil fuels in transport and industry sectors, alternative source of energy is necessary. Such implications have driven the industrial and scientific community to search for a more sustainable and renewable source of energy (Cherubini, 2010). As such, biomass has been identified as a potential alternative to fossil fuel resources as a feedstock for industrial productions, addressing both energy and non-energy sectors (Naik et al., 2010).

According to Demirbas (2009), biomass comprises biological materials which can be found in natural and derived materials. It can be defined as organic matters in which solar energy is stored. Biomass contains varying amounts of cellulose, hemicellulose and lignin which are made up from hydrogen, carbon, oxygen, nitrogen and sulphur which presents in minor proportions. Saxena et al. (2009) categorises biomass resources into three main categories, which exist depending on different geographic conditions.

- Energy crops which include edible and non-edible crops
- Standing forest which comprises various intermediate products and residual wastes of different nature
- Wastes which consists of agricultural, agro industrial and municipal solid wastes

Since ancient times, biomass has always been a major source of energy for mankind. Traditionally, biomass had been utilised through direct combustion. At present, biomass can be converted into three main products of heat/electrical energy, transportation fuels and feedstock for chemical production. In recent decades, biomass utilisation as a source of energy is experiencing a huge upsurge in commercial and research interest due to several reasons. First of all, biomass is a renewable, potentially sustainable and relatively environmentally benign source of energy (Yuan et al., 2013). In addition, biomass can be converted into a huge array of diverse materials and value-added products. It provides rooms for exploitation to be explored and converted into different forms and products (Bozell, 2008). Moreover, the combustion of forestry and agricultural biomass for energy production is an effective use of waste products. Hence, waste disposal problem can be significantly reduced (Saxena et al., 2009).

1.2. Integrated Biorefinery

Biomass can be converted into useful forms of energy and value-added products by using a number of different processes. Presently, various well-established standalone biomass conversion processes and technologies are available to convert biomass into different value-added products. These conversion processes include physical/mechanical, thermochemical, chemical and biological/biochemical processes. Biorefinery, a concept analogous to petroleum refinery can be applied to explain the utilisation of biomass as a feedstock to produce multiple products (Fernando et al., 2006). According to Kamm et al. (1998), biorefinery can be defined as a complex system made up from sustainable and environmentally benign technologies to exploit and utilise biological raw materials. Similar to a petroleum refinery, a biorefinery integrates a range of processing technologies to produce multiple products by using various biomass resources as raw materials. The implementation of the biorefinery concept has been a key to chemical industries' gradual shift towards the use of biomass resources for industrial chemical manufacturing (Frost and Draths, 1995). As biomass is available in different forms and characteristics, many possible processing technologies are available to convert biomass into different value-added products. Hence, significant effort in the research and development for the synthesis and design of biorefineries has been focused on integrating the broad range of biomass conversion platforms (physical/mechanical, thermochemical, chemical and biological/biochemical conversion processes) to produce a wide spectrums of value-added products. In order to enhance the productivity, cost effectiveness and overall process performances, Fernando et al. (2006) proposed the concept of integrated biorefinery which integrates multiple biomass conversion platforms as a whole. Through the concept of integrated biorefinery, the waste generated from a biorefinery can be minimised while the energy and material recovery can be maximised. Hence, the concept of integrated biorefinery has the potential to improve economic, environmental and social sustainability while converting biomass into energy and different chemical products efficiently.

To date, there are a large number of established biomass conversion pathways available for implementation in an integrated biorefinery to convert biomass into a wide spectrum of potential products. As such, there is a need to screen all potential pathways systematically and determine the optimum conversion pathways that produce the desired products. Various approaches have been developed for process synthesis and screening of potential conversion pathways for integrated biorefineries (Bao et al., 2011; Halasz et al., 2005; Ng et al., 2009; Ng et al., 2014; Santibañez-Aguilar et al., 2011; Wang et al., 2013; Zhang et al., 2014; Zondervan et al., 2011). While significant amount of research attention have been focused in the area of synthesis and design of integrated biorefinery, limited research works have been carried out in the area of product design in integrated biorefinery. According to Skibar et al. (2009), chemicals derived from biomass have the potential to form the foundation of a huge range of products coming from chemical industries. The number of potential value-added chemicals, either in the form of end products or as intermediate products is tremendous (Werpy and Petersen, 2004). In addition to being utilised to produce the conventional and market available products (i.e. biopolymers, biodiesel, solvents etc.), biomass has the ability to be designed and converted into various novel chemical products (Holladay et al., 2007). Thus, in order to convert biomass into value-added products efficiently, product design aspect is essential to be taken into consideration in the synthesis and design of integrated biorefinery. This can only be achieved by integrating the design of integrated biorefinery with chemical product design.

1.3. Chemical Product Design

A chemical product can be defined as a system consists of different chemical substances which is designed and manufactured for one or more purposes (Cisternas and Gálvez, 2006). According to Cussler et al. (2010), chemical products can be generally categorised into three types. The first type is commodities such as acids and alcohols. Most of these chemical products are relatively simple to produce, and the manufacturing processes involved are stable and well-established. Therefore, the design goal of commodities is to manufacture products at minimum cost. The second type of chemical products is molecular products such as pharmaceutical drugs. The selling point for this type of products is the rate of innovation and introduction of the products into the market. In order to compete with the rival companies, the speed in discovering and developing the products is more vital than the manufacturing cost of the products. The third type of chemical products is performance products. The value of this type of products is dependent on its functions, which are normally defined by the structure of the products. Table 1.1 summarised the classification of chemical products.

Table 1.1: Classification of chemical products

	Commodities	**Molecular products**	**Performance products**
Design key	Cost	Speed	Function
Design basis	Unit Operations	Chemistry	Microstructure
Design risk	Feedstock	Discovery	Science

Although these distinct categories of chemical products differ in their design key steps, selling points and possible risks encountered during the product design process, the design procedures for these chemical products are identical and similar. According to Cussler and Moggridge (2001), the main purpose of chemical product design is to identify the optimal product to be made for a specific application. Moggridge and Cussler (2000) proposed that the entire chemical product design process can be represented by four principal steps as follows:

- Identify customer needs
- Generate ideas to meet the needs
- Select among ideas
- Manufacture products

The first step is to define the needs or functionalities that the product should fill. This is followed by generating all possible ideas to meet the identified needs and selecting the most promising one among the generated ideas. The final step in the design process is to determine the ways and methods to manufacture and test the product before introducing it to the market.

Traditionally, bottom-up approaches are used in searching for new chemical products with optimal performance. For example, a solvent is designed to provide maximum separability during separation process. Bottom-up product design approaches are usually based on design heuristics, experimental studies and expert judgements or experiences (Odele and Macchietto, 1993). In bottom-up approaches, all feasible molecules are first generated from the raw materials and subsequently tested for the required product needs. As they are mainly based on trial and error approaches, these traditional methods are intrinsically inefficient, time consuming and costly (Venkatasubramanian et al., 1994). Furthermore, these approaches are largely dependent on the available information and knowledge. Thus, it is challenging to search for new chemical products which possess optimal properties without systematic selection tools (Churi and Achenie, 1996). On the other hand, new chemical products can be designed via top-down approaches. Top-down approaches are reverse engineering approaches where the design process begins with the identification of needs to fulfil, and search for the molecules that possess the properties which can meet the product needs (Gani et al., 1991).

As discussed earlier, the goal of chemical product design is to identify a product that gives a particular performance. In most cases, performance and suitability of a product are defined in terms of physical properties rather than chemical structure of the product. For example, to design an effective refrigerant, the volumetric heat capacity for the designed refrigerant should be high so that the amount of refrigerant required is reduced for the same refrigeration duty. Besides, the viscosity of the designed refrigerant should be low to achieve a low pumping power requirement. Hence, as long as the product possesses high volumetric heat capacity, low viscosity and fulfils other product needs, it is suitable to be used as an effective refrigerant regardless of its chemical structure. Therefore, chemical product design problems can be considered as inverse property prediction problems where the preferred product attributes are represented in terms of physical target properties. The objective for the inverse property prediction problems is to determine the molecule that matches the defined properties (Gani and O'Connell, 2001).

As stated by Stephanopoulos (2003), one of the important sources of product specifications and requirements in product design is customer needs. Thus, it is required to translate descriptive customer requirements into measurable physical properties of a product (Achenie et al., 2003). For example, in order to design a chemical product which is non-hazardous, toxic limit concentration of the product should be measured. Another example would be the design of a product which will not cool easily. In order to fulfil the requirement, the heat capacity of the product is measured and taken into consideration during the design process. In addition, there are situations where a product needs can only be fulfilled by measuring and taking more than one physical property into consideration; for example, design of a transportation fuel. The consistency of the fluid flow has to be considered to make sure that the fuel can flow continuously from the fuel tank to the combustion chamber. Hence, the density and viscosity of the fuel have to be considered during the design stage. Moreover, engine efficiency is one of the important parameters which should be considered in designing the fuel so that the fuel can be burnt to run the engine efficiently. Based on such requirement, octane rating and heating value of the fuel are taken into account. After the required product attributes are represented with measurable product properties, chemical product that meets the product needs can be designed based on the identified product properties. The design of chemical products based on product properties can be done by using computer-aided molecular design (CAMD) techniques.

In general, CAMD techniques predict and estimate the properties of molecules by using property prediction models. According to Gani and Pistikopoulos (2002), property prediction models estimate product properties from structural descriptors, which are numerical values that contains chemical information of a molecule. Some of the commonly used structural descriptors to quantify a molecular structure include chemical bonds and molecular geometry (Randić et al., 1994). As CAMD techniques are able to design chemical products having a set of desirable product properties, they have been developed as powerful techniques in the field of chemical product design

(Harper and Gani, 2000). Currently, most of the CAMD techniques utilise property prediction models based on group contribution (GC) methods to verify that the generated molecules possess the specified set of target properties (Harper et al., 1999). Besides GC methods, established methods in developing property prediction models include the application of topological indices (TIs). TIs are used to correlate the chemical structure to physical properties of a molecule. The correlated relationships are called quantitative structure property/activity relationships (QSPR/QSAR) (Kier & Hall, 1986).

To date, most of the developed and available chemical product/molecular design approaches emphasise on designing optimal chemical products/molecules. In most cases, the optimal product is designed in terms of optimum target property(s). This optimality of product properties is the main factor that defines the quality of a product. Hence, in inverse property prediction chemical product design problems, the product with optimal predicted target property(s) will be regarded as the optimal product. As mentioned earlier, most of the CAMD techniques involve property predictions which are done by using property prediction models. It is noted that property prediction models are developed with certain accuracy and uncertainties. The accuracy of these property prediction models are usually expressed in terms of correlation coefficient (r^2) and standard deviation (σ). In general, the accuracy of property prediction models is used as an indicator of the models' ability in predicting the properties or the expected error that the models might cause. Hence, while utilising CAMD techniques in designing chemical products with optimal predicted target property(s), the expected accuracy can be known.

In addition, most of the established chemical product design methodologies are focusing on optimising a single product property while designing an optimal chemical product. It is aware that in some situations, there are several important product properties to be considered and optimised in order to design an optimal chemical product. For example, during the design of an effective solvent, the solvent should be designed with maximum separability or solubility. Besides, the flammability limit of the designed solvent should fall within the safety operating limit and the toxicity of the solvent should meet the environmental regulations (Harini et al., 2013). Refrigerant design is another example where multiple product properties are important. In order to design an effective refrigerant, the volumetric heat capacity for the designed refrigerant should be high so that the amount of refrigerant required is reduced for the same refrigeration duty (Samudra and Sahinidis, 2013). Besides, the designed refrigerant should possess low viscosity to achieve low pumping power requirement. Since more than one design objective is involved in designing these products, these chemical product design problems have to be solved as multi-objective optimisation problems.

In many occasions, chemical products exist in the form of mixtures of different components rather than as single component products. According to

Churi and Achenie (1997), the main purpose of designing mixtures is that mixtures have the potential for giving a good mix of target properties which is unattainable by individual chemical components. For example, for refrigerant design, although difluoromethane (CH_2F_2) is a better refrigerant in terms of low compressor displacement and zero ozone depletion, its vapour pressure is too high for an efficient refrigerant. Therefore, in order to overcome this limitation, mixture of chloromethane (CH_3Cl) and CH_2F_2 is introduced as mixtures offer greater flexibility in matching multiple target properties (Duvedi and Achenie, 1997). As pointed out earlier, various biomass conversion pathways are available to convert biomass into a wide range of products. In cases where the desired properties cannot be met by a single component product, an optimal mixture of chemicals would be required.

1.4. Problem Statement

It is realised that the synthesis and design of integrated biorefineries which focus on the product design aspects are yet to be examined thoroughly. Many established approaches have been developed by the research community in the realm of integrated biorefinery. However, most of the available approaches emphasise on the identification of optimal processing routes that lead to the products without addressing the product design aspects of the biorefinery. This serves as the main motivation in this thesis. In chemical product design problems, there are cases where multiple product properties are required to be considered and optimised to design an optimal product. In such cases, the chemical product design problems have to be solved as multi-objective optimisation problems. Moreover, property prediction models are developed with certain range of accuracy. The accuracy of property prediction models is necessary to be taken into consideration while utilising CAMD techniques for chemical product design problems. On the other hand, while converting biomass into value-added products in an integrated biorefinery, there are situations where the desired product needs cannot be fulfilled by a single component product. In such situations, design of optimal mixture from biomass would be required. All of the abovementioned remain as research gaps to be filled within this thesis.

1.5. Research Objectives

Based on the identified research gaps, the primary objectives of this research work can be summarised as follows.

i. To develop a conceptual framework for the identification of chemical product and its production routes in integrated biorefineries.

ii. To develop a systematic methodology for the design of optimal chemical product in terms of target product properties as well as the identification of optimal conversion pathways based on different optimisation objectives in integrated biorefineries.

iii. To develop a multi-objective optimisation approach for optimal chemical product design problems where multiple product properties are required to be considered and optimised simultaneously.

iv. To develop a robust chemical product design methodology that considers the accuracy of property prediction models while designing an optimal chemical product in terms of target product properties.

v. To develop a systematic methodology for optimal mixture design in terms of multiple product properties via optimal conversion pathways based on different optimisation objectives.

1.6. Outline of Thesis

In this thesis, introductions to integrated biorefinery and chemical product design are presented in Chapter 1. In addition, Chapter 1 also highlights the main research gap and the objectives of this research work. Chapter 2 presents a critical and thorough literature review on the potential chemical products that can be produced from biomass, different CAMD techniques as well as the current status in the area of CAMD. This is followed by the discussion of research scopes and research methodologies, which are presented in Chapter 3.

Chapters 4 – 8 discuss various novel integrated design techniques for biorefineries with emphasis on chemical product design aspects. A conceptual design for the synthesis of chemical product from biomass in integrated biorefineries is presented in Chapter 4. The objective for the conceptual design is to identify chemical product from biomass and its production routes in integrated biorefineries. Chapter 5 extends the conceptual design into a systematic methodology for optimal chemical product design in integrated biorefineries. The systematic methodology designs the optimal chemical product in terms of target product properties. After the design of the chemical product, the optimal conversion pathways based on different production objectives in converting the biomass into the chemical product are identified. Chapter 6 presents a multi-objective optimisation approach for the design of optimal chemical products in terms of multiple product properties. The presented approach provides solutions for chemical product design problems where multiple product needs are required to be considered and optimised simultaneously. In chapter 7, a robust chemical product design approach is introduced. The approach identifies optimal chemical product in terms of optimality of the product properties while considering property prediction model accuracy. Chapter 8 further extends the systematic methodology presented in Chapter 5 for the design of optimal mixture from biomass which meets the product needs as well as the identification of optimal conversion pathways in producing the mixture in terms of different production objectives.

Chapter 9 presents the summary of the accomplishments and contributions of this research work. In addition, potential future works that can be done based on the techniques developed in this research work are highlighted in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1. Potential Products from Biomass

In near decades, the feedstock utilised in chemical industries for the production of organic chemicals has been gradually shifting from petroleum to biomass. Factors causing this shift include the awareness of finite fossil fuel resources, environmental imperatives, discovery of renewable energy resources and advancements in technologies (Xu et al., 2008). As discussed in Chapter 1, the concept of integrated biorefinery can be utilised to convert biomass into biofuel, bioenergy and value-added products such as bulk chemicals, specialty chemicals and pharmaceutical products. According to Cherubini (2010), the products of integrated biorefineries can be divided into two main categories of energy products and chemical/material products. Energy products include products which are utilised for their energy content. These products are usually used to generate electricity, heat and energy for transportation purposes. Some of the important energy products which can be produced from biomass in integrated biorefinery are:

- Gaseous biofuels (biogas, biomethane, hydrogen, syngas etc.)
- Liquid biofuels (biodiesel, bioethanol, bio-oil, FT-fuels etc.)
- Solid biofuels (charcoal, lignin, pellets etc.)

While energy products are products which are utilised for their energy content, chemical/material products are utilised for their functionalities based on their chemical or physical properties. Some of the common chemical/ material products that can be derived from biomass are shown as follows.

- Chemicals (building blocks, bulk chemicals, fine chemicals etc.)
- Organic acids (itaconic, lactic, succinic, sugar derivatives etc.)
- Polymers and resins (furan resins, phenol resins, starch-based plastics etc.)
- Biomaterials (cellulose, paper, pulp, wood panels etc.)
- Food and animal feed
- Fertilisers

According to Xu et al. (2008), the most common biomass feedstock utilised for the production of commodities and specialty chemicals is carbohydrates. Carbohydrates exist primarily in the form of polysaccharides which includes starch and cellulose (Lichtenthaler and Mondel, 1997). Conventionally, starch and its monosaccharide derivative (D-glucose) have been used as basic organic raw materials by chemicals industries in producing bulk chemicals and polymers (Wilpiszewska and Spychaj, 2007). However, starch is an edible food based resource. Utilisation of starch for the production of chemical products has raised concern about the competition between industrial and food applications of starch. Therefore, utilisation of lignocellulosic biomass for the production of biochemical products has become more attractive since lignocellulosic biomass is mostly waste plant matter (Xu et al., 2008). Lignocellulosic biomass is comprised of cellulose, hemicellulose and lignin. Through different conversion technologies, lignocellulosic biomass can be converted into value-added products such as ethanol and various chemicals (Wyman, 2003). In addition, lignocellulosic materials could also be liquefied into chemical intermediates which are rich in hydroxyl groups (Liang et al., 2006).

Viewing the opportunity to convert starch and lignocellulosic biomass into different chemical products, various research works have been conducted to identify potential chemicals to be made from these biomass. Elliott (2004) discussed the chemicals derived from biomass based on different biomass conversion technologies. The potential chemicals are generally categorised into fermentation products, carbohydrate chemical derivatives, pyrolysis products, gasification products, development fermentations, catalytic/ bioprocessing and plant derived. Werpy and Petersen (2004) presented a report that identifies twelve major building block chemicals that can be produced from starch via different conversion technologies. These building blocks possess the potential to be transformed into new families of useful molecules. Therefore, the identified twelve building blocks can be subsequently converted into various bio-based chemicals that suit the market/product needs (Werpy and Petersen, 2004). Holladay et al. (2007) discussed about the potential of lignin recovery for production of macromolecules, aromatics as well as miscellaneous monomers. Some of the potential products which can be produced from lignin include various fuel additives, carbon fibre, adhesives, phenol, quinone, cyclohexane etc. Skibar et al. (2009) presented a report to highlight the future of biomass by discussing the efforts done by the industrial sectors in utilising biomass for the production of value-added products. According to Skibar et al. (2009), other than the traditional polymer production, production of specialty chemicals for beauty and personal care markets will be one of the most important future markets for the utilisation of biomass.

Based on the abovementioned previous works, it can be seen that the utilisation of biomass is no longer limited to produce energy and bulk chemicals. There has been intensive research on the development of utilisation of biomass in producing fine chemicals as well as specialty chemicals. Hence, there is ample opportunity to produce various chemical products from biomass.

2.2. Synthesis and Design of Integrated Biorefinery

In order to synthesis and design an integrated biorefinery, different conversion processes and technologies from different platforms have to be integrated systematically and efficiently. According to Nishida et al. (1981), process synthesis can be defined as *an act of determining the optimal interconnection of processing units as well as the optimal type and design of the units within a process system*. Since the initiation of the research of process synthesis, intense focus and huge effort have been put in by the scientific community in exploring and studying different elements and aspects of process synthesis and design. In general, process synthesis can be divided into seven categories based on the design aspects the category focuses in. These seven categories are heat exchanger network (HEN) synthesis, mass exchange network (MEN) synthesis, material synthesis, reaction pathway synthesis, reactor network synthesis, separation network synthesis and total flow sheet synthesis (Douglas, 1992).

According to Kokossis and Yang (2010), process systems engineering (PSE) approaches have the potential to support process synthesis and design, which can be applied and utilised in the design of integrated biorefinery. PSE is the field that covers the actions and activities involved in the *engineering of systems consist of physical, chemical and/or biological processing operations* (Stephanopoulos and Reklaitis, 2011). Throughout the years, various PSE approaches have been developed for the synthesis and design of integrated biorefinery, each with its own advantages and disadvantages. Some of the commonly used approaches are discussed as follows.

i) Hierarchical approaches which solve the process synthesis and design problems by using a series of hierarchical decisions and short cut models at different stages of the synthesis of process (Douglas, 1985). They emphasise on the strategy of decomposition and screening in identifying the solution. Although they provide quick solution for process synthesis and design problems, hierarchical approaches do not guarantee an optimal solution due to their sequential decomposition strategy (Li and Kraslawski, 2004).

ii) Heuristic searches that utilise engineering knowledge and experiences to generate promising solutions. By first identifying a good base case design, subsequent modification, adjustment and refinement can be applied to enhance the overall process performance (Stephanopoulos and Westerberg, 1976). Though heuristic searches are proven to be effective in generating appropriate configurations for process synthesis and design problems, they do not guarantee the generation of optimal configuration (Frangopoulos et al., 2002).

iii) Insight-based approaches that consist of approaches such as pinch analysis, distillation residue curve map, ternary diagram etc. These insight-based approaches provide insights and visualisation of the process performance which are useful in helping the users to visualise the overall process performance. However, the applications of insight-based approaches in solving complex process synthesis and design problems are often constrained by the limited parameters that can be taken into consideration (Voll, 2013).

iv) Algorithmic approaches such as process graph (P-graph) method. These approaches perform a step by step set of operations based on automated reasoning, calculation and data processing for the identification of solutions (Oppenheim, 2010). Algorithmic approaches serve as powerful and reliable tools in solving process network synthesis problems in terms of search space reduction, which leads to faster solutions for extensive problems. However, the applicability of algorithmic approaches is reduced for complicated process synthesis and design problems (Lam et al., 2013).

v) Mathematical optimisation approaches that formulate process synthesis and design problems as mathematical models (i.e., linear programming (LP), nonlinear programming (NLP) models etc.) and solve them via different optimisation methods and strategies. Based on the nature and required level of detail for the problems, different mathematical programming models range from LP, mixed-integer linear programming (MILP), NLP and mixed-integer nonlinear programming (MINLP) models can be formulated and solved to identify the process configuration with optimal performance (Grossmann, 2002). While mathematical optimisation approaches are useful and effective in solving process synthesis and design problems, most of the time, these approaches require intensive computational effort when rigorous process modelling is required (Caballero et al., 2007).

Throughout the years, numerous PSE approaches have been developed and applied in the synthesis and design of integrated biorefineries. These approaches are proven to be effective in screening and determining potential conversion pathways to synthesise an integrated biorefinery. For example, Halasz et al. (2005) adapted P-graph method in developing a green biorefinery by considering processing technology as well as raw material utilisation. Ng et al. (2009) presented a hierarchical approach to synthesise and screen the potential alternatives for an integrated biorefinery. In the presented work, two screening tools (evolutionary technique and forward-reverse synthesis tree) are proposed to reduce the process alternatives systematically. Mansoornejad et al. (2010) introduced a hierarchical methodology to optimise the economic performance of forest biorefinery by integrating the design of process/product portfolio, manufacturing flexibility and supply chain network. On the other hand, insight-based approaches are also utilised in the synthesis and design of integrated biorefinery. For instance, Tan et al. (2009) presented a graphical pinch approach for the analysis of water footprint constraints on biofuel production systems. The developed approach provides valuable insights for the allocation of energy crops to different geographical regions based on the regional energy demand and available water resources. Pinch analysis is later adapted to develop an automated targeting approach for finding maximum biofuel production and revenue targets of an integrated biorefinery (Ng, 2010). Later, the automated targeting approach was further extended by Tay and Ng (2012) to develop a multiple-cascade automated targeting approach. The approach is proposed to determine the maximum economic performance of a gasification-based integrated biorefinery. Meanwhile, Tay et al. (2010) presented a C-H-O ternary diagram in determining the overall performance of the synthesised integrated biorefineries. The work proposed by Tay et al. (2010) acts as a quick targeting tool that aids in the evaluation and analysis of integrated biorefinery based on the C-H-O diagram. Besides, Svensson and Harvey (2011) adapted heat pinch analysis in identifying energy efficiency improvements and practical retrofit solutions in a biorefinery in pulp and paper industry. Martinez-Hernandez et al. (2013) later developed an integration approach based on mass pinch analysis for the analysis and design of product exchange networks formed in biorefinery pathways featuring a set of processing units. Recently, Abdelaziz et al. (2015) proposed a hierarchical design approach with the use of mass and heat pinch analysis for Organocat biorefinery. By integrating mass and heat exchanger networks, the proposed systematic approach improves the existing biorefinery designs by enhancing the efficiency of mass and energy utilisation.

In addition to hierarchical and insight-based approaches, numerous mathematical optimisation approaches have been developed for the synthesis and design of integrated biorefineries. For example, Sammons et al. (2007) and Sammons et al. (2008) introduced a flexible framework for optimal biorefinery product allocation by utilising mathematical optimisation techniques in evaluating and identifying optimal combination of production routes and product portfolios. Bao et al. (2009) presented a systematic approach based on technology pathway to determine the optimum pathway that achieves the highest conversion of the desired products. Tay et al. (2011) developed a modular optimisation approach that utilises thermodynamic equilibrium models to evaluate the performance and ultimately, design an integrated biorefinery based on the assessed performance. Odjo et al. (2011) presented a joint disjunctive-genetic algorithm representation approach for process network synthesis to determine optimal product allocation in a biorefinery. Later, Pham and El-halwagi (2012) presented a systematic two-stage approach in synthesising and optimising biorefinery configurations. The presented approach is based on the concept of “forward and backward” approach which involves forward synthesis of biomass that leads to possible intermediates and backward synthesis that starts with the desired products and identifies potential pathways that produce the products. Ng and Ng (2013) adapted the concept of industrial symbiosis (IS) to develop a palm oil processing complex (POPC). The developed POPC integrates the entire palm oil processing industry in maximising material recovery between processing technologies to achieve maximum economic performance. Ng et al. (2013b) later extended the concept of IS to synthesise a POPC with different owners. The proposed work identifies optimum network configuration that addresses individual interest of different owners in the synthesised POPC. Tay et al. (2013) proposed a robust optimisation approach for the synthesis of integrated biorefineries that considers the uncertainties in raw material supply and product demand. Detailed allocation of biomass, intermediates and final products are determined by solving the generated single-step MINLP formulation. Kasivisvanathan et al. (2014) presented a heuristic framework based on algebraic approach for the debottlenecking of palm oil-based integrated biorefinery. By taking the safety and operating capacity of the unit operations into consideration, the framework identifies the bottleneck of the system and provides measures to relieve the process bottleneck. Dansereau et al. (2014) presented an integrated framework for margins-based planning for forest biorefinery. By utilising a superstructural optimisation approach, the presented framework helps the decision makers to identify different supply chain policies to maximise profit in a price-volatile environment.

Besides economic performance, design aspects such as product portfolio, raw material allocation, environmental, safety and health impacts are considered during the synthesis and design of integrated biorefineries. Santibañez-Aguilar et al. (2011) presented a multi-objective optimisation model for the optimal planning of biorefinery. The model simultaneously maximises economic performance and minimises environmental impact while considering different feedstock, processing technologies as well as end products. Zondervan et al. (2011) proposed a superstructure-based optimisation model for the design of optimal processing routes for multi-product biorefinery system by considering different feedstock, processing steps, final products and optimisation objectives. Tay et al. (2011b) adapted fuzzy optimisation approach in designing an integrated biorefinery which considers economic performance and environmental impact simultaneously. Shabbir et al. (2012) presented a hybrid optimisation model which combines insight-based automated targeting and superstructure-based optimisation approaches for the synthesis of sustainable integrated biorefinery while considering both economic and environmental performance. Later, Ponce-Ortega et al. (2012) presented a disjunctive programming approach in designing an optimal integrated biorefinery. The proposed approach (Ponce-Ortega et al., 2012) decomposes and solves a complex biorefinery design problem as a set of subproblems to identify the optimal pathway configuration for a given criterion. You et al. (2012) developed a multi-objective MILP model to determine the optimum configuration in cellulosic ethanol supply chain while considering economic, environmental and social objectives. In the work of You et al. (2012), the economic objective is measured by total annualised cost, the environmental objective is measured by life cycle greenhouse gas emissions while the social objective is measured by the number of accrued local jobs.

Meanwhile, Ng et al. (2013a) extended fuzzy optimisation approach to develop a systematic multi-objective optimisation approach for synthesis of integrated biorefinery which takes into consideration economic performance, environmental, safety and health impacts. Murillo-Alvarado et al. (2013) adapted the disjunctive programming approach to identify optimal reaction pathways of a biorefinery while taking into account the maximisation of the net profit and minimisation of greenhouse gas emissions. El-halwagi et al. (2013) introduced an approach that considers the techno-economic factors as well as the effects of associated risk into the selection, sizing and supply chain network development of a biorefinery. Wang et al. (2013) proposed a superstructure-based multi-objective MINLP optimisation model for a biorefinery via gasification pathway that simultaneously maximises economic objective and minimises environmental concern. By solving the MINLP model with the ε-constraint method, the optimal solution is identified in terms of maximised economic objective measured by net present value (NPV) and minimised environmental impact measured by global warming potential (GWP). Similar consideration are taken into account by Gebreslassie et al. (2013a) to design an optimum biorefinery via fast pyrolysis, hydrotreating and hydrocracking. Optimum NPV and GWP were determined by solving the generated bi-criteria NLP model with ε-constraint method. Gebreslassie et al. (2013b) later extended the approach in synthesising and designing an algae-based biorefinery with maximised NPV and minimised GWP. Similarly, Zhang et al. (2014) adapted the ε-constraint method to solve a bi-criteria MINLP model for the synthesis of a biorefinery through fast pyrolysis and hydroprocessing subject to NPV and GWP objectives. Recently, Gong and You (2014) developed a detailed superstructure-based optimisation model for algae-based biorefinery that considers carbon sequestration and utilisation. Based on the developed superstructure, the optimal design of algae-based biorefinery is determined by minimising the unit carbon sequestration and utilisation costs.

Based on the above review, it is noted that the research works on the synthesis and design of integrated biorefinery have been intense and comprehensive. Design aspects such as economic, environmental, safety and social consideration have been taken into account in the available research works. It can be seen that the aforementioned works have focused on process design aspects of an integrated biorefinery. In addition, the abovementioned works have applied developed approaches in solving realistic and specific case studies. However, most of the aforementioned contributions focused mainly on identifying and designing the optimal processing routes that lead to the products without emphasising on the product design aspects of the biorefinery. It can be seen from the literature review that biomass has the potential to be converted into value-added products which include commodities, fine chemicals as well as new and novel products. Most of the time these products are designed to fulfil customer requirements and product needs (Achenie et al., 2003). Hence, in order to synthesise an optimal integrated biorefinery, the product design aspects have to be considered such that the integrated biorefinery would produce products which satisfy product needs. This can be achieved by integrating the design of integrated biorefinery with chemical product design.

2.3. Computer-Aided Molecular Design

Chemical product design problems can be defined as the identification of chemical products that satisfy a set of desired product needs. According to Venkatasubramanian et al. (1994), the traditional chemical product design methods have been considered as an iterative approach. Most of the time, the traditional approaches require a search which involves a large number of potential candidate molecules. During the product design process, the scientists or product designers first hypothesise a target molecule as the potential product that possesses the desired product needs. This is followed by the synthesising of the product and testing for the desired product needs. Redesigning of the target molecule is required if the desired product needs are not met. As these approaches are iterative in nature, they are expensive and time consuming, which result in low performance in terms of efficiency and cost effectiveness (Venkatasubramanian et al., 1994). A generalised framework of the traditional chemical product design approach is shown in Figure 2.1.

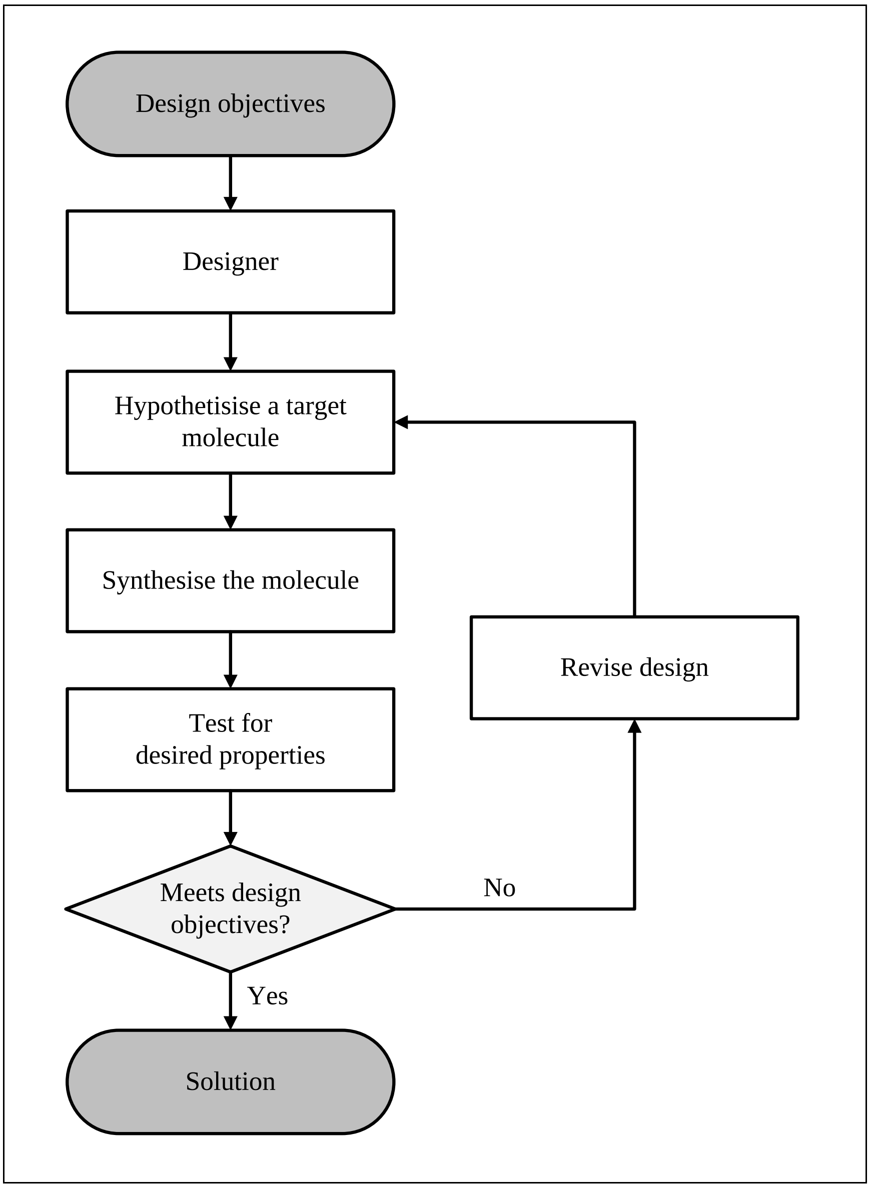


Figure 2.1: Traditional molecular design approach

In view of this, computer-aided molecular design (CAMD) techniques are efficient alternatives to the traditional iterative approaches for the design of chemical products. As discussed in Chapter 1, most of the time the suitability and performance of a chemical product are defined in terms of physical properties rather than chemical structure of the product. Hence, chemical product design problems can be considered as inverse property prediction problems where the desired product attributes are represented in terms of physical properties. The objective of the inverse property prediction problems can then be defined as the searching for the molecules that possess the required physical properties (Gani and O'Connell, 2001). In recent years, CAMD techniques have attracted much attention and emerged as powerful techniques for their ability to identify promising molecules that possess the desired physical properties (Samudra and Sahinidis, 2013).

In general, a CAMD problem can be formulated as the process of identifying all compounds which match a specified set of physical properties that give the required product needs. Throughout the years, various approaches have been developed, applied and extended in solving a wide range of chemical product design problems. These methodologies and approaches for CAMD can be classified into different categories. One of the main categories is generate-and-search approaches (Gani et al., 1991). In generate-and-search approaches, molecular groups and target properties which correspond to the product needs are first identified. This is followed by the generation of feasible set of compound structures and the prediction of target properties of the generated compound structures. The desired product can then be designed and selected among the identified compounds with the predicted target properties. A typical framework of generate-and-search approach used for chemical product design problem is illustrated in Figure 2.2 (Harper et al., 1999).

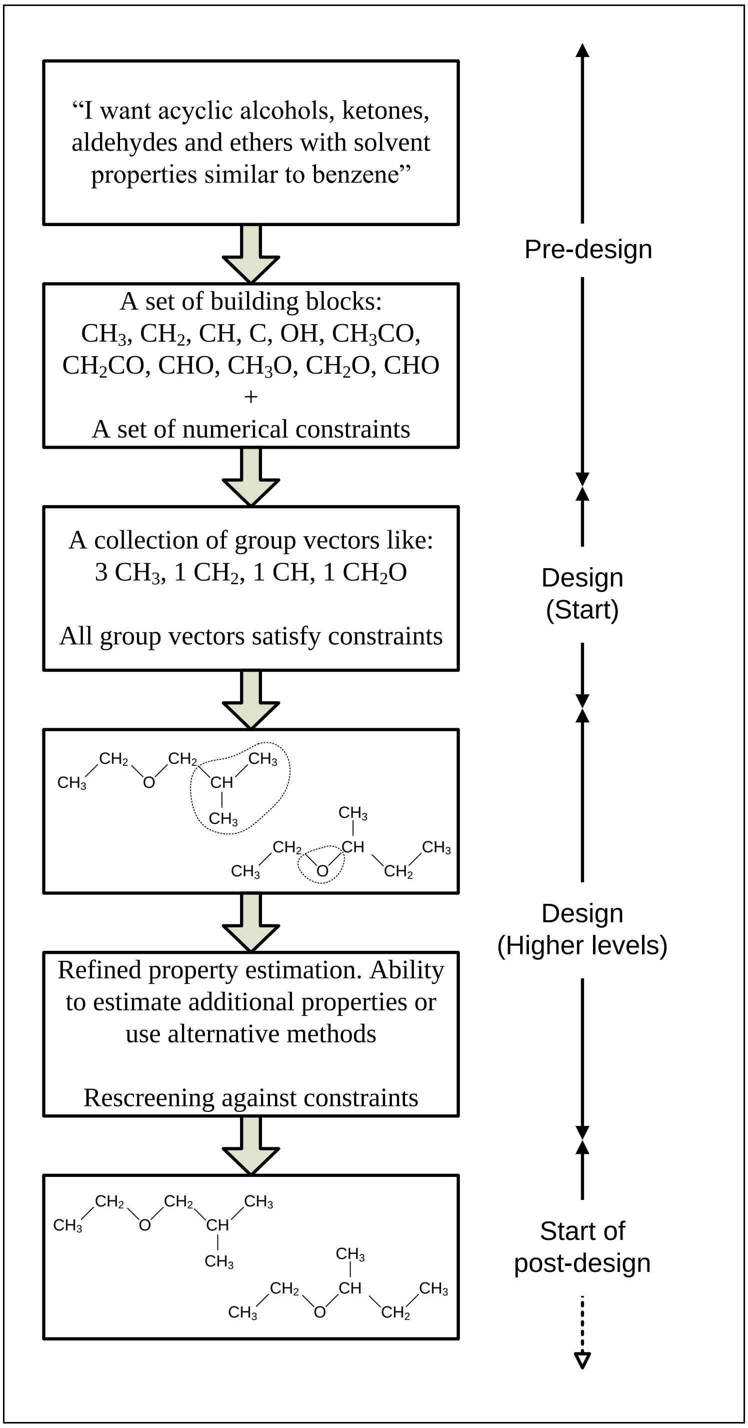


Figure 2.2: Basic steps in generate-and-search CAMD approach

As shown in Figure 2.2, the generate-and-search CAMD framework can be divided into pre-design, design and post-design phases. In pre-design phase, product needs are determined. Required functionalities of the product and the basic molecular groups that form the product are identified in this stage. This information is used in the design phase to determine the feasible candidates. If necessary, property estimation and product analysis can be performed at higher level in post-design phase. The post-design phase may also address the question of synthesis and manufacturing of the chemical product.

In addition to generate-and-test approaches, mathematical programming approaches are also among the well-known approaches for solving CAMD problems (Macchietto et al., 1990). The basic concept of mathematical programming approach can be shown by using generalised mathematical expression as shown below.

Objective function:

$$\text{Maximise} \quad f(p,n) \tag{2.1}$$

Subject to:

$$g_1(p,n) \le 0 \tag{2.2}$$

$$g_2(p,n) \le 0 \tag{2.3}$$

Here, p is the target property and n is the frequency of the structural descriptor in the molecule. $g_1(p, n)$ is a set of property constraints subject to the target property ranges to make sure the molecule fulfils the product needs while $g_2(n)$ is a set of structural constraints to ensure the structural feasibility of the molecule. The objective $f(p, n)$ is a function of property targets and structural components of the molecule to be optimised. In mathematical programming approaches, the chemical product design problem is formulated as a mathematical programming model which is solved to identify the molecule in terms of appropriate performance index. Depends on the nature of the design problem, constraints such as material balances, process and design limitation can be incorporated during the generation of molecule.

Other than the deterministic approaches, stochastic approaches are utilised in solving CAMD problems as well. Some of the widely used stochastic optimisation techniques include genetic algorithm (GA), simulated annealing (SA) and Tabu search (TS). Based on Darwinian models of natural selection and evolution, the basic concept behind GA is the evolutionary creation of a new population of entities from an earlier generation through processes of evolution namely crossover, mutation and selection (Holland, 1975). By using these processes of evolution, GA handles the linear and bound constraints by generating only feasible newer points. The ultimate goal of GA is to generate better and fitter generations through evolution in achieving the design objective. Meanwhile, SA is a combinatorial optimisation technique for solving unconstrained and bound-constrained optimisation problems. SA solves optimisation problems based on random estimation of objective function and evaluation of the problem constraints. While requiring a great number of function evaluations to determine the optimal solution, the application of SA increases the possibility for the generation of global optimal solution even for problems with multiple local minima. In TS, short-term memory function is incorporated to make sure that the visited solutions are prevented while searching for better solutions. This enables the searching of solutions to be done in wider search space. In general, these heuristic search methods are applied for problems when the deterministic branch and bound (BB) and outer approximation (OA) approaches result in slow convergence or are difficult to apply. For example, Lin et al. (2005) proposed a detailed implementation of the TS algorithm for CAMD of transition metal catalysts. Compared to the deterministic approach, the proposed approach shows that TS is able to provide a list of good candidate molecules while using a smaller amount of computational time. Song and Song (2008) presented an optimisation approach for the design of environmentally friendly solvents for separation processes using CAMD approach based on SA technique. By solving several case studies, it is shown that the presented optimisation approach can solve the design problems with significantly reduced amount of computational time.

In addition to mathematical programming and stochastic approaches, visual approaches are developed in solving product and process design problem as well (Eljack et al., 2005). Visualisation of the design problem is achieved by employing property clustering techniques which satisfy intra- and inter-stream conservation through linear mixing rules. Hence, for problems that can be satisfactorily described by only three properties, the molecular and process design problem can be simultaneously solved visually on a ternary diagram.

2.4. Types of Properties and Estimation Techniques

CAMD techniques are important for chemical product design problems for their ability in predicting, estimating and designing molecules with a set of predefined target properties (Harper and Gani, 2000). According to Gani and Constantinou (1996), properties of a chemical product (pure compound and mixture) can be divided into different categories based on the nature of the property. Table 2.1 shows the classification of chemical product properties.

Table 2.1: Classification of chemical product properties

Property type	**Property**
Primary	Critical temperature, critical pressure, critical volume, normal boiling point, normal melting point, heat of vaporisation at 298 K, heat of fusion at 298 K, Gibbs energy of formation at 298 K,
Secondary	Surface tension, vapour pressure, density, volume, viscosity, heat capacity
Functional	Vapour pressure, liquid density, conductivity, solubility
Mixture	Liquid density, saturation temperature, saturation pressure, liquid solubility, solid solubility

As shown in Table 2.1, chemical product properties are categorised into primary, secondary, functional and mixture properties. Primary properties are properties that can be estimated from the molecular structure of the product. For example, the estimation of properties such as normal boiling point and heat of vaporisation at 298 K can be done directly based on the product molecular structure. Meanwhile, secondary properties are pure component properties which are dependent on other properties. For example, density at a fixed temperature and pressure is dependent on the mass and volume of the product. Functional properties are pure component properties which are dependent on the temperature and/or pressure of the system such as density and vapour pressure. Mixture properties are properties of a mixture which are dependent of the composition of the mixture constituents. Properties such as saturation temperature and saturation pressure are important for the estimation of mixture properties.

Depending on the types of product properties and the required estimation accuracy, different types of property prediction models can be utilised for chemical product design problems. According to Gani and Constantinou (1996), property prediction models can be classified in terms of reference and approximate methods. Reference methods are methods that can verify a theory and/or validate other simpler/approximate methods. These methods usually provide accurate property estimation. However, they are often computationally intensive. On the other hand, approximate methods estimate property by matching a theory within a limited range of experimental data. Though these approximate methods are less accurate, they are computationally inexpensive compared with reference methods (Gani and Constantinou, 1996). Property prediction models can be further categorised into mechanical, semi-empirical and empirical models, each with its advantages and disadvantages. These models provide property estimation for different chemicals such as pure compounds, mixtures and polymers with varying degrees of accuracy. Achenie et al. (2003) arranged the classification of property prediction models, which can be shown in Figure 2.3.

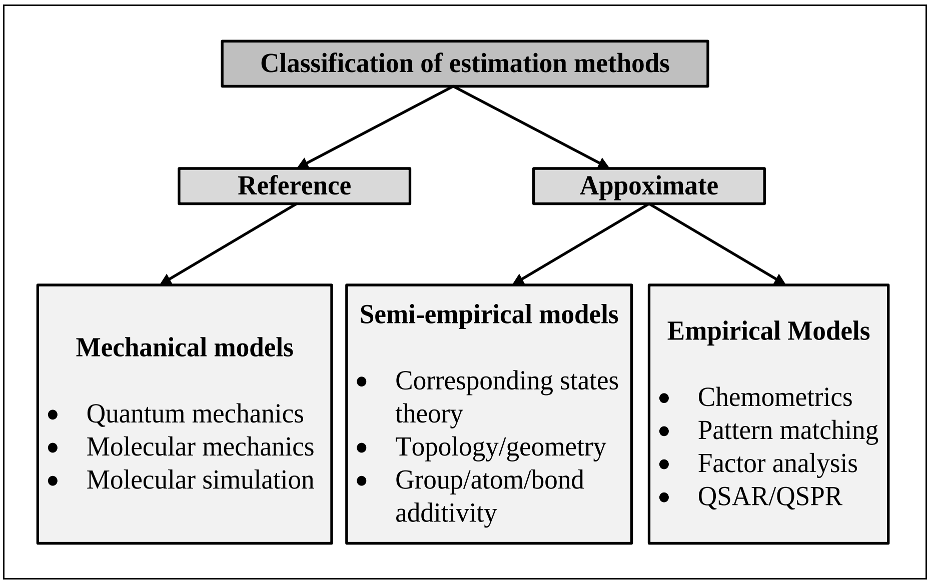


Figure 2.3: Classification for property estimation methods

2.4.1. Group Contribution Methods

One of the important classes of semi-empirical property models is group contribution (GC) models. Currently, most of the CAMD techniques use property prediction models based on GC methods to verify and ensure that the generated molecules possess the specified set of desirable properties (Harper et al., 1999). By utilising molecular groups as structural descriptors, GC methods estimate the property of the molecule by summing up the contributions from the molecular groups in the molecule according to their appearance frequency (Ambrose, 1978; Horvath, 1992; Joback and Reid, 1987). Property prediction models based on GC methods are widely used for property estimation because these models are simple to apply yet provide reasonably accurate predictions for many properties. Moreover, they can provide quick property estimations without significant errors and expensive computational effort (Constantinou et al., 1993).

However, the early GC property prediction models become less reliable as the complexity of the molecule increases. As molecular groups were assumed to be independent and non-overlapping, resonance, conjugation and proximity effects were not taken into account (Mavrovouniotis, 1990). Hence, the models cannot differentiate between isomers and capture the interactions among different molecular groups. Constantinou and Gani (1994) presented an improved GC approach by defining the molecular groups as first and second order molecular groups. The basic level is called as first order molecular groups while the next higher level is known as second order molecular groups. Second order molecular groups are developed and defined by having the first order molecular groups as their building blocks. These second order molecular groups represent different types of interactions and the effect of these interactions among the first order molecular groups. Hence, isomers and compounds with functional groups can be distinguished. Later, GC methods are further extended by Marrero and Gani (2001) by identifying and incorporating third order molecular groups into the property prediction models. The formation of third order molecular groups is analogous to the second order molecular groups, but their contribution have been correlated to focus on molecular fragments or compounds whose description is insufficient through first and second order molecular groups. These include polyfunctional and structural groups such as multi-ring compounds, fused ring compounds and compounds which consist of various functional groups. A general representation of property model by using GC methods can be shown with the following equation.

$$f(p) = \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \qquad (2.4)$$

In Equation (2.4), $f(p)$ is a function of the target property p, z^{I} and z^{II} are binary coefficients depending on the levels of estimation, N_i, N_j, N_k are the numbers of occurrence of first, second and third order molecular groups correspondingly and C_i, C_j, C_k are contributions of first, second and third order molecular groups respectively.

GC methods have been widely applied in estimating thermodynamic properties of organic compounds. Ambrose (1978) presented GC methods in estimating property values for critical temperature, critical pressure as well as critical volume. Marrero and Gani (2001) developed GC methods for the prediction of thermodynamic properties such as normal melting and boiling points, critical properties, heat capacity and enthalpy of organic compounds. GC method in predicting heat capacity, liquid viscosity and other thermodynamic properties is presented as well (Joback and Reid, 1987). Apart from thermodynamic properties, GC methods are also utilised to develop property prediction models for non-thermodynamic properties such as acute toxicity (Martin and Young, 2001), surface tension and viscosity (Conte et al., 2008), and 22 other environmental-related properties of organic chemicals (Hukkerikar et al., 2012a).

2.4.2. Topological Indices and Group Contribution$^+$ Method

In addition to GC methods, established methods in developing property models include the application of topological indices (TIs). TIs are molecular descriptors calculated based on principles in chemical graph theory (Trinajstić, 1992). In chemical graph theory which considers the molecules as the vertices and edges in a graph, atoms in the graph are named vertices while the bonds used to connect them are called edges (Wilson, 1986). This method allows the capture of molecular information such as types of atoms and bonds, total number of atoms and bonding between the atoms. Hence, interactions among different atoms/molecular groups and their effects can be captured and utilised in describing a molecular graph as an index. This index is used to correlate the chemical structure to physical properties of a molecule. These correlated relationships are called quantitative structure property/activity relationships (QSPR/QSAR) (Kier and Hall, 1986). Figure 2.4 shows a simple schematic representation of the property prediction by using a QSPR model formed from first order connectivity index (CI), which is one of the commonly used TIs. The model as shown in Figure 2.4 is formed from first order CI. The molecule is first converted into a hydrogen-suppressed graph (molecular graph without considering hydrogen vertices), where vertices and edges of the molecule are identified at the same time. Next, each edge is characterised by the reciprocal

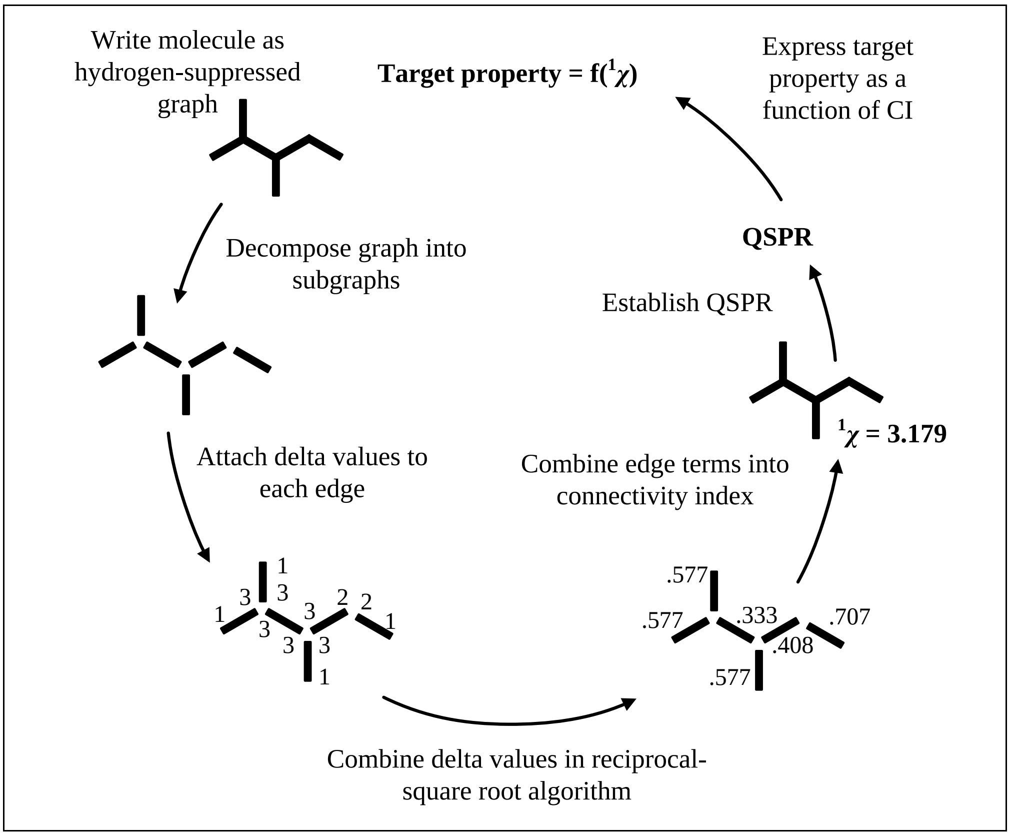


Figure 2.4: Property prediction by using QSPR model

square root product of the vertex valencies. The index can then be determined by summing up the values obtained, which can be used to develop a QSPR model to express the target property as a function of CI.

Some of the well-known TIs which can correlate the chemical structure to physical properties of a molecule are Wiener indices (Wiener, 1947), Randić's molecular CI (Randić, 1975), Kier's shape indices (Kier, 1985) and edge adjacency indices (Estrada, 1995). Some of the properties which can be estimated by using property models developed from TIs include toxic limit concentration (Koch, 1982), soil sorption coefficient (Bahnick and Doucette, 1988), molar volume (Dai et al., 1998), octanol-water partition coefficient, melting point and water solubility (Siddhaye et al., 2004) and flash point (Patel et al., 2009). Knowing the shortcoming of GC methods that the required molecular groups to describe a chemical compound are not always available, Gani et al. (2005) utilised CI to develop a group contribution$^+$ (GC$^+$) model in addressing the issue of unavailability of molecular groups and the respective contributions in the GC model. The model is able to create the unavailable molecular groups and create the respective contributions for the estimation of property. Zeroth and first order CIs are used in GC$^+$ model to predict the contribution of the missing molecular groups (Gani et al., 2005).

As discussed previously, chemical product design problems can be considered as inverse property prediction problems. The design goal of the inverse property prediction problem is to determine the molecular structure of a chemical product from the desired product properties by using property prediction models. In some chemical product design problems, the desired target properties could not be estimated by using a single class of property prediction models. Hence, different classes of property prediction models are required for the estimation of different target properties in the design problems. Although property prediction models are useful in estimating target product properties, applying different classes of property prediction models together in an inverse molecular design problem is a computationally challenging task (Camarda and Maranas, 1999). This is because the mathematical formulations involved are exclusive to certain property prediction models. While GC methods estimate property by summing the frequency of each molecular groups occurring in the molecule times its contribution, estimations of TIs involve the operations on vertex-adjacency matrix (Raman and Maranas, 1998). Therefore, it is not easy to utilise different property prediction models by using a similar calculation method. Moreover, as second and third order molecular groups of GC methods are formed by using first order molecular groups as their building blocks, it is challenging to consider the property contributions from second or third order molecular groups without the knowledge of the complete molecular structure. In addition, the inverse relationships between TIs result in high degeneracy in the approach. This means there could be many possible molecular structures for a specific solution. Hence, this approach is unable to guarantee a unique and distinctive molecular structure as a final solution. Furthermore, most of the property prediction models are non-linear in nature. The nonlinearity of the property prediction models leads to the formulation of MINLP model, which requires exhaustive computational effort to solve. All of these aforementioned limitations make it difficult to utilise different classes of property prediction models in an inverse molecular design problem.

2.5. Molecular Signature Descriptor

To overcome the abovementioned problems and utilise different classes of property prediction models simultaneously in a design problem, a descriptor known as molecular signature descriptor is utilised (Visco et al., 2002). The signature is a systematic coding system to represent the atoms in a molecule by using the extended valencies to a pre-defined height. The relationship between a TI and its signature can be represented in Equation (2.5):

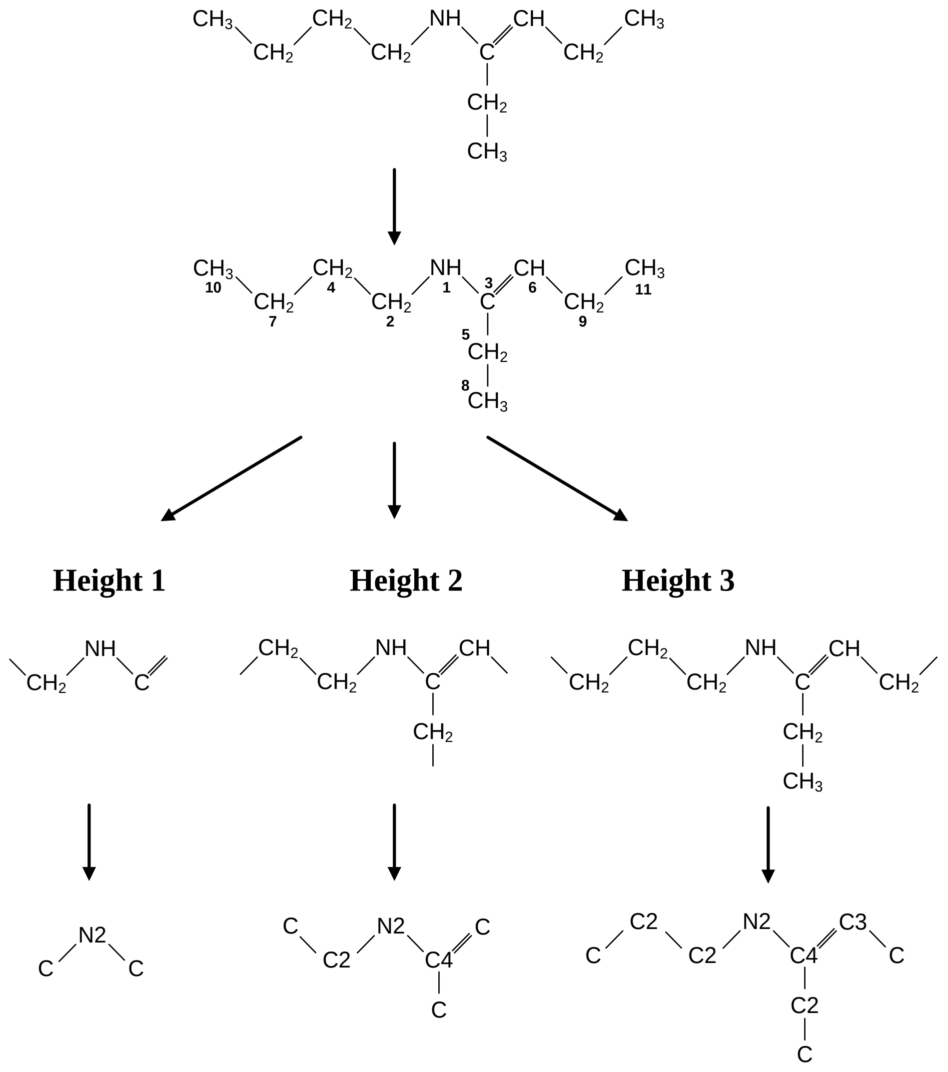
$$\mathrm{TI}(G) = u\,{}^{h}\alpha_G \cdot \mathrm{TI}[\mathrm{root}({}^{h}\Sigma)] \tag{2.5}$$

Here, ${}^{h}\alpha_G$ is vector of the occurrence number of each signature of height h, TI[root (${}^{h}\Sigma$)] is the vector of TI values for each signature root while u is a constant specific to TI. Equation (2.5) can be represented in terms of number of appearances of signatures by using Equation (2.6) as shown below.

$$\mathrm{TI} = \sum_{d=1}^{N} {}^{h}\alpha_d L_d \tag{2.6}$$

In Equation (2.6), α is the occurrence number of each signature of height h while L is the TI values for each signature root. Signature of a molecule can be obtained as a linear combination of its atomic signatures by representing a molecule with atomic signatures. As signature descriptor carries information of their neighbouring atoms, it is related to the rest of the building blocks in the molecule while representing individual building block for a complete molecule. Therefore, TIs can be described by using molecular signature (Faulon et al., 2003).

To utilise molecular signature descriptor, the molecular structures of chemical products are represented in terms molecular signatures, which serve as the building block of the molecule. Figure 2.5 shows how signature for a molecule is formed. The procedure for obtaining the atomic signature of atom



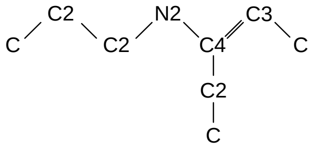
Atomic signature at:

Height 1	N2(CC)
Height 2	N2(C2(NC)C4(=CCN))
Height 3	N2(C2(N2(CC)C1(C))C4(=C3(=CC)C1(C)N2(CC)))

Figure 2.5: Illustration of atomic signatures up to height 3

N up to height 3 in the molecule as shown in Figure 2.5 is explained as follows. To construct an atomic signature for an atom *x* (atom N in Figure 2.5) in a molecule, the molecule is first transformed into a molecular graph *G*, and the atoms in the molecule are labelled/numbered to distinguish them from each other. The atomic signature of a distance *h* from *x* can be represented as a subgraph containing all atoms that are at height (distance) *h* of *x* in the molecular graph *G*. This subgraph is the atomic signature at different height, annotated as ${}^{h}G(x)$. For example, since signatures up to height 3 are constructed, all the atoms at height 3 from atom N are extracted, as shown in Figure 2.5. To obtain signature of height 1, only the atoms bonded to atom N (atoms *y* for example/atom C no.2 and C no.3 in Figure 2.5) are considered; to obtain signature of height 2, atoms *y* and atoms bonded to atoms *y* (atoms *z* for example/atom C no.4, C no.5 and C no.6 in Figure 2.5) are included; to obtain signature up to height 3, all the atoms *y*, *z* and atoms bonded to atoms *z* (atom C no.7, C no.8 and C no.9 in Figure 2.5) are taken into account. By representing a molecule with atomic signatures, signature of a molecule can be obtained as a linear combination of its atomic signatures (Faulon et al., 2003; Visco et al., 2002). In Figure 2.5, it can also be seen that graph colouring has been used to differentiate between different types of atoms. Here, the graph colouring function used is the valency of each atom at all levels. A more detailed explanation is shown in Figure 2.6.

Molecule



Height 3 signature

Without colouring
N(C(N(CC)C(C))C(=C(=CC)C(C)N(CC)))

With colouring
N2(C2(N2(CC)C1(C))C4(=C3(=CC)C1(C)N2(CC)))

Figure 2.6: Molecular graph colouring of atomic signature

By writing the property prediction models in terms of signature, GC methods and TIs with different mathematical formulations can now be expressed and used on a common platform. Another important application of molecular signature descriptor is its ability to account for the contributions of second and third order molecular groups in property models developed based on GC methods. The procedure to identify the contributions of higher order molecular groups can be explained in Figure 2.7.

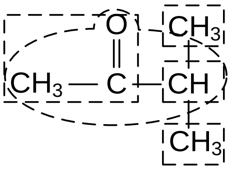
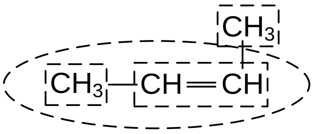
Molecule:		
Height three signatures:	C4(=O2(=C)C1(C)C3(CCC))	C3(=C3(=CC)C1(C))
First order molecular groups:	CH_3, CH, CH_3CO	CH_3, CH=CH
Corresponding second order molecular groups:	CH_3COCH	$CH_3CH=CH$

Figure 2.7: Expression of higher order molecular groups with signatures

In the first step, the signatures are generated based on first order molecular groups without considering higher order molecular groups. Signatures that carry higher order group contributions can then be identified among the generated signatures. For those identified higher order molecular groups, property contributions of the actual molecular groups as well as the contributions of the higher order groups are assigned. Figure 2.7 shows two examples of expressing higher order molecular groups by using signatures. After generating the height three signatures correspond to the first order molecular groups (shown in dotted squares), signatures which carry the contributions corresponding to the second order molecular groups (shown in dotted circles) are identified. With the available first order molecular groups, the signature distinctly represents second order molecular groups of CH_3COCH and $CH_3CH=CH$, as illustrated in Figure 2.7. Therefore, by utilising molecular signature descriptor, higher order molecular groups in GC methods can now be differentiated from the first order molecular groups and represented with signatures. More importantly, property models developed by GC methods can be applied together with property models developed from TIs in an inverse molecular design problem.

Based on this approach, it is possible to represent different types of structural descriptors on the same platform by utilising molecular signatures. Examples for the application of molecular signature descriptor are provided in Appendix A of this thesis. Since target properties in a product design problem might not be able to be estimated by using only a single class of property prediction models, the application of molecular signature allows the utilisation of different classes of property prediction models in a chemical product design problem. This is particularly useful for chemical product design problem which involve multiple target properties (Chemmangattuvalappil et al., 2010).

2.6. Current Status in Computer-Aided Molecular Design

Over the last decades, numerous CAMD techniques have been intensively developed and their applications include the design of different types of chemical products. For example, CAMD techniques are applied in the design of polymers. Vaidyanathan and El-Halwagi (1996) presented a systematic procedure for the synthesis of polymers with specific properties. By formulating the design problem as MINLP model and solving the model by using global optimisation technique, aliphatic and aromatic polymers with desired properties can be synthesised. Camarda and Maranas (1999) developed an algorithm with includes structure-property correlation of polymer repeat unit in an optimal polymer design problem. The optimisation problem is formulated as MINLP model. Zeroth and first order CIs are then employed for the design of polymers with optimal levels of macroscopic properties. Eslick et al. (2009) developed a computational molecular design framework for cross-linked polymer networks. By utilising QSPR in describing the relationship between the polymer and the desired properties, the developed work applies TS in determining the polymers with desired properties. Pavurala and Achenie (2014) proposed a CAMD approach for generating molecular structures of polymer candidates which have the potential to be effective polymer carriers in drug delivery. A MINLP optimisation technique is used for the generation of novel polymer structures which are not available in the literature.

In addition to polymer designs, the designs of refrigerant are also explored by using CAMD techniques. Duvedi and Achenie (1996) presented a mathematical programming-based CAMD approach for the design of environmentally safe refrigerants. By using augmented-penalty/outer-approximation algorithm in solving the MINLP model, compounds with optimum performance that meet molecular structural constraints, physical property constraints and process design limitations are designed. Sahinidis et al. (2003) proposed a MINLP model which can handle large number of preselected molecular groups and search for global optimal solution for an alternative refrigerant design problem. Property prediction models based on GC methods are utilised to calculate the target properties in the design of alternative refrigerants. The design of refrigerant is further explored by Samudra and Sahinidis (2013). The proposed CAMD approach identifies efficient refrigerant components that fulfil not only the process targets, but also environmental and safety guidelines such as biodegradability and lethal concentration. Other than the abovementioned works, there has been an extensive amount of effort being put in the design of industrial solvent. Karunanithi et al. (2009) proposed a systematic methodology in crystallisation solvent design of carboxylic acids by combining targeted bench scale experiments, CAMD approach and database search approach. Mac Dowell et al. (2011) applied statistical associating fluid theory for potentials of variable range (SAFT-VR) to describe the fluid phase behaviour in the modelling of amines and mixtures of amines with water and carbon dioxide. Struebing et al. (2013) proposed a systematic methodology that identifies improved reaction solvents by combining quantum mechanical computations of reaction rate constant with CAMD procedure. The developed methodology allows the identification of high performance solvent within a large set of possible molecules. Papadopoulos et al. (2014) presented an approach for the screening and selection of post combustion carbon dioxide capture solvents. In the presented approach, the optimal capture solvents are selected based on the performance criteria of several thermodynamics, reactivity and sustainability properties.

In addition to the design of polymers, refrigerants and solvents, the application of CAMD techniques is also further extended to design of pharmaceutical compounds. Siddhaye et al. (2000) utilised zeroth and first order CIs to relate the molecular structure to physical properties of pharmaceutical products while searching for the optimal molecule from the formulated MILP model. Siddhaye et al. (2004) developed a two-step method in designing novel pharmaceutical products by developing structure-based correlations using zeroth and first order CIs for physical properties and solving the developed MILP formulation in search for optimal solution. Harini et al. (2013) presented a review of the available literatures on computational schemes for rational solvent design focusing on solvent extraction and crystallisation in pharmaceutical industry. Properties of interest and the property prediction methods available for the estimation of those properties are discussed and reviewed in the paper.

Furthermore, the design of working fluids for organic Rankine cycle (ORC) is investigated. Design approach on ORC working fluid has first been presented by Papadopoulos et al. (2010). The presented approach utilises

CAMD and process optimisation techniques for the generation of optimum working fluid candidates with respect to important economic, operating, safety and environmental indicators. Lampe et al. (2014) presented a framework for the design of an ORC working fluid. The presented work applies continuous-molecular targeting approach (CoMT-CAMD) approach to integrate the selection of working fluid with process optimisation into a single optimisation problem in designing process and working fluid for a geothermal ORC. Recently, the design of ionic liquids (ILs) via CAMD techniques has also been intensively reported. For instance, McLeese et al. (2010) presented an approach for ILs design which includes the development of QSPR for target properties and searching for optimal solution by using combinatorial optimisation approach. Karunanithi and Mehrkesh, (2013) proposed a computer-aided IL design framework to design and select an optimum structure for IL via GA and problem decomposition approach. As only limited structure-property correlations are available, most of the current research works on IL are focusing on the development of such correlations for physical and chemical properties estimation of IL.

2.6.1. Integrated Process and Molecular Design

In chemical product design problems, chemical products are usually designed on the basis of chemical components. In such cases, the design goal is to identify the chemical component that possesses certain properties that gives the required functionalities. In addition, there are also situations where the main purpose of a chemical product design process is to design a product that drives a particular process. In such situations, the focus is emphasised on the process performance which is driven by the chemical product. Traditionally, process design and molecular design have been decoupled and treated as two separate problems with little or no interactions between both process and molecular design approaches. This results in inefficient or suboptimal solution while solving a process and product design problem. For example, during a separation process design, the solvent is usually selected from a list of pre-defined potential components. Thus, the performance of the process is limited to the performance of the listed components. In contrary, during the design of a chemical product, the target properties for the product are usually decided by following design heuristics or expert judgments with limited input from the perspective of process design. This often results in the generation of suboptimal product. In order to bridge the gap and overcome the limitations caused by solving the process and molecular design problems separately, Eden et al. (2004) proposed a simultaneous approach by integrating the process design problem with molecular design problem. This enables the identification of the preferred product properties that provide optimum process performance without pre-deciding to any specific compounds during the solution step (Eden et al., 2004). In the proposed approach, molecular building blocks that form the chemical product are used as the input for molecular design problem while the desired process performance is fed into the process design problem. As both of the design problems are interlinked with each other, this can be considered as an integrated chemical process-product design problem where the process target values are used as the supporting information to design the product while the product target values provide additional input for the generation of process data. This can be shown in Figure 2.8 as follows.

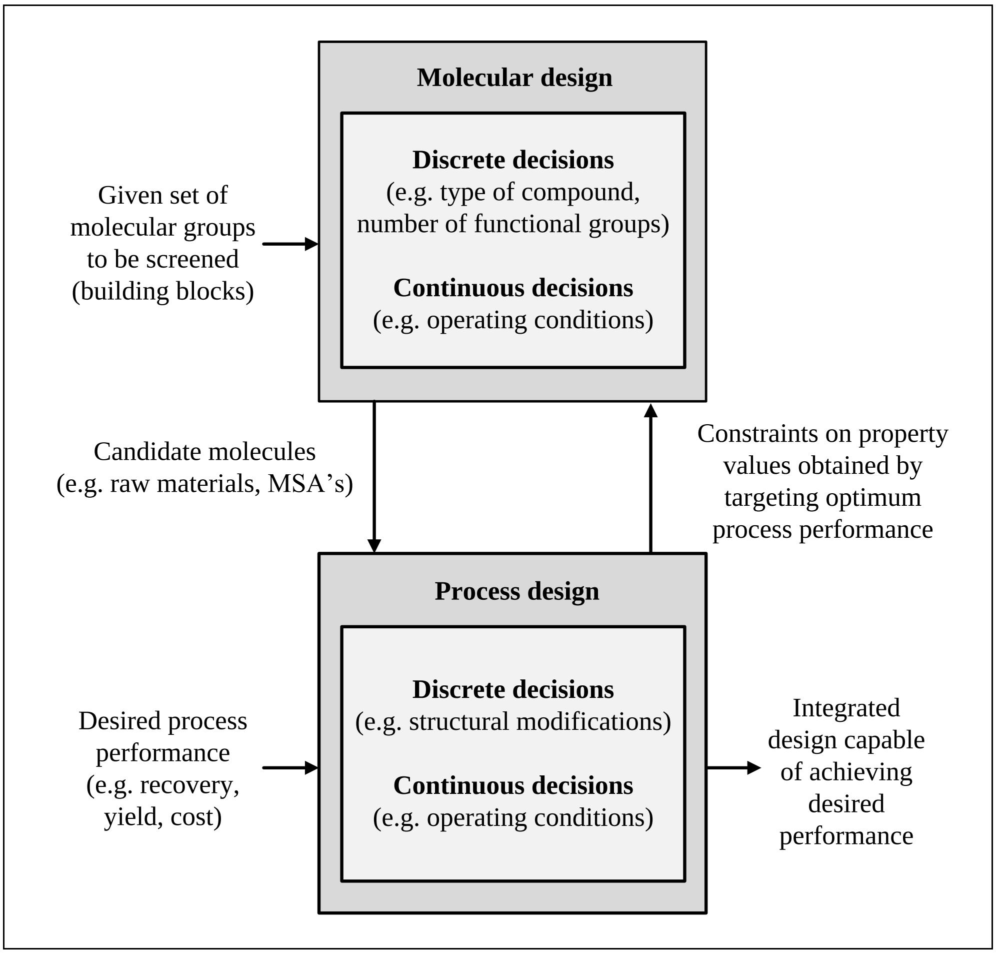


Figure 2.8: Integrated process-product design for reverse problem formulations

In order to expand the applicability of CAMD techniques in integrated process and product design problems, the concept of integrated process and product design approach has been widely applied and extended. For instance, Hostrup et al. (1999) presented a hybrid method which integrates mathematical modelling with heuristic approaches for solving the optimisation problem related to separation process synthesis and solvent design and selection. Lee et al. (2002) developed a combined nonlinear programming/thermodynamic approach in identifying the optimal refrigerant mixture and the optimal operating conditions for the refrigerant mixture in mixed-refrigerant systems. Eden et al. (2004) introduced a systematic framework for simultaneous solution of process and product design for separation design problems by utilising property clustering approach. The approach reformulated the conventional forward problems into two reverse formulations. The first reverse problem identifies the design targets by solving the reverse formulation problem while the second reverse problem designs the process and product by solving the identified design targets. Papadopoulos and Linke (2005) proposed a unified framework for integrated design of solvent molecules and process systems that allows the identification of solvent molecules based on process performance criteria. Later, Papadopoulos and Linke (2006) utilised a molecular clustering approach for the efficient incorporation of solvent design information into process synthesis in the integrated design of solvent and process systems. The proposed work adapted multi-objective optimisation approach in identifying Pareto optimal solvent candidates that are evaluated in the process synthesis stage. Karunanithi et al. (2006) presented a novel methodology in designing and selecting solvents and anti-solvents for solution crystallisation. In the presented work, the MINLP model is solved with the process and product performance objectives along with the consideration of potential recovery of the solvents. The same method is also adapted by Conte et al. (2011) in developing a virtual product-process design laboratory software for the design of formulated liquid products which is able to design/verify a formulated product.

Meanwhile, Bommareddy et al. (2010) developed an algebraic approach for product design problems by solving the process and molecular design problems as two reverse problems. The approach identifies the input molecules' property targets based on the desired process performance in the first reverse problem while determining the molecular structures that match the identified targets in the second reverse problem. Bardow et al. (2010) presented a CoMT-CAMD approach which utilises perturbed chain polar (PCP) statistical associating fluid theory equation of state for an integrated solvent and process design problem. By using SAFT to describe the fluid phase behaviour, the developed approach is applied in designing optimal solvent and process for carbon dioxide capture. Pereira et al. (2011) developed a computer-aided molecular and process design (CAMPD) for solvent and process design for high-pressure separation of carbon dioxide and methane based on SAFT-VR. By utilising SAFT-VR to represent the liquid and gas phases simultaneously, the work identifies the optimum solvent blend and operating condition with maximum purity and maximum net present value. Bommareddy et al. (2012) later presented an integrated framework by combining computer-aided flow sheet design (CAFD) and CAMD tools. The integrated framework addresses and evaluates the effect of changes involved in both product and process on each other while designing a chemical product.

2.6.2. Mixture Design

As mentioned previously, in chemical product design problems, there may be cases where all the desired properties cannot be met by a single component molecule. In such cases, an optimal mixture/blend of chemicals would be an ideal solution. Generally, these mixtures contain one (or more) liquid chemical as the main component and a set of additional chemicals which acts as additive components. The main component performs the key functionalities of the mixture while the additive components enhance the quality of the mixture. Hence, by mixing the main component with additive components, mixture which possesses target properties that satisfy the product needs can be designed. CAMD techniques are widely applied in the design of multi-component mixture. Klein et al. (1992) proposed an algorithm for the identification of solvent mixtures with desirable properties by integrating optimisation algorithms with CAMD techniques. Duvedi and Achenie (1997) applied mathematical programming approach in designing environmentally benign refrigerant mixtures. Churi and Achenie (1997) developed a MINLP approach which greatly reduces the required computational effort in identifying the optimal design of refrigerant mixtures for a two-evaporator refrigerant system. Sinha et al. (2003) presented a systematic framework for the design of cleaning solvent blends by solving a MINLP problem with simultaneous consideration of associated process constraints, property requirements and environmental restrictions. Karunanithi et al. (2005) proposed a decomposition-based solution strategy for the design of optimal solvent mixtures by formulating the design problem as MINLP problem and solving the problem as a series of subproblems. Solvason et al. (2009)

developed a visual mixture design of experiments by using property clustering techniques. In the work (Solvason et al., 2009), component properties are transformed to conserved surrogate property clusters described by property operators which can be mixed by following linear mixing rules. The mixture can then be identified by mixing the components until the mixture falls within the feasibility target region described by product and process property targets. Papadopoulos et al. (2013) presented a two-stage CAMD method for the synthesis and selection of binary working fluid mixtures used in ORC. The method identifies the first component with optimal mixture performance of the mixture in the first stage while designing the required matching molecules and selecting the optimum mixture concentration in the second stage. Yunus et al. (2014) developed a decomposition-based systematic methodology for the design of tailor-made blended products. The methodology designs the blended products by selecting the promising components, mixing the shortlisted components and verifying the target properties of the designed mixture.

2.6.3. Multi-objective Chemical Product Design

It is aware that the focus of most of the current product/molecular design methodologies is on designing molecule(s) with a single optimum target property. In order to design an optimal product, there can be situation where multiple product properties are needed to be considered and optimised simultaneously. As more than one design objective is involved, the design problems have to be solved as multi-objective optimisation problem. In general, the result of a multi-objective optimisation problem is a set of Pareto optimal solutions, referred as Pareto set. A solution for a multi-objective optimisation problem is Pareto optimal if no other solution that improves at least one of the objective functions without deteriorating the performance in any other objective function(s) can be found. In multi-objective decision-making problems, the Pareto optimality is a necessary condition in order to guarantee the rationality of a decision. Hence, the Pareto set represents all reasonable actions that a rational decision maker can take to obtain the optimal solution(s) in a multi-objective optimisation problem (Jiménez and Bilbao, 2009).

According to Kim and de Weck (2006), the most commonly used approach in solving multi-objective optimisation problem is the weighted sum method. This method can be explained mathematically as below (Fishburn, 1967).

$$A^{\text{weighted sum}} = a_1 A_1 + a_2 A_2 + \cdots + a_y A_y \tag{2.7}$$

In Equation (2.7), $A^{\text{weighted sum}}$ is the overall objective function while a_y is the weighting factor for the individual objective function A_y. This method converts multiple objectives into an aggregated scalar objective function by first assigning each objective function with a weighting factor, and later summing up all the contributors to obtain the overall objective function. Methods which utilise the concept of weightage allocation include goal programming technique (Charnes et al., 1955) and normal boundary intersection method (Das and Dennis, 1998). By using these techniques, each of the objectives is given a weight to differentiate their relative importance during the aggregation of the overall objective function. According to Ehrgott and Gandibleux (2002), the major drawback of these methods is that a decision maker is required in finding the appropriate weighting factor to be assigned to each objective. As a result, these methods tend to be biased as the weighting factors assigned to the objective are based on expert knowledge or personal subjective preferences of the decision maker (Korte, 2003).

In the context of chemical product design, while considering the design problems as decision-making problems, the weighting factor for each property are assumed to be deterministic/crisp when the conventional multi-objective optimisation methods are used (Deckro and Hebert, 1989; Deporter and Ellis, 1990). However, the relative importance of each property to be optimised in chemical design problems is not always definable. Hence, the significance of each product property to design an optimal product in a design problem is normally uncertain/fuzzy. Furthermore, these objectives might be incomplete, unclear or contradictory in nature.

2.6.3.1. Bi-level Optimisation

Bi-level optimisation approach is one of the potential approaches for solving multi-objective optimisation problems. Different from the general multi-objective optimisation approaches which perform optimisation of several objectives simultaneously, bi-level optimisation approach orders and arranges the objectives in a multi-objective optimisation problem to a hierarchy and solves them in a hierarchical order (Caramia and Dell’Olmo, 2008). Introduced based on static Stackelberg game with leader-follower strategy, the concept of bi-level optimisation is to obtain an optimised solution for the main optimisation problem while independently optimising the second level optimisation problem (von Stackelberg, 1952). In other words, in order to optimise the multi-objective decision-making problems, the objectives of the problems are categorised into upper-level objective (leader's objective) and lower-level objectives (follower's objective). The overall optimised solution for the problems can then be identified by first optimising the lower-level objective, followed by the optimisation of the upper-level objective. A general formulation of bi-level optimisation problem can be written as follows.

Objective function:

$$\text{Maximise/Minimise} \quad F(p,n) \tag{2.8}$$

Subject to:

$$G(p,n) \leq 0 \tag{2.9}$$

$$\text{Maximise/Minimise} \quad f(p,n) \tag{2.10}$$

Subject to:

$$g(p,n) \leq 0 \tag{2.11}$$

Here, the objective $F(p, n)$ is the upper-level objective function while $f(p, n)$ is/are the lower-level objective function(s). $G(p, n)$ and $g(p, n)$ are sets of property and structural constraints for upper-level and lower-level respectively. Problems that can be modelled by means of bi-level optimisation approach are those for which the variables of the upper-level problem are constrained by the optimal solution(s) of the lower-level problem (Caramia and Dell'Olmo, 2008). Bi-level optimisation approach has been utilised in various research fields. Takama and Umeda (1980) developed an algorithm for solving a water allocation and wastewater treatment problem. By using bi-level optimisation approach, two independent subsystems which concern about water allocation and control system reliability are solved and the overall optimal solution is determined. Cao and Chen (2006) proposed a two-level decision-making process in a capacitated plant selection problem under decentralised manufacturing environment. By considering opportunity cost and the independent relationship between the principal firm and the selected plants, an optimal solution is obtained by solving the two-level nonlinear programming model which are transformed and linearised into an equivalent single level model. Roghanian et al. (2007) adapted bi-level multi-objective programming model to solve a supply enterprise-wide chain planning problem which considers market demand, production capacity and resources availability for each plant. Later, Aviso et al. (2010b) presented a bi-level fuzzy optimisation model to explore the effect of charging fees for the purchase of freshwater and the treatment of wastewater in a water exchange network of an eco-industrial park.

2.6.3.2. Fuzzy Optimisation

In addition to bi-level optimisation approach, fuzzy optimisation approach is another commonly utilised multi-objective optimisation approaches in solving multi-objective decision-making problem. In order to solve a decision-making problem, fuzzy set theory was developed by Zadeh

(1965). As the theory systematically defines and quantifies vagueness and uncertainty, it is possible to solve problems which require decision-making under fuzzy environment. Bellman and Zadeh (1970) developed fuzzy optimisation approach that is able to select the preferred alternative in a fuzzy environment by solving an objective function on a set of alternatives given by constraints. Zimmermann (1976) then adapted fuzzy set theory into linear programming problems by solving the problems under fuzzy goals and constraints. Later, Zimmermann (1978) extended the approach to address linear programming problems which involve multiple objectives. This extended fuzzy optimisation approach integrates several objectives into a single objective and solves the overall objective based on the predefined fuzzy limits to obtain an optimised solution in a multi-objective optimisation problem.

In order to utilise fuzzy optimisation approaches, the objectives in a multi-objective optimisation problem can be written as fuzzy optimisation models, which can be described by their membership function. These membership functions represent the relationships between the degree of satisfaction of the objectives (λ) and the objective values within the target ranges. In general, the fuzzy membership functions can be categorised into maximum, minimum, trapezoidal and triangular membership functions (Zimmermann, 2001). The different types of fuzzy membership functions are shown in Figure 2.9.

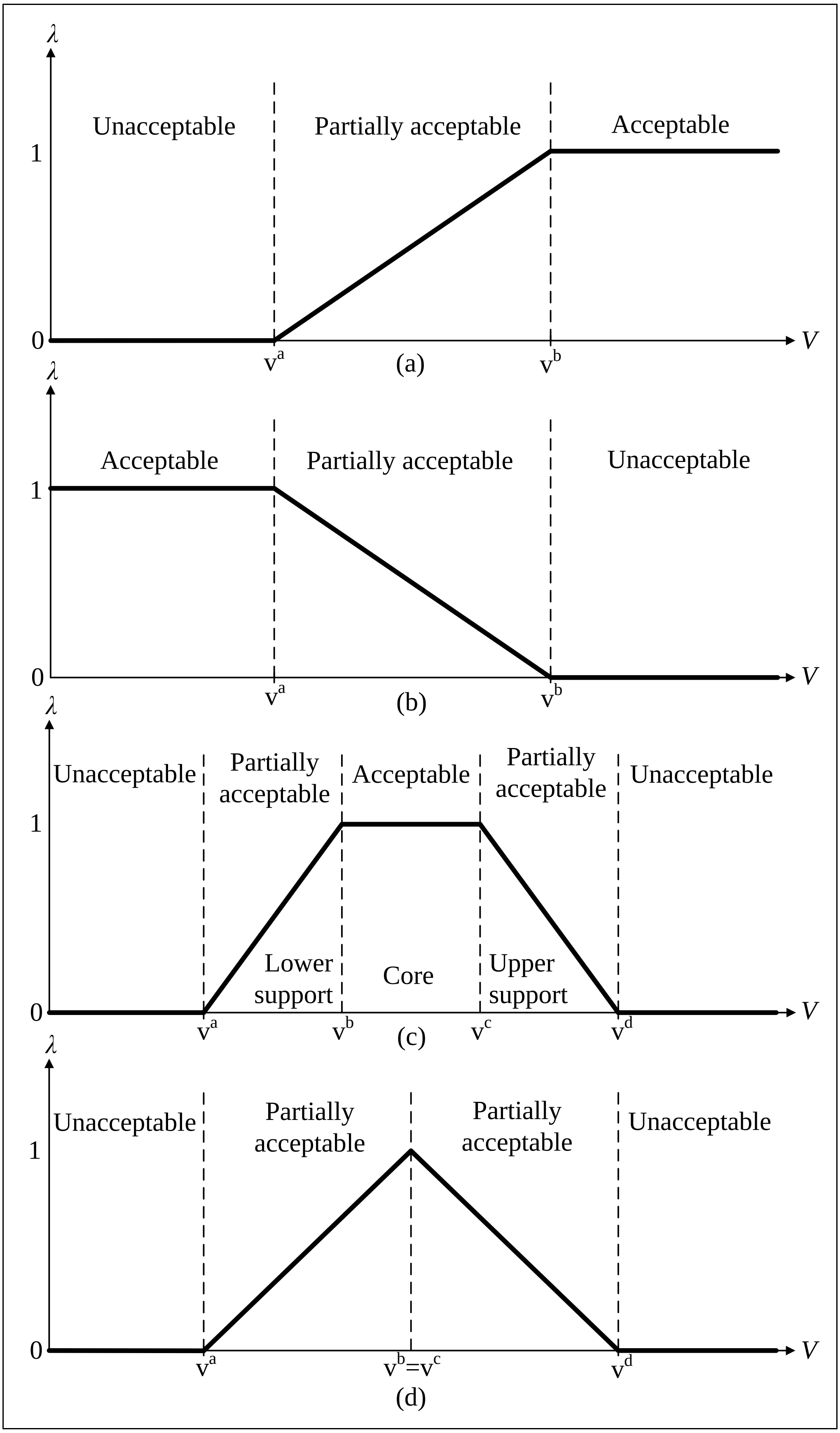


Figure 2.9: Fuzzy membership functions for: (a) maximising; (b) minimising; (c) trapezoidal-shaped; (d) triangular constraints

In Figure 2.9, v^a, v^b, v^c, and v^d are different values which can be used to represent different target ranges for the objective *V*. As shown in Figure 2.9 (a) and (b) respectively, within a target range bounded by v^a and v^b, the maximum fuzzy membership function is used for objectives where higher values are preferred while minimum fuzzy membership function is utilised for objectives where lower values are desirable. Objectives where the values are preferred to fall within a certain target range can be modelled as trapezoidal fuzzy membership functions, as shown in Figure 2.9 (c). The trapezoidal fuzzy membership function is characterised by its core and supports. The core (bounded by v^b and v^c) represents the target range of highly plausible values while the supports which consist of lower support (bounded by v^a and v^b) and upper support (bounded by v^c and v^d) cover the values that are at least marginally plausible. When the objective value of v^b in a trapezoidal fuzzy membership function equals to the value of v^c, the objective can be modelled as triangular fuzzy membership function, as shown in Figure 2.9 (d).

In fuzzy optimisation approaches, by writing the objectives in a multi-objective optimisation problem as fuzzy membership functions, trade-off between the objectives can be introduced. Therefore, an optimal compromise solution can be obtained by solving the multi-objective optimisation problem. Fuzzy optimisation approaches are useful to address the vagueness and ambiguity in multi-objective optimisation problems due to the incompleteness and unavailability of relevant information. In general, vagueness is associated with the difficulty of making precise distinction. For example, an objective is vague if it cannot be delimited by a target range. On the other hand, ambiguity is associated with one-to-many relations. For instance, a situation is ambiguous when there are two or more alternatives such that the selection between them is left unspecified (Klir, 1987). In order to address the vagueness in a multi-objective decision-making problem, fuzzy mathematical programming developed by Bellman and Zadeh (1970) is utilised to treat the decision-making problem under fuzzy goals and constraints. The fuzzy goals and constraints represent the flexibility of the target values of the objectives and the elasticity of the constraints in order to obtain an optimal solution under fuzzy environments. This type of fuzzy mathematical programming is called flexible programming. The second type of fuzzy mathematical programming treats the ambiguity of the coefficients of objective and constraints in a multi-objective decision making problem. Dubois (1987) introduced inequality indices between fuzzy coefficients based on possibility theory. As the fuzzy coefficients can be regarded as possibility distributions on coefficient values, this type of fuzzy mathematical programming is called possibilistic programming. The last type of fuzzy mathematical programming treats the vagueness and ambiguity of fuzzy coefficients in a multi-objective decision-making problem. This can be address by using the fuzzy mathematical model first developed by (Negoita et al., 1976). The model represents the vagueness as fuzzy satisfactory region and a fuzzy function value is required to be included in the given region. The developed fuzzy mathematical programming is called robust programming. Inuiguchi and Ichihashi, (1990) later extended the flexible programming into fuzzy coefficients case based on possibility theory to address both vagueness and ambiguity in a multi-objective decision-making problem. In addition to addressing the vagueness and ambiguity, fuzzy optimisation approaches are suitable for cases where the objectives in a multi-objective optimisation problem are contradictory (Liang et al., 2012).

Fuzzy optimisation approaches have been widely extended and applied in numerous industries and research disciplines. One of the widely utilised approaches is max-min aggregation approach (Zimmermann, 1983, 1978). Tan et al. (2009a) utilised max-min aggregation approach and developed a fuzzy multi-objective approach in determining optimal bioenergy system configuration while simultaneously considering the land use, water and carbon footprints. Aviso et al. (2010) applied the approach in fuzzy mathematical programming to address the contradictory objectives from several decision makers while designing eco-industrial water exchange networks. Later, Kasivisvanathan et al. (2012) adapted the approach to retrofit a palm oil mill into a sustainable biorefinery which fulfils the conflicting objectives of economic performance and environmental impact. Andiappan et al. (2014) utilised fuzzy optimisation approach in developing an integrated biorefinery which simultaneously address and optimise the contradicting objectives of economic performance, environmental impact and energy requirement of the biorefinery.

In addition to max-min aggregation approach, two-phase approach developed by Guu and Wu (1999, 1997) is also widely applied. Liang (2009) developed a two-phase fuzzy mathematical programming approach to simultaneously minimise project cost, completion time and crashing cost in a project management decision problem. Aviso et al. (2011) presented an approach to design eco-industrial resource conservation networks while considering individual fuzzy goal of participating plants in the presence of incomplete information. Lu et al. (2012) proposed an inexact two-phase fuzzy programming approach for municipal solid waste management where solution with high satisfactory level is obtained through relaxation of objective functions and constraints. Ng et al. (2013a) incorporated the approach in synthesis of an integrated biorefinery in optimising economic, environmental, inherent safety and inherent occupational health performances simultaneously. Later, Ng et al. (2014) adapted two-phase approach in solving a multi-objective chemical product design problem to identify the optimal product in terms of multiple target properties.

2.6.4. Robust Chemical Product Design

CAMD techniques utilises property prediction models to predict, estimate and design molecules which possess a set of required target properties (Harper and Gani, 2000). In general, property prediction models are developed from regression analysis over a set of compounds. In the context of chemical product property prediction, regression analysis is a process of estimating the relationship between the product property and the TI/molecular groups from GC methods that correlate with each other. According to Kontogeorgis and Gani (2004), development of property models is an iterative process of theory/hypothesis definition, model equations solving, validation of model against experimental data, and modification of theory/model parameters if required. While providing relatively simple and accurate methods in property predictions, it is noted that these property prediction models are approximate in reality, and there are always some discrepancies between experimental measurements and model predictions. The disagreement between the prediction and experimental values applies to all property estimation methods such as factor analysis, pattern recognition, molecular similarity, different TIs and GC methods (Maranas, 1997a). From the cyclic process of property prediction models, it can be said that the accuracy of a model is affected by the uncertainties, which can arise from deficiency in theories or models and their parameters, and insufficient of knowledge of the systems.

It is noted that the effectiveness and usefulness of these property prediction models in estimating a property and eventually identifying the optimum molecule rely heavily on the accuracy of the property prediction models. In general, the performance or accuracy of property prediction models is evaluated and shown in terms of statistical performance indicators. Some of the commonly used pointers include standard deviation (σ), average absolute error (AAE), average relative error (ARE) and coefficient of determination (R^2). Traditionally, the accuracy of property prediction models is only used as an indicator of the models' ability in predicting the product properties or the expected error that the model might produce. As long as the property prediction models provide reasonable precision, the accuracy of the property prediction models is seldom taken seriously.

Few works have been published to address the issue of property prediction uncertainty. Attempt to analyse, address and improve the uncertainty of property prediction models have been carried out. For example, Maranas (1997b) presented a systematic methodology that quantifies property prediction uncertainty by using multivariate probability density distributions to model the likelihood of different realisations of the parameters of GC methods. The proposed work describes the disagreement between experimental measurements and GC predictions by recognising that the contribution of molecular groups to various properties is dependent of molecular structure around some nominal value, depending on the particular molecular structure. By imposing chance constraints in the developed methodology, optimal molecule can be identified through stochastic property matching or stochastic property optimisation formulation. The developed methodology is applied in solving different cases of polymer design problems (Maranas, 1997b, 1996). Kim et al. (2002) proposed the incorporation of uncertainty factor (discrepancy percentage between literature and experimental values) to define property prediction uncertainty of GC methods in solving a solvent selection problem. The developed approach utilises Hammersley stochastic annealing (HSTA) algorithm in tackling the problems of solvent selection under uncertainty and searching for reliable candidate solvents. The use uncertainty factor for the quantification of uncertainties in property prediction models is further extended by Xu and Diwekar (2005). The proposed optimisation framework uses and compares the performance of efficient genetic algorithm (EGA) and Hammersley stochastic genetic algorithm (HSGA) in solving the computer-aided solvent design problems. Folić et al. (2007) presented a method in assessing the impact of uncertainty in the developed hybrid experimental/computer-aided methodology for the design of solvents for reactions. The presented work applied global sensitivity methods to explore the uncertain parameter space in identifying the key parameters and the most likely solvent candidates in the solvent design problem.

While works have been presented in carrying out uncertainty analysis of property prediction models, most of the attention is focused in addressing property prediction uncertainty for property prediction models developed from GC methods. In addition, most of the developed approaches utilise stochastic programming approach in solving the design problem. According to Bertsimas et al. (2011), though stochastic programming approach provides comprehensive solution with consideration of probabilistically realised uncertainty, it often results in the formulation of multistage problem which can be computationally intensive. On the other hand, robust optimisation is suited for problems under uncertainty which the uncertainty model is deterministic. As robust programming is a single stage optimisation where the uncertainties are expressed as user-defined probability, there are no recourse action involve in the programming model. Hence, computational effort required in solving the design problem can be greatly reduced (Bertsimas et al., 2011).

2.7. Conclusions

Based on the literature review presented in this chapter, it is clearly shown that the synthesis and design of integrated biorefinery which focus on product design aspect have yet to be explored by many. In addition, rooms for improvement have been identified in the research area of CAMD. These research gaps provide opportunities for the development of approaches in synthesising integrated biorefinery with emphasis on product design aspects.

From the literature review, although there are numerous research works on the synthesis and design of integrated biorefinery, it is found out that the development of simultaneous process and product design of integrated biorefinery is still in its early stages. It is realised that most of the previous works do not consider customer needs in producing value-added products in integrated biorefinery. Most of the works have focused on process design aspects in designing an integrated biorefinery where the attention is mainly on identifying and designing the optimal processing routes that lead to the products without incorporating the product design aspects into the synthesis of biorefinery. Therefore, there is a need to fill the research gap by synthesising an integrated biorefinery that is able to produce value-added products that meet customer requirements. This can be achieved by integrating the design of integrated biorefinery with chemical product design.

In addition, other than optimising a single property while designing a chemical product, there are cases where more than one product property is considered important and required to be optimised simultaneously. As the traditional multi-objective optimisation approaches are mainly based on the weighting factors assigned by decision makers, these approaches tend to be biased. To address this problem, a systematic methodology for the design of chemical products which optimises multiple product properties simultaneously without any favouritism and prejudice is needed.

CAMD generally utilise property prediction models in predicting the product property and ultimately designing the optimum molecules. Most of the time, the optimality of product property is the only factor considered while designing optimal products by using CAMD techniques. However, it is noted that property prediction models are developed with certain accuracy and uncertainty. As the accuracy of property prediction models can affect the effectiveness of CAMD techniques in predicting the product properties, the effects of property prediction uncertainty have to be considered while applying CAMD techniques. Therefore, a comprehensive robust optimisation approach for chemical product design which considers the optimality of product properties as well as the inherent uncertainty of different classes of property prediction models is required.

Moreover, in many occasions, a single component/molecule product is insufficient to meet desired product needs. Therefore, mixture of chemicals would be required to address the product needs. In such cases, there exist an opportunity to explore the potential of designing an optimal mixture from biomass in an integrated biorefinery. Together with the abovementioned opportunities, these research gaps are further investigated and addressed in the following chapters.

CHAPTER 3

RESEARCH SCOPES AND METHODOLOGIES

3.1. Research Scopes

Based on the identified research gaps, this research work is divided into five main scopes with the intention to synthesise and design integrated biorefineries which focus on different aspects of chemical product design. The five research scopes to be explored and presented in this thesis are summarised as below:

i. Conceptual design for synthesis of chemical product from biomass in integrated biorefineries

   Due to the increase in the number of potential products, new reactions and technologies, determining of optimum chemical products and processing routes in an integrated biorefinery have become more challenging. Therefore, it is essential to consider product design aspects in the synthesis and design of integrated biorefineries. A conceptual framework is presented to design chemical products from biomass in an integrated biorefinery. The conceptual framework integrates different technologies and conversion pathways in an integrated biorefinery with product design techniques to convert biomass into valuable chemical products.

ii. Systematic methodology for optimal chemical product design in integrated biorefineries

The conceptual framework proposed in the previous research scope is further explored and extended in this scope. In order to synthesise and design an efficient integrated biorefinery, optimal chemical products in terms of target product properties as well as optimal conversion pathways based on different optimisation objectives (e.g. highest product yield, lowest environmental impact etc.) are required to be determined. A systematic optimisation approach that integrates chemical product design with chemical reaction pathway synthesis is developed to address this issue.

iii. Multi-objective optimisation approach for optimal chemical product design

The presented approaches for the design of optimal chemical products from biomass focus on the optimisation of a single product property. In order to design an optimal chemical product, it is aware that there are situations where multiple product properties are needed to be considered and optimised simultaneously. In cases where more than one product property is to be considered and optimised concurrently, the product design problems are required to be solved as multi-objective optimisation problems. The usual practise of weighted sum method in solving multi-objective optimisation problems tends to be biased as it relies heavily on heuristic and personal preferences. Hence, there is a need for an answer to identify optimal chemical products in multi-objective optimisation problems systematically without bias. A systematic multi-objective optimisation approach for the design of chemical products with optimal properties is developed to address this problem.

iv. Robust chemical product design via multi-objective optimisation approach

In general, the optimality of product property is the only factor considered while designing optimal products by using computer-aided molecular design (CAMD) techniques. However, it is noted that property prediction models are developed with certain accuracy and uncertainty. As the accuracy of property prediction models can affect the effectiveness of CAMD techniques in predicting the product properties, the effects of property prediction uncertainty have to be considered while applying CAMD techniques. A systematic multi-objective optimisation based chemical product design methodology is developed for the design of optimal chemical products. The optimal chemical products are designed by optimising the optimality of product properties while taking the effect of property prediction model accuracy into consideration.

v. Systematic methodology for optimal mixture design in integrated biorefinery

Most of the time, chemical products exist as mixtures of different components rather than single component products since mixtures provide a good mix of target properties which are unattainable by individual chemical components. In this respect, product and process design in an integrated biorefinery would be a challenging task. A systematic optimisation approach is developed to convert biomass into optimal mixture in terms of multiple product properties via optimal conversion pathways based on different optimisation objectives (e.g. highest product yield, lowest environmental impact etc.).

3.2. Research Methodology

Based on the identified research gaps, various process system engineering (PSE) approaches, CAMD techniques and mathematical optimisation approaches are utilised in addressing the proposed research scopes. Extensive literature review on the technologies and conversion pathways of integrated biorefineries as well as the potential chemical products to be produced from biomass is to be carried out. By using the information gathered from literatures, a chemical reaction pathway map (CRPM) will be developed to identify the conversion pathways for the production of chemical products which meet the product needs. Mathematical optimisation approach will be utilised to identify optimal conversion pathways for the production of optimal chemical products in terms of target product properties.

In addition, various multi-objective optimisation approaches will be developed for the design of optimal chemical products in terms of multiple target product properties. These approaches are targeted for chemical product design problems where multiple target product properties are to be considered and optimised simultaneously as well as chemical product design problems where the property prediction model accuracy is to be taken into account.

As the research progresses, approaches for the identification of optimal products, optimal biomass conversion pathways as well as optimal products in terms of multiple target product properties will be developed. Based on these approaches, a methodology for the design of optimal mixture in integrated biorefineries will developed to identify optimal mixture in terms of multiple target product needs and the optimal conversion pathways for the production of the mixture in terms of different production objectives. Figure 3.1 shows the graphical representation of the research strategy.

3.2.1. Conceptual Design for Synthesis of Chemical Product from Biomass in Integrated Biorefineries

To convert biomass into valuable chemical products in an integrated biorefinery, a conceptual framework is introduced by integrating chemical reaction pathways in a biorefinery with product design techniques. For a chemical product with specified product needs, the product needs are expressed in terms of measurable product properties. To identify the

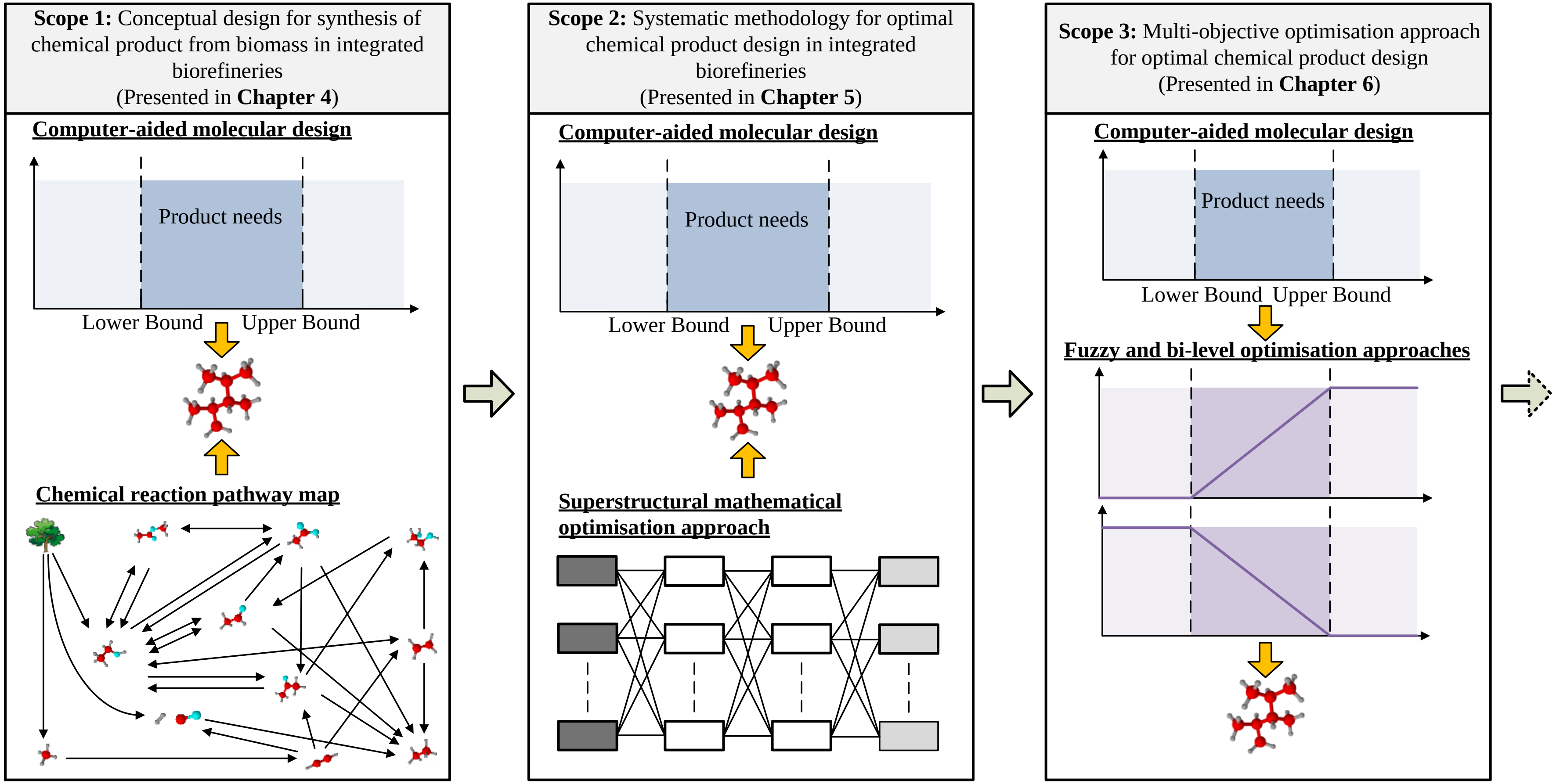


Figure 3.1: Research methodology

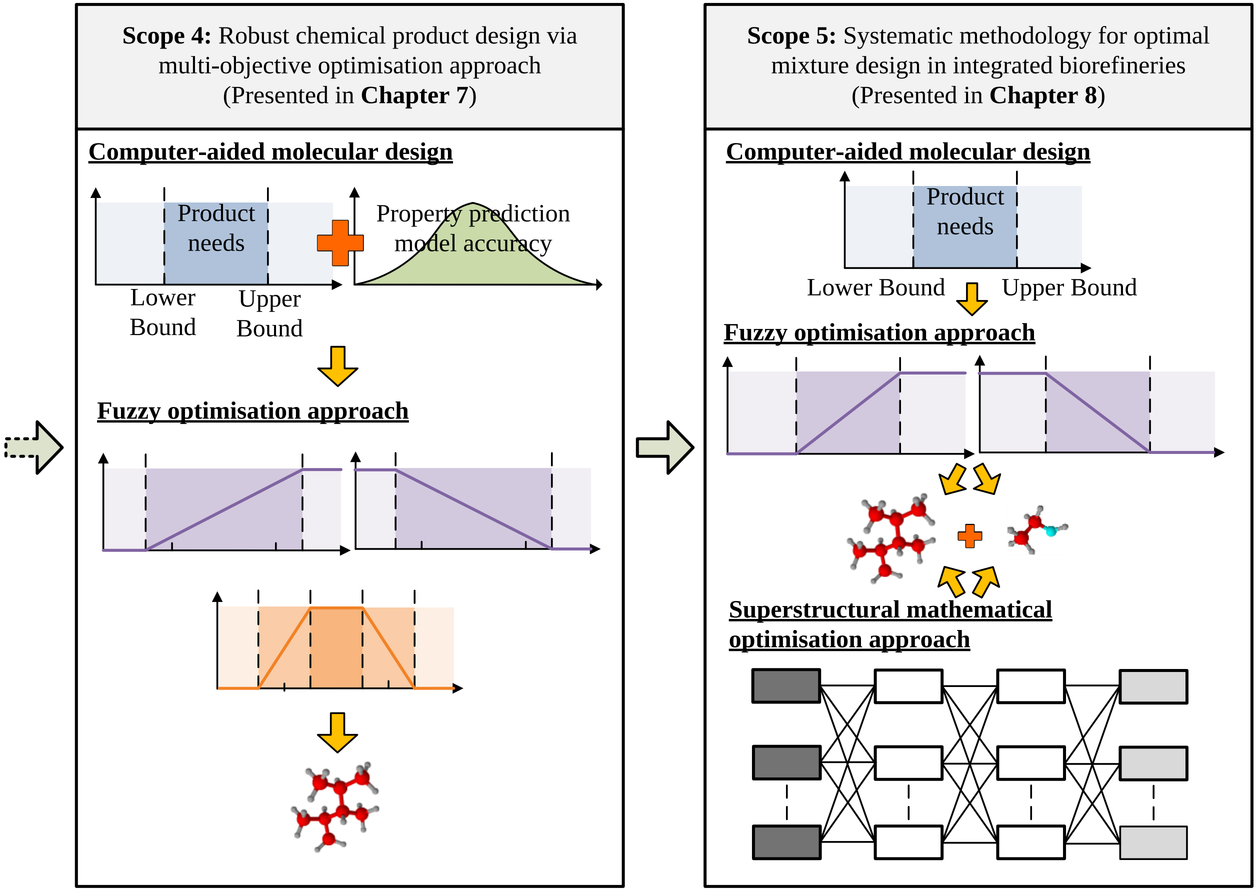


Figure 3.1: (continued) Research methodology

molecular structure of the product which fulfils the product needs, product properties can be estimated by using different classes of property prediction models. It is known that different types of structural descriptors can be represented on the same platform by utilising molecular signature descriptor. Hence, in order to utilise different classes of property prediction models together in a chemical product design problem, signature based CAMD techniques are adapted. This is followed by the identification of reaction pathways that convert biomass into the identified chemical product, which is done by using CRPM. This is accomplished by categorising the potential chemical products based on their functional groups and selecting the pathways from CRPM based on the objective of chemical reaction pathway selection.

3.2.2. Systematic Methodology for Optimal Chemical Product Design in Integrated Biorefineries

The conceptual framework proposed in the previous scope is extended for the design of optimal chemical products in integrated biorefineries. A systematic two-stage optimisation approach is developed to design optimal chemical products from biomass. In the presented approach, optimal chemical products in terms of target product properties are determined via signature based CAMD techniques. In order to systematically identify the optimal conversion pathways that convert biomass into the identified chemical products, superstructural mathematical optimisation approach of chemical reaction pathway synthesis is utilised. Superstructural mathematical optimisation approach provides systematic mean to identify the optimal conversion pathways by optimising and selecting the conversion pathways based on different optimisation objectives. Hence, by integrating CAMD techniques with superstructural mathematical optimisation approach, the systematic two-stage optimisation approach identifies the optimal chemical products in terms of target product properties as well as the optimal conversion pathways in an integrated biorefinery.

3.2.3. Multi-objective Optimisation Approach for Optimal Chemical Product Design

To design an optimal chemical product where multiple product needs are considered and optimised, a multi-objective optimisation approach is proposed. As discussed previously, the relative importance of each target property to be optimised in chemical product design problems is not always definable. Furthermore, the target property ranges of the design problems might be incomplete or unclear. In order to solve multi-objective chemical product design problems under such situations, fuzzy and bi-level optimisation approaches are incorporated into signature based CAMD techniques in developing the multi-objective optimisation approach. By utilising signature based CAMD techniques, different classes of property prediction models are expressed in terms of molecular signatures and utilised in a chemical product design problem. By incorporating fuzzy optimisation approach into the product design methodology, property weighting factors in a multi-objective optimisation problem are able to be addressed systematically without predefining the weighting factors. Meanwhile, bi-level optimisation approach is utilised to determine the target property ranges which are undefined. Thus, optimal chemical products can be identified by solving the multi-objective optimisation problem. While solving the chemical product design problem, max-min aggregation approach is first applied to optimise the product properties. Two-phase approach is then employed to discriminate the chemical products for cases where more than one chemical product possesses similar least satisfied property.

3.2.4. Robust Chemical Product Design via Multi-objective Optimisation Approach

In order to design a chemical product with consideration of the accuracy of property prediction model, a systematic multi-objective optimisation approach is developed. The approach is developed for the design of optimum chemical products by optimising property superiority with consideration of property robustness. Property superiority is quantified by property optimality of the chemical product. Meanwhile, the effect of the accuracy of property prediction models is measured as property robustness. In the developed approach, property robustness is expressed by the standard deviation of a property prediction model, which is a measure of average variation between the experimental data and the estimated value of product property by using the property prediction model. Signature based CAMD technique is adapted to identify the optimal product in terms of multiple target product properties. Fuzzy optimisation approach is applied to address and trade off property superiority and robustness simultaneously. Therefore, optimal chemical product is designed based on how much the product satisfies the criteria of property superiority and robustness.

3.2.5. Systematic Methodology for Optimal Mixture Design in Integrated Biorefineries

In chemical product design problems, there may be cases where the design of mixture is preferred as mixtures provide a good mix of target properties which are unattainable by single component chemical products. To identify the optimal conversion pathways in an integrated biorefinery which convert biomass into an optimal mixture in terms of target product properties, a two-stage optimisation approach is developed. In the first stage, the optimal mixture in terms of target product properties is designed via signature based CAMD techniques. The main component of the mixture is first identified from the target properties. This is followed by the design of additive components to form an optimal mixture with the main component based on the desired product properties. Fuzzy optimisation approach is incorporated into the CAMD techniques to address the consideration and optimisation of multiple product properties during the mixture design stage. Once the optimal mixture is identified, the second stage determines the optimal conversion pathways via superstructural mathematical optimisation approach. With such approach, the optimal conversion pathways for the production of optimal mixture can be determined based on different optimisation objectives.

3.3. Conclusions

The identified research gaps have been divided into five research scopes, as presented and discussed in this chapter. These research scopes will be discussed and addressed in detail in the following chapters by using the proposed research methodologies with respective case studies.

CHAPTER 4

CONCEPTUAL DESIGN FOR SYNTHESIS OF CHEMICAL PRODUCT FROM BIOMASS IN INTEGRATED BIOREFINERIES

4.1. Introduction

With the awareness of global environmental issues and the search for a sustainable and renewable energy as an alternative source for fossil fuels, biomass is seen as a potential solution. An integrated biorefinery is used for the conversion of biomass into energy and a wide range of value-added products in order to ensure a sustainable utilisation of biomass. However, due to the increase in the number of potential products, new reactions and technologies, determining of chemical products and processing routes in an integrated biorefinery have becoming more challenging. Therefore, it is essential to develop a systematic approach to address the abovementioned issues. In this chapter, a conceptual approach which integrates computer-aided molecular design (CAMD) techniques with chemical reaction pathway synthesis is developed to design biochemical products from biomass. Based on the presented approach, biochemical products that meet the product needs can be determined via signature based molecular design techniques. In addition, chemical reaction pathways that convert biomass into the biochemical products can be determined. A case study of biofuel production from palm-based biomass is solved to illustrate the proposed approach.

4.2. Integration of Molecular Design Techniques and Chemical Reaction Pathway Synthesis

In order to identify the conversion pathways that convert biomass into value-added products that fulfil the product needs, a two-stage conceptual approach for integrating molecular design techniques with chemical reaction pathway synthesis is presented. In the first stage, biochemical products which meet the customer requirements are identified via molecular design technique. Next, a chemical reaction pathway map (CRPM) is developed and used to determine the conversion pathways to produce the identified products. Figure 4.1 shows the integration of the synthesis of integrated biorefinery with biochemical product design by using CRPM and molecular design techniques.

As shown in Figure 4.1, in order to utilise this two-stage conceptual approach, the biochemical products that meet the product needs are first identified in the first stage of the approach. The product needs are translated into a set of measurable physical properties. This set of physical properties is used as property constraints which represent product specifications. In order to form a complete molecular structure of the product, structural constraints are applied in the molecular product design problems together with property constraints. The biochemical products which satisfy property and structural constraints are identified by utilising signature based molecular design technique developed by Chemmangattuvalappil et al. (2010). Once the biochemical products are determined, identification of the chemical reaction pathways that convert biomass into the products can be analysed and

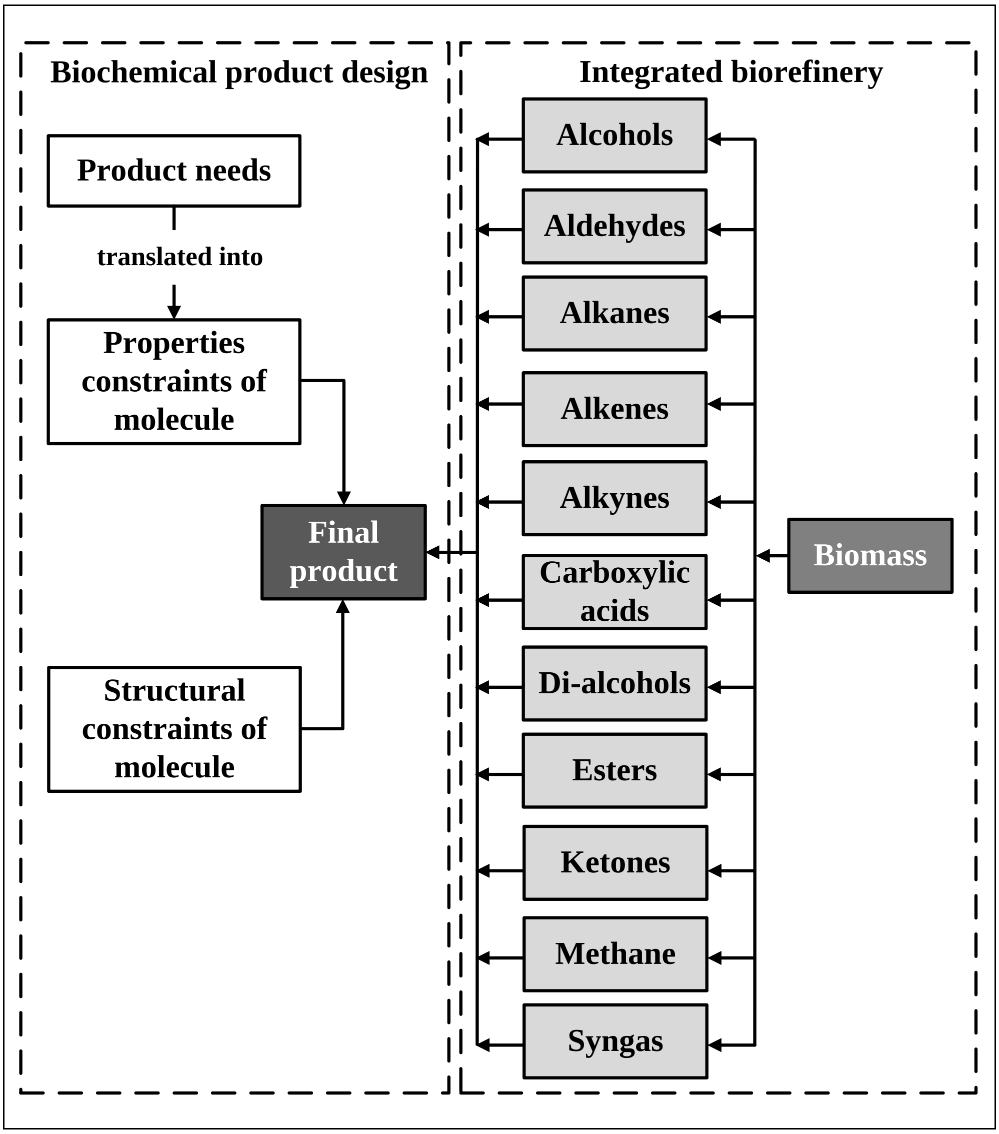


Figure 4.1: Integration of integrated biorefinery and molecular product design

determined in the second stage of the conceptual approach. As shown in Figure 4.1, based on the result from the design of biochemical product, biomass can be converted into different products (alcohol, alkane, carboxylic acid etc.) in an integrated biorefinery. In order to identify the chemical reaction pathways that convert biomass into the identified biochemical products, a CRPM is developed as a representation of an integrated biorefinery based on the available chemical reactions and technologies. By using the CRPM, the reaction pathways that convert biomass into the biochemical products identified in the first stage of the conceptual approach can be determined. By integrating molecular product design techniques with the synthesis of integrated biorefinery, this conceptual approach provides chemical reaction pathways that convert biomass into biochemical products that fulfil product needs. The proposed two-stage conceptual approach is further discussed in the following subsections.

4.2.1. Design of Biochemical Product: Signature Based Molecular Design Technique

In this stage, the biochemical products are designed by utilising signature based molecular design techniques. The step by step procedure involved in the optimal product design is represented in a flowchart as shown in Figure 4.2. Note that the procedure is designed specifically for product design problems where different classes of property prediction models are used and the molecular structure of the product is represented by using molecular signature descriptor. The details of each step are discussed as follows.

4.2.1.1.Define Objective for the Product Design Problem

The first step in solving a product design problem is to define the objective. This is done by identifying the product needs. These product needs

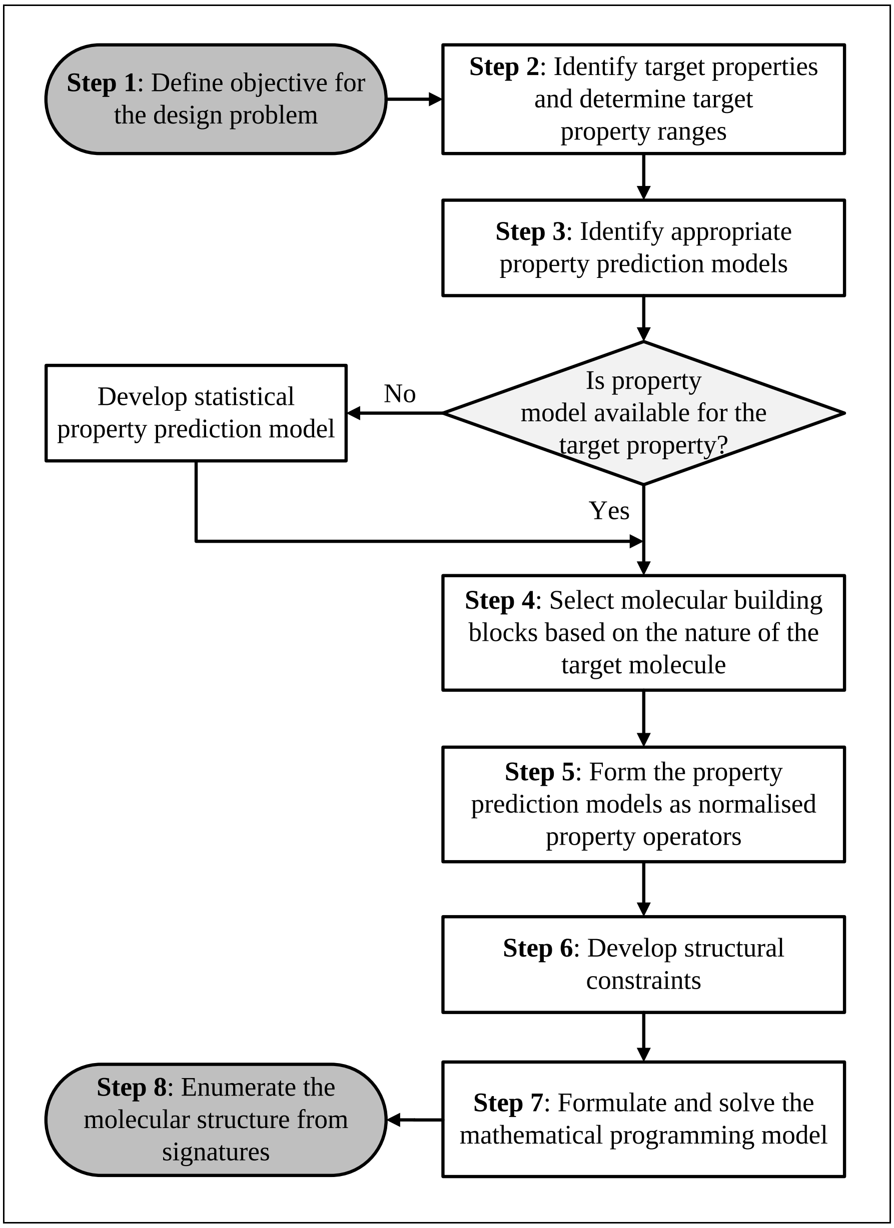


Figure 4.2: Procedure for solving a chemical product design problem

can be extracted from the operating conditions of an industrial process or from the customer requirements. The product needs cover the physical properties which are responsible for a particular functionality of the product as well as the properties that make sure that the product fulfils the environmental and safety regulations. For example, in order to design an effective refrigerant, the performance of the refrigerant should be high while the power requirement for the refrigerant is preferred to be low. In addition, it has to make sure that the refrigerant is not harmful to the environment and safe to be used. Hence, the objective of the design problem can be the optimisation of any target property or performance criterion.

4.2.1.2.Identify Target Properties and Determine Target Property Ranges

Once the product needs and the objective of the product design problem have been identified, the identified descriptive product needs are translated into measurable physical properties. For example, during the design of refrigerant, the performance of the refrigerant can be expressed as volumetric heat capacity while the power requirement of the refrigerant can be measured as viscosity. The volumetric heat capacity should be high so that the amount of refrigerant required is reduced for the same refrigeration duty whilst the viscosity is preferred to be low to achieve low pumping power requirement. On the other hand, ozone depletion potential (ODP) and median lethal dose/concentration (LD_{50}/LC_{50}) can be measured to ensure that the designed refrigerant is environmentally benign and safe to be used. These target properties are then expressed as property specifications, which can be written as a set of property constraints bounded by upper and lower limits. The target property ranges can be fixed based on the customer or process requirements. For example, while designing a gasoline blend, the Reid vapour pressure is designed to fall within 45 kPa and 60 kPa while the desired viscosity should fall within 0.30 cP and 0.60 cP. The property specifications for a product design problem can be generalised and shown in Equation (4.1).

$$v_p^{\mathrm{L}} \le V_p \le v_p^{\mathrm{U}} \qquad \forall p \in P \tag{4.1}$$

Here, p is the index for the target property, V_p is the target property value, v_p^{L} is the lower limit and v_p^{U} is the upper limit for the product target property. By following Equation (4.1), optimal solution in terms of target product properties is identified within the predefined target property ranges while solving a product design problem.

4.2.1.3.Identify Appropriate Property Prediction Models

After the identification of target properties from the product needs, property prediction models which estimate the target properties of the product can be identified. As this conceptual approach utilises signature based molecular design techniques, different classes of property prediction models such as property prediction models developed from group contribution (GC) method or topological indices (TIs) are utilised for the prediction of target properties. Hence, the target properties can be written as functions of property prediction models developed from GC method or TIs, as shown in the following equation.

$$\theta_p = f(\mathrm{GC/TI}) \qquad \forall p \in P \tag{4.2}$$

In Equation (4.2), θ_p is the property function corresponding to the target property p. For target properties where property prediction models are unavailable, models which combine experimental data and available property prediction models can be developed to estimate the respective target properties. These target properties can be represented as functions of other physical properties. The information of the physical properties can be obtained from the experimental data or predicted by using the available property prediction models. Therefore, by using these physical properties as the source, statistical property prediction models can be developed based on the correlation between the target properties and the physical properties using statistical models such as fitting regression model, factorial design etc.

4.2.1.4.Select Molecular Building Blocks

Suitable molecular building blocks for the product design problem are determined in this step. The molecular building blocks have to be chosen such that the properties and molecular structure of the new product are similar to the available product from where the molecular building blocks are selected. It is assumed that by designing a new molecule with the chosen molecular groups as building blocks, the designed product will possess the properties and functionalities of the desired product. For example, in order to design an alcohol solvent, molecular group -OH is chosen as one of the molecular building blocks as it is the functional group of alcohol. As the product design methodology employs signature based molecular design technique, signatures corresponding to the selected molecular groups are then generated.

4.2.1.5.Form Property Prediction Models as Normalised Property Operators

The next step is to express the property prediction models as normalised property operators. Normalised property operators are dimensionless property operators, which are required so that different target properties can be expressed and compared together on the same property platform (Shelley and El-Halwagi, 2000). According to Shelley and El-Halwagi (2000), property operators are functions of the original properties tailored to obey linear mixing rules. Hence, property operators will follow simple linear mixing rules regardless of the linearity of the original properties. Property specifications in Equation (4.2) can be written as normalised property operators as shown in Equation (4.3).

$$\Omega_p^{\mathrm{L}} \leq \Omega_p \leq \Omega_p^{\mathrm{U}} \qquad \forall p \in P \tag{4.3}$$

Here, Ω_p is the normalised property operator for the target property p, Ω_p^{L} is the lower limit and Ω_p^{U} is the upper limit for the normalised property operator. As signature based molecular design technique is employed in this developed methodology, normalised property operators are used to express molecules as linear combinations of atomic signatures.

4.2.1.6.Develop Structural Constraints

Apart from satisfying the property constraints, the targeted molecule should have a feasible and stable chemical structure which is formed from a collection of molecular signatures (Chemmangattuvalappil et al., 2010). Hence, structural constraints are generated based on graph theory principles in order to enable the formation of a complete molecule. Firstly, it is ensured that the generated molecule is complete without any free bond in the structure

(Trinajstić, 1992). This can be explained mathematically by using handshaking lemma as follows.

$$\sum_{d=1}^{n_1}\alpha_d + 2\sum_{n_1}^{n_2}\alpha_d + 3\sum_{n_2}^{n_3}\alpha_d + 4\sum_{n_3}^{n_4}\alpha_d = 2\left[\left(\sum_{d=1}^{N_S}\alpha_d + \frac{1}{2}\sum_{d=0}^{N_{DB_d}}\alpha_d + \sum_{d=0}^{N_{MB_d}}\alpha_d + \sum_{d=1}^{N_{TB_d}}\alpha_d\right) - 1 + O\right] \tag{4.4}$$

In Equation (4.4), n_1, n_2, n_3 and n_4 are the number of signatures of valency one, two, three and four respectively, N_s is the total number of signatures in the molecule, N_{DB_d} , N_{MB_d} and N_{TB_d} are the signatures with one double bond, two double bonds and one triple bond, O is the number of circuits in the molecular graph.

In addition to handshaking lemma, it must be ensured that the signatures in the solution set are consistent. Handshaking dilemma is used to ensure the consistency of the signatures, which is shown by using the following equation.

$$\sum (l_d \rightarrow l_{d'})_h = \sum (l_{d'} \rightarrow l_d)_h \tag{4.5}$$

In Equation (4.5), $(l_d \rightarrow l_{d'})_h$ is one colouring sequence $l_d \rightarrow l_{d'}$ at a level h. Equation (4.5) must be obeyed for all colour sequences at each height. This guarantees that the number of bonds in each signature will match with the bonds in the other signatures. This is explained in Figure 4.3.

List of signatures [colouring sequence]			**Handshaking di-lemma**		
d_1	C1(C2(CC))	[1→2]			
d_2	C2(C2(CC)C1(C))	[2→2, 2→1]	Σ[1→2]	=	Σ[2→1]
d_3	C2(C3(CCC)C1(C))	[2→3, 2→1]	d_1	=	$d_2+d_3+d_4$
d_4	C2(C4(CCCC)C1(C))	[2→4, 2→1]			

Figure 4.3: Explanation of handshaking dilemma

In Figure 4.3, the edges of the signatures have the colours of 1, 2, 3 and 4. The reading of colouring sequence for signature d_1 will be 1→2, 2→2 and 2→1 for signature d_2, 2→3 and 2→1 for signature d_3 and 2→4 and 2→1 for signature d_4. Hence, by following Equation (4.5), the handshaking dilemma can be written. Each colour sequence (e.g. 1→2) has to be complemented with another colouring sequence in reverse order (e.g. 2→1) to ensure linkage and consistency of the signatures. By obeying the structural constrains, a complete structure without any free bonds can be formed from the combination of signatures. The using of molecular signatures and the connectivity rules of signatures in molecular product design are discussed in detail by Chemmangattuvalappil and Eden (2013).

4.2.1.7.Generate Feasible Solutions by Solving Mathematical Model

Once the property and structural constraints have been constructed, mathematical model can be formulated to solve the molecular design problem. The objective function of the mathematical model is to maximise/minimise the preferred target property Ω_p, as shown in Equation (4.6).

$$\text{Maximise/Minimise } \Omega_p \tag{4.6}$$

For example, in order to design a refrigerant with high volumetric heat capacity, the objective function for the mathematical model can be formulated to maximise the volumetric heat capacity of the refrigerant while fulfilling other target properties. On the other hand, the objective function can be formulated to minimise the viscosity of the refrigerant in order to achieve low pumping power requirement. Subject to property and structural constraints, the objective function is solved to determine the solution for the product design problem. The solution is obtained in terms of the number of appearances of signatures. Additional solutions can be generated by using integer cuts. Integer cuts work by adding additional constraints in the mathematical programming model to ensure that the generated solution (in terms of combination of molecular signatures) will not appear again when the model is solved. This step may be continued until no feasible solution can be found. This indicates that all possible combinations of signatures that make up the molecules which satisfy all the property and structural constraints have been identified.

4.2.1.8.Enumerate Molecular Structure

With the signatures obtained by solving the design problem, molecular graph can now be generated from the set of signatures based on the graph signature enumeration algorithm by Chemmangattuvalappil and Eden (2013). By using the graph signature enumeration algorithm, molecular structure is generated from the list of signatures and the name of the molecule can then be identified. Figure 4.4 shows an example for the enumeration of molecular structure for propan-1-ol.

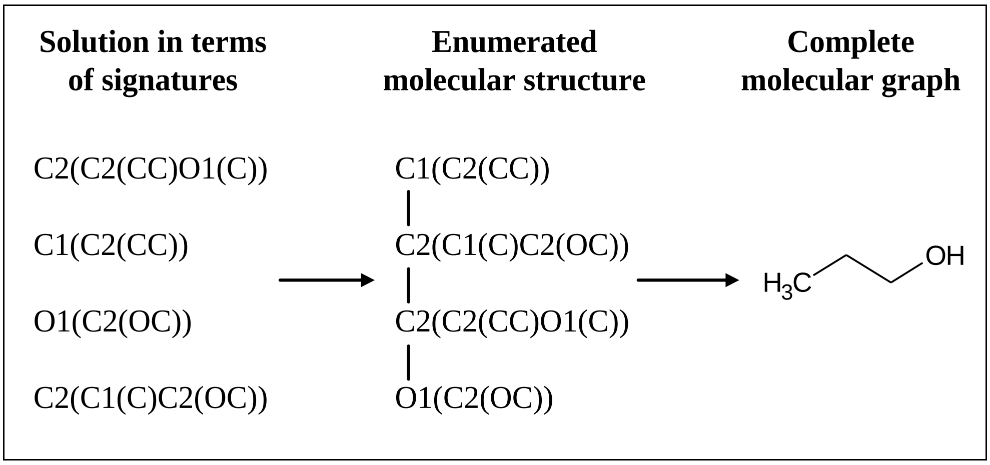


Figure 4.4: Enumeration of molecular structure for propan-1-ol

4.2.2. Design of Integrated Biorefinery: Chemical Reaction Pathway Synthesis

Once the biochemical product which fulfils the product needs is identified in the first stage, chemical reaction pathways that convert the biomass into the identified product are determined in the second stage of the conceptual approach. Biomass CRPM proposed by Ng et al. (2009) is adapted for the identification of chemical reaction pathways. As most of the reactions of organic chemicals are heavily dependent on the reactivity of functional groups (e.g. alcohol, alkene, carboxylic acid, ester etc.), the intermediates and final products of an integrated biorefinery are classified based on the functional groups of the chemical products. By using mainly organic chemical reactions and experiment data as the foundation of development, a biomass

CRPM is constructed as shown in Figure 4.5. The details of the chemical reactions and technologies for the construction of the CRPM are tabulated in Table 4.1.

A total of 25 potential chemical reaction pathways that convert biomass into intermediates and the desired products are selected in developing the CRPM. These reaction pathways consist of thermochemical, chemical and biochemical processes. As shown in Figure 4.5, the intermediates and final products in the CRPM are organic chemicals which are categorised into nine functional groups namely alcohol, aldehyde, alkane, alkene, alkyne, carboxylic acid, di-alcohol, ester and ketone. In addition to the nine functional groups, two common intermediate/final products which can be found in a biorefinery, i.e. methane and syngas are included in the CRPM as well. Syngas is a mixture of gases that contains of carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), steam (H_2O) and hydrogen (H_2) (Ciferno and Marano, 2002). It is recognised as one of the most promising intermediates to produce biochemical products (Khodakov et al., 2007). Methane and syngas are included in CRPM since they can be derived from biomass and they have the potential to be further converted into other value-added products through various technologies. As shown in Figure 4.5, syngas can be produced via gasification or pyrolysis or gasification of biomass (Pathway 2). After conditioning of syngas, it can be further converted into different products such as methanol and biofuel (alkanes). On the other hand, methane can be produced from anaerobic digestion of biomass. It can be considered as final product or intermediate if further conversion process is

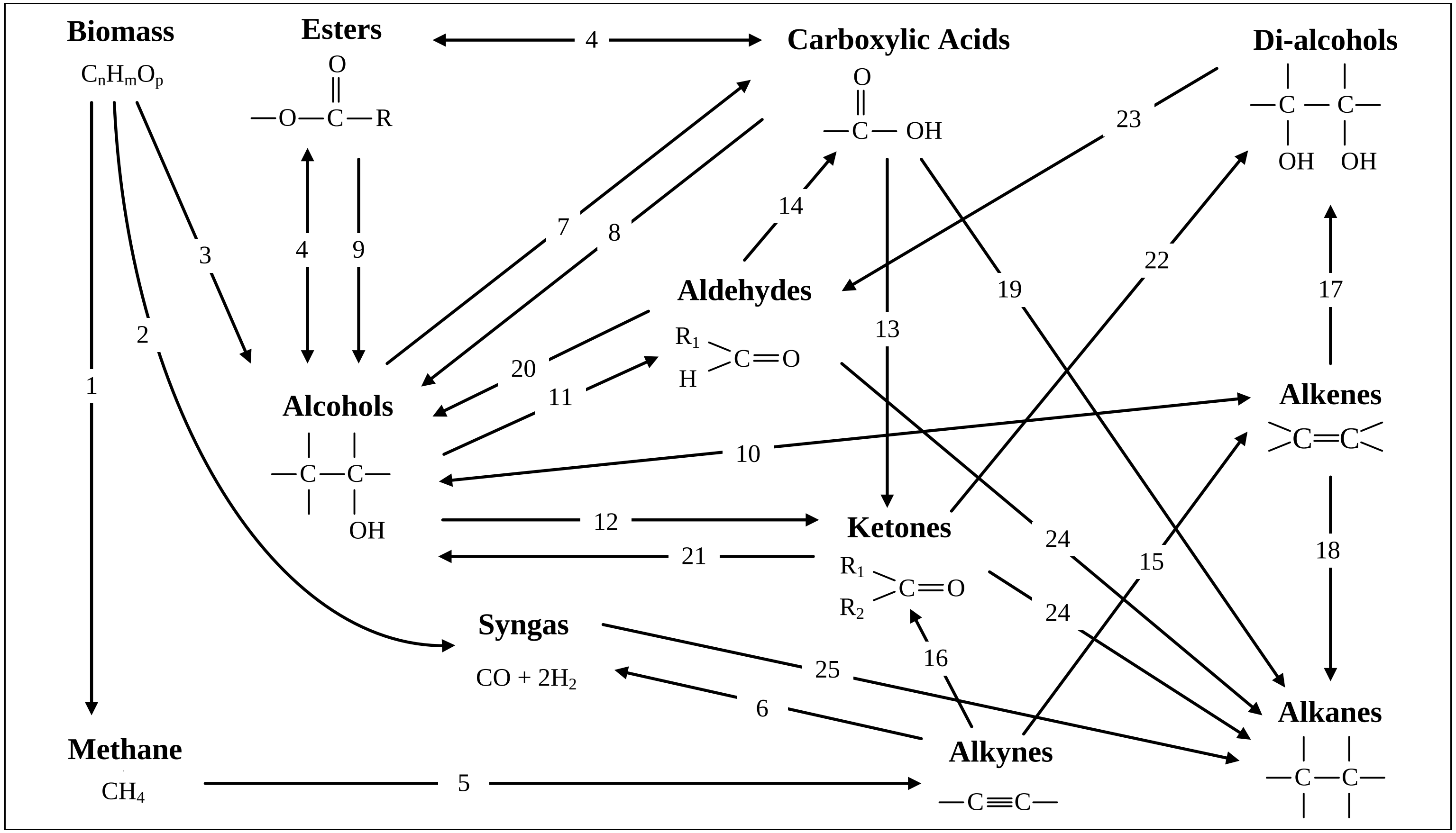


Figure 4.5: Biomass chemical reaction pathway map

Table 4.1: List of pathways and specifications for the developed CRPM

Pathway	Chemical reaction/ technology	Major process requirement/ specification
1	Anaerobic digestion	-
2	Gasification	Temperature : 1200 - 1300 ^{o}C Pressure: 1 atm
	Pyrolysis	Temperature: 200 – 300 ^{o}C Pressure: 1 atm
3	Fermentation	-
4	Esterification	-
5	Cracking	Temperature: 1200 - 1300 ^{o}C
6		
7	Oxidation	Reagent: $KMnO_4$ or $NaCr_2O_7$ / H_2SO_4
8	Carboxylic acid reduction	Catalyst: $LiAlH_4$
9	Ester reduction	Catalyst: Na-EtOH
10	Dehydration	Catalyst: Acids
11	Oxidation of alcohol	Oxidant: Derivatives of Cr (VI), Mn (VII), Mn (IV)
12		
13	Reaction with organometallic reagent	Catalyst: H_3O^+ Temperature: -75 ^{o}C
14	Oxidation	Reagent: Ammoniacal silver nitrate
15	Alkyne reduction	Catalyst: Pd
16	Hydration	Catalyst: $HgSO_4/H_2SO_4$ (aq.)
17	Oxidation	Catalyst: HCO_2H, Potassium permanganate
18	Hydrogenation	-
19	Decarboxylation	Temperature: 100 - 200 ^{o}C Catalyst: H_2O
20	Aldehyde reduction	Catalyst: Pt; $NaBH_4$ or $LiAlH_4$
21	Ketone reduction	
22	Ketone reduction	Catalyst: Mg/Hg
23	Oxidative cleavage	Catalyst: $NaIO_4$ & H_2O
24	Clemmensen reduction	Catalyst: Zn-Hg, HCl, boil
	Wolff-Kishner reduction	Catalyst: KOH, $(HOCH_2, CH_2)_2O$ Temperature: 200 ^{o}C
25	Fischer-Tropsch process	Temperature: 250 ^{o}C Pressure: 25 atm Catalyst: Co

required. It is showed in Figure 4.5 that methane can be converted into alkynes via cracking (Pathway 5). It can be further converted into syngas and alkenes via cracking (Pathway 6) and reduction (Pathway 15) respectively.

CRPM is a useful tool in screening and selecting the desired conversion pathways. By using the CRPM, alternative pathways to produce the desired product can be analysed. Besides, total number of stages for the conversion from biomass to the preferred products can be estimated by utilising the CRPM. CRPM shown and used in this chapter serves as a general representation of an integrated biorefinery. It considers only a portion of the available chemical reactions/technologies and potential products. Thus, the presented CRPM can be updated to include and accommodate information such as new processing technologies, potential products, side products, wastes generated etc. The application of the proposed conceptual approach is shown by using a case study in the following subsection.

4.3. Case Study

A design problem of producing bio-based fuel with improved antiknock quality from palm-based biomass is solved and presented. In this case study, palm-based biomass is chosen as the feedstock of the integrated biorefinery. In the first stage of the approach, signature based molecular design techniques are used to represent different classes of property prediction models in designing bio-based fuel which fulfils the product needs. In the second stage, conversion pathways which fulfil the production objective that convert the biomass into the designed bio-based fuel are identified by utilising the developed CRPM. For the ease of illustration, the bio-based fuel is targeted and designed as a single component bio-based fuel in this case study.

4.3.1. Identification of Bio-based Fuel

Antiknock quality, which is normally expressed as octane number is a measure of a fuel's ability to resist auto-ignition and knock in a spark-ignited engine conditions (Anderson et al., 2012). Note that antiknock quality is the main property that set the price of biofuel. Hence, bio-based fuel with high antiknock quality is desired. In this case study, research octane number (*RON*) is used as the indication of antiknock quality of the bio-based fuel. In addition, it is very important for a fuel to be safe to use. Therefore, other than *RON* which is used as the measurement of the bio-based fuel quality, the flammability characteristics of the synthesised biofuel are taken into consideration (Albahri, 2003a). Auto-ignition temperature (T_{ig}) is taken as one of the important properties of the bio-based fuel. It is the lowest temperature in which the substance will self-ignite with air at atmospheric pressure without external source of ignition such as spark or flame. Furthermore, flash point (T_f), latent heat of vaporisation (H_v), boiling point (T_b) and flammability limits of the bio-based fuel are properties that need to be considered to ensure the stability and safety of the biofuel. T_f is defined as the lowest temperature where the biofuel will vaporise to form an ignitable mixture in air. Meanwhile, flammability limits is the range of biofuel concentration that can ignite in the air at 298K. The range is normally bounded by upper flammability limit (*UFL*) and lower flammability limit

(*LFL*). H_v is the amount of heat required to convert a unit mass of a liquid into vapour at its boiling point, while T_b of a liquid is the temperature at which the liquid starts to boil at a fixed pressure.

Bio-based fuel with high *RON* is desired as higher *RON* indicates higher engine efficiency (Anderson et al., 2012). Therefore, the objective of this case study is to design a fuel with a maximised *RON* subjected to other property constraints as given in Table 4.2.

Table 4.2: Upper and lower bounds for bio-based fuel design

Property	**Target property range**	
	v_p^{L}	v_p^{U}
T_{ig} (K)	600	800
UFL (Volume %)	6.0	20.0
LFL (Volume %)	1.0	5.0
T_b (K)	300	500
H_v (kJ/mol)	25	55
T_f (K)	230	350

Following the proposed approach, property constraints of the bio-based fuel are represented in terms of GC models and TIs. For T_f, a connectivity index (CI) is available (Patel et al., 2009).

$$T_f = 33.638(^0\chi) + 164.386 \tag{4.7}$$

In Equation (4.7), ${}^0\chi$ is the zeroth order CI. GC models for the prediction of H_v and T_b are represented by Equations (4.8) and (4.9) respectively (Marrero and Gani, 2001).

$$H_v = H_{v0} + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \tag{4.8}$$

$$T_b = T_{b0} \cdot \ln\left(\sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \right) \tag{4.9}$$

In Equations (4.8) and (4.9), H_{v0} and T_{b0} are adjustable parameters, z^{I} and z^{II} are binary coefficients, N_i, N_j, N_k are the number of occurrence of first, second and third order molecular groups correspondingly and C_i, C_j, C_k are contributions of first, second and third order molecular groups respectively. For *RON*, T_{ig}, *UFL* and *LFL* of the biofuel, reliable GC models are available and utilised (Albahri, 2003a, 2003b).

$$\begin{aligned} f(p) = w^{\mathrm{I}} + w^{\mathrm{II}}\left(\sum_i N_i C_i\right) - w^{\mathrm{III}}\left(\sum_i N_i C_i\right)^2 + \\ w^{\mathrm{IV}}\left(\sum_i N_i C_i\right)^3 + w^{\mathrm{V}}\left(\sum_i N_i C_i\right)^4 + w^{\mathrm{VI}} / \left(\sum_i N_i C_i\right) \end{aligned} \tag{4.10}$$

In Equation (4.10), w^{I}, w^{II}, w^{III}, w^{IV}, w^{V} and w^{VI} are the correlation constants. Since the values of the constant w^{III}, w^{IV}, w^{V} and w^{VI} are relatively insignificant, only the first two terms of Equation (4.10) will be considered for this case study.

The next step is to select the suitable molecular building blocks for the design problem. Since the product to be designed is biofuel, alkanes are set as the target molecule. Therefore, only atom C and atom H will be considered during the design process. As molecular signature descriptor is utilised in solving the chemical product design problem, only signatures with single bond are considered in this design problem to design the bio-based fuel. Signatures of height one is required since property prediction model of zeroth order CI is utilised. The generated signatures can be classified into first order groups of carbon with zero (C-), one (CH-), two (CH_2-) and three (CH_3-) hydrogen atoms. For signature C-, as it is bonded with zero hydrogen atoms, it can be connected to four other matching signatures. Same concept applies for others signatures as well, where signature CH- can be connected to three other matching signatures, signature CH_2- can be connected to two other matching signatures and signature CH_3- can be connected to one matching signature. The list of the signatures is given in Table 4.3.

Table 4.3: List of signatures for bio-based fuel design

No.	**Signature**
1.	C(C)
2.	C(CC)
3.	C(CCC)
4.	C(CCCC)

With the identification of property prediction models and molecular building blocks, the next step is to transform the property prediction models into their respective normalised property operators. Property prediction models as shown in Equations (4.7) – (4.10) are written as normalised property operators. Normalised property operators and the normalised target property ranges are shown in Table 4.4.

Table 4.4: Normalised property operators and normalised target property ranges for the bio-based fuel design problem

Property	$\boldsymbol{\Omega_p}$	**Normalised target property range**	
		$\boldsymbol{\Omega_p^{\mathrm{L}}}$	$\boldsymbol{\Omega_p^{\mathrm{U}}}$
RON	$\frac{RON-103.6}{0.231}$	To be maximised	
T_{ig}	$\frac{T_{ig}-780.42}{26.78}$	-6.7371	-0.7311
UFL	$\frac{UFL-18.14}{3.4135}$	-3.5565	0.5449
LFL	$\frac{LFL-4.174}{0.8093}$	-3.9219	-1.0206
T_b	$e^{\frac{T_b}{222.543}}$	3.8499	9.4570
H_v	$H_v - 11.733$	13.2670	43.2670
T_f	$\frac{T_f-164.386}{33.638}$	1.9506	5.5180

The next step is to formulate the bio-based fuel design problem as a mathematical model. In this case study, the molecular design problem is written as a mixed-integer linear programming (MILP) model. Since the objective of this case study is to design a bio-based fuel with maximised *RON*, objective function for the case study can be written as shown in Equation (4.11).

$$\text{Maximise} \quad \Omega_{RON} \tag{4.11}$$

To ensure the formation of a feasible molecule with no free bonds in the final molecular structure, structural constraints are employed. Equations (4.4) and (4.5) are modified according to the case study and utilised to guarantee the generation of a complete molecular structure. The objective function can now be solved together with property and structural constraints to generate the bio-based fuel with maximised *RON*. Commercial optimisation software LINGO version 13, in Asus N56V with Intel Core i5-3210M (2.50 GHz) processor and 4 GB DDR3 RAM is used to solve the MILP model. The average central processing unit (CPU) time for the generation of solutions is 0.1 s. The solution from solving the mathematical model is obtained in terms of combination of signatures. Additional solutions are generated by using integer cuts. The list of possible combinations of signatures is shown in Table 4.5. By utilising graph signature enumeration algorithm discussed in the previous section, the molecular structure of all five solutions is formed. The list of products and their respective properties are given in Table 4.6 while Table 4.7 shows the molecular structure of the solutions.

From Table 4.6, it can be seen that all of the bio-based fuel properties fall within the target property ranges as shown in Table 4.2. As the objective of the design problem is to identify the bio-based fuel with maximised *RON* while having other properties fall within the preferred target property ranges, the solutions in Table 4.6 are arranged with decreasing *RON*. For this case study, the best solution identified is 2,2,3,3,4,4-hexamethylpentane with *RON*

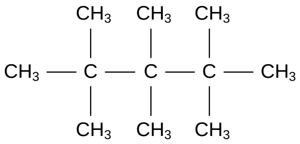
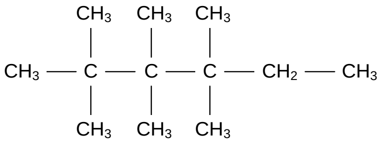
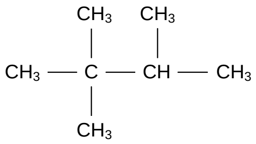
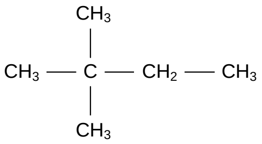
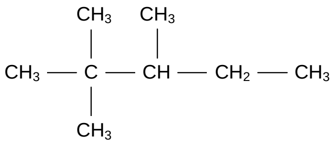
Table 4.5: Bio-based fuel design solutions in terms of signatures

Solutions	**Signature**	**Number of occurrence**
A	C(C)	8
	C(CC)	0
	C(CCC)	0
	C(CCCC)	3
B	C(C)	8
	C(CC)	1
	C(CCC)	0
	C(CCCC)	3
C	C(C)	5
	C(CC)	0
	C(CCC)	1
	C(CCCC)	1
D	C(C)	4
	C(CC)	1
	C(CCC)	0
	C(CCCC)	1
E	C(C)	5
	C(CC)	1
	C(CCC)	1
	C(CCCC)	1

Table 4.6: Bio-based fuel design solutions in terms of product specifications

Sol.	**Name**	**Property**						
		RON	**T_{ig} (K)**	***UFL* (vol%)**	***LFL* (vol%)**	**T_b (K)**	**H_v (kJ/mol)**	**T_f (K)**
A	2,2,3,3,4,4-hexamethylpentane	103.6	785	18.7	4.3	420	46	324
B	2,2,3,3,4,4-hexamethylhexane	103.3	747	13.8	3.1	443	51	336
C	2,2,3-trimethylbutane	103.2	729	11.5	2.6	333	32	261
D	2,2-dimethylbutane	103.0	713	9.6	2.1	311	28	252
E	2,2,3-trimethylpentane	102.8	691	6.8	1.5	366	36	278

Table 4.7: Bio-based fuel design solutions in terms of molecular structures

Sol.	Name	Molecular structure
A	2,2,3,3,4,4-hexamethylpentane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$
B	2,2,3,3,4,4-hexamethylhexane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$
C	2,2,3-trimethylbutane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3$
D	2,2-dimethylbutane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$
E	2,2,3-trimethylpentane	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{CH}-CH_2-CH_3$

of 103.6 while the fifth best solution identified is 2,2,3-trimethylpentane with *RON* of 102.8. The mathematical formulation and result for this case study can be found in Appendix B of this thesis.

4.3.2. Identification of Chemical Reaction Pathway

Once the bio-based fuel is identified, the chemical reaction pathways that convert the palm-based biomass into the identified product are determined in stage two of the conceptual approach by using the developed CRPM. In order to demonstrate the application of the proposed approach, the objective of the integrated biorefinery is to produce the bio-based fuel through chemical reaction pathways with highest product yield. As this proposed approach acts as a conceptual approach, it is assumed that the overall pathways with fewest conversion stages give the overall pathways with highest product yield.

In this case study, since the objective of the case study is to design bio-based fuel, the product of the integrated biorefinery is identified as alkanes. As shown in the developed CRPM (Figure 4.5), there are several alternative pathways that can convert the palm-based biomass into the targeted alkanes. By utilising the CRPM, the chemical reaction pathways with fewest conversion stages are identified as Pathway 2 followed by Pathway 25. This can be shown in Figure 4.6. In Pathway 2 (gasification of biomass), palm-based biomass is gasified with H_2O to produce syngas in a gasifier in the temperature range of 1200 – 1300 ^{o}C at 1 atm. Next, the product syngas is further converted into alkanes via Fischer-Tropsch process, which is Pathway 25 in the CRPM at temperature of 250 ^{o}C and pressure at 25 atm. The product alkanes can then be further converted and designed into the bio-based fuel identified in the first stage of the approach. It can be clearly seen from the CRPM that compared with other possible alternatives, the conversion stages involved in this overall reaction (gasification followed by Fischer-Tropsch process) is the fewest. Therefore, gasification of biomass followed by Fischer-Tropsch process is identified as the chemical reaction pathways with highest productivity to convert palm-based biomass into the bio-based fuel. Following the two-stage conceptual approach, it is ensured that the bio-based fuel which fulfils the product needs is produced. In the integrated biorefinery,

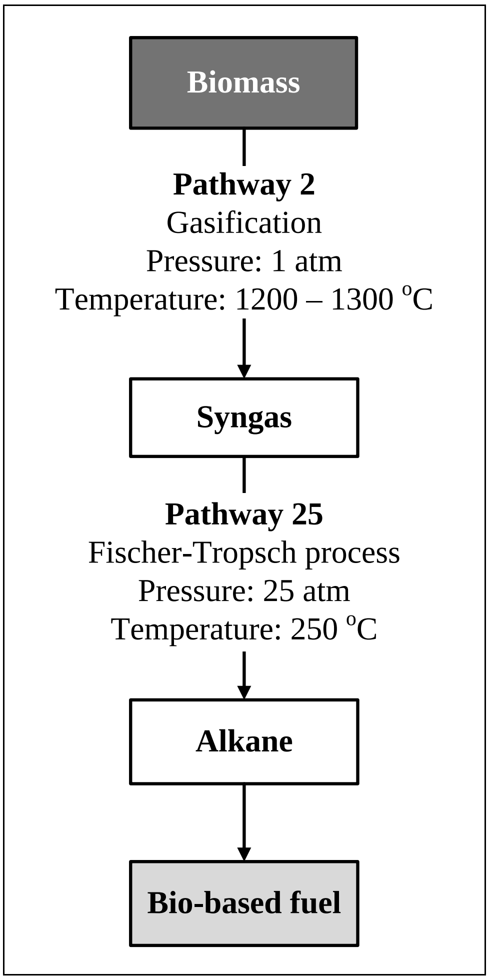


Figure 4.6: Chemical reaction pathway for the conversion of palm-based biomass into bio-based fuel

palm-based biomass is converted into alkanes by following the chemical reaction pathways with highest productivity of alkane. Product alkane can be further designed into the bio-based fuel which possesses optimised *RON* and other target properties that fall within the target property ranges. This case study which serves as a proof of concept shows how the proposed approach converts biomass into value-added bio-based fuel with preferred product properties while following the desired chemical reaction pathways.

4.4. Conclusion

In this chapter, a conceptual approach to integrate chemical reaction pathway synthesis with molecular product design techniques is presented to convert biomass into valuable chemical products in an integrated biorefinery. To design a product which fulfils the product needs, signature based molecular design techniques which can handle different classes of property prediction models are employed to determine the optimum product in terms of target properties. Subsequently, chemical reaction pathways that convert biomass into the identified product have been chosen by using the CRPM. This is accomplished by categorising the designed product based on its functional groups and selecting the conversion pathways from the CRPM based on the production objective. In order to identify the optimal conversion pathways that convert biomass into the identified chemical product based on different production objectives, the proposed conceptual approach is extended and discussed in Chapter 5.

CHAPTER 5

SYSTEMATIC METHODOLOGY FOR OPTIMAL CHEMICAL PRODUCT DESIGN IN INTEGRATED BIOREFINERIES

5.1. Introduction

The recent developments of process synthesis and design for integrated biorefineries have significantly increased the potential of biomass to be utilised as a sustainable and renewable source of energy. To date, various biomass conversion pathways are available to convert biomass into numerous value-added products. This has made the identification of optimum products and conversion pathways in an integrated biorefinery a complicated and difficult task. While the conceptual approach presented in Chapter 4 addresses the product design aspects in an integrated biorefinery, the approach does not identify the optimal conversion pathways that convert the biomass into the optimal biochemical product. In order to synthesise an efficient integrated biorefinery, it is important that the integrated biorefinery is able to provide optimal performances while accommodating to different production objectives. Therefore, a systematic approach is required for the design of optimal biochemical products in terms of target properties and the synthesis of optimum conversion pathways from biomass. In this chapter, the conceptual approach introduced in Chapter 4 is extended into a novel two-stage optimisation approach. This is achieved by integrating signature based molecular design technique with superstructural mathematical optimisation approach. A case study of bio-based fuel production from palm-based biomass is solved to illustrate the efficacy of the proposed approach.

5.2. Two-stage Optimisation Approach for Synthesis of Optimal Biochemical Products

In order to ensure the optimum conversion pathways that convert biomass into biochemical products with optimised target product properties, a novel two-stage optimisation approach has been developed by integrating molecular design technique with the synthesis and design of integrated biorefinery. In the first stage of the optimisation approach, optimal biochemical products in terms of target product properties are determined via signature based molecular design techniques. Optimum conversion pathways in terms of different production objectives that convert biomass into the identified biochemical products can then be determined via superstructural mathematical optimisation approach in the second stage of the optimisation approach. The idea of integration of the synthesis and design of integrated biorefinery with molecular product design techniques are previously discussed in Chapter 4, which is shown in Figure 4.1.

Once the optimal biochemical product is determined, identification of the optimum conversion pathways that convert biomass into the determined product can be determined in the second stage of the optimisation approach. Based on the available conversion pathways and technologies, a superstructure is constructed as a representation of an integrated biorefinery. By using superstructural mathematical optimisation approach, optimal conversion pathways based on different design goals such as economic potential, production yield, environmental impact etc. can be determined in this stage. By combining the strengths from both sides, this two-stage optimisation approach is able to determine the optimum conversion pathways that convert biomass into the optimal biochemical product that possesses the required product needs. Details of the proposed two-stage optimisation approach are discussed in the following subsections.

5.2.1. Stage 1: Design of Optimal Biochemical Product

In this stage, the optimal biochemical product that possesses optimal target properties is designed by utilising signature based molecular design techniques. As the approach adapted in identifying the optimal biochemical product is similar to the approach proposed in Chapter 4, the details of the approach will not be discussed in this section. The step by step procedure involved in the identification of optimal biochemical product can be found in Section 4.2.1.

5.2.2. Stage 2: Design of Integrated Biorefinery

Once the optimal biochemical product which fulfils the product needs is identified in the first stage, optimal biomass conversion pathways to produce the biochemical product are identified in the second stage of the optimisation approach. This is done by utilising superstructural mathematical optimisation approach. First, all of the possible conversion pathways and technologies that convert biomass into intermediates and from intermediates into the final products are compiled. A superstructure which includes all the conversion pathways and technologies can then be constructed as the representation of an integrated biorefinery, as shown in Figure 5.1. Figure 5.1 illustrates a general superstructure of an integrated biorefinery with biomass feedstock *b* converted through conversion pathways *q* to produce intermediates *s*, and further processed via conversion pathways *q'* to produce products *s'*. The mathematical model which relates the flow of biomass through different conversion pathways to produce the products can now be formulated. This is explained and discussed as follows.

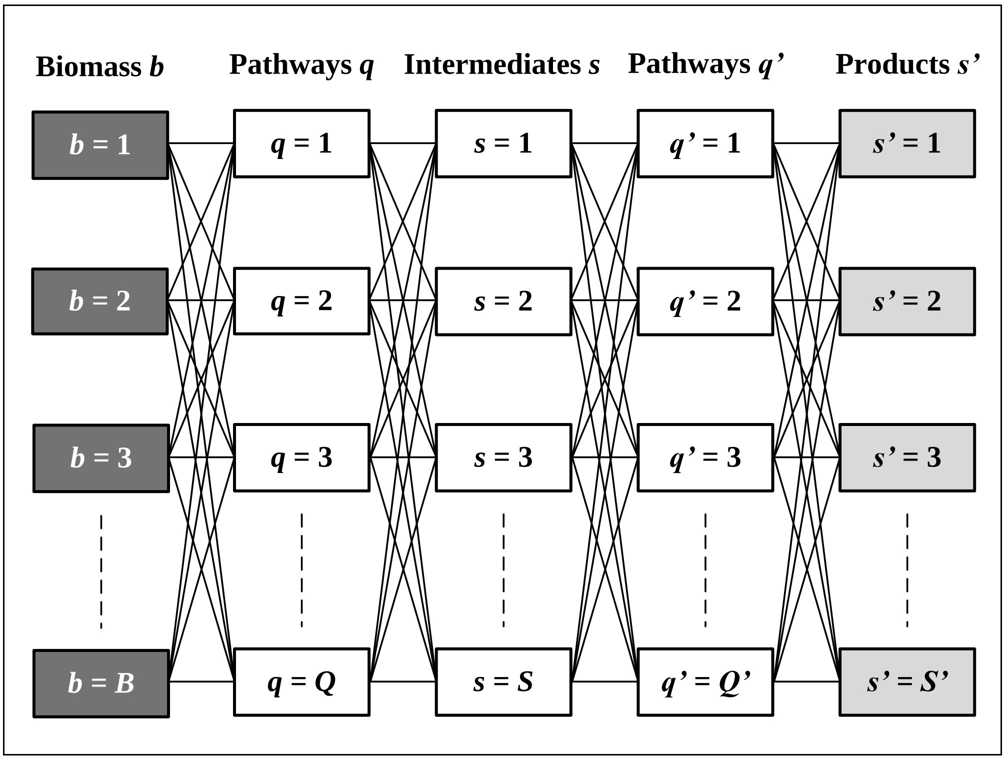


Figure 5.1: Superstructure as representation of integrated biorefinery

Biomass feedstock *b* can be split to biomass conversion pathway *q* with their respective flow rate F_{bq}^{I}.

$$B_b^{\mathrm{Bio}} = \sum_q F_{bq}^{\mathrm{I}} \qquad \forall b \tag{5.1}$$

In Equation (5.1), B_b^{Bio} is the available total flow rate of biomass feedstock *b*. After going through the biomass conversion pathway *q*, intermediate *s* is generated based on conversion rate of conversion pathway *q*, R_{bqs}^{I}. This gives a total intermediate production rate of T_s^{Inter}, as shown in Equation (5.2).

$$T_s^{\mathrm{Inter}} = \sum_{\mathrm{q}} \sum_{\mathrm{b}} \left(F_{bq}^{\mathrm{I}} R_{bqs}^{\mathrm{I}} \right) \qquad \forall s \tag{5.2}$$

Subsequently, the intermediate *s* is then further converted to product *s’* via biomass conversion pathway *q’*. The splitting of total production rate of intermediate T_s^{Inter} to all possible conversion pathway *q’* with flow rate $F_{sq'}^{\mathrm{II}}$ can be represented by Equation (5.3).

$$T_s^{\mathrm{Inter}} = \sum_{q'} F_{sq'}^{\mathrm{II}} \qquad \forall s \tag{5.3}$$

The total production rate of product *s’*, $T_{s'}^{\mathrm{Prod}}$ can be determined based on given conversion rate of conversion pathway *q’*, $R_{sq's'}^{\mathrm{II}}$ via Equation (5.4).

$$T_{s'}^{\mathrm{Prod}} = \sum_{q'} \sum_{s} \left(F_{sq'}^{\mathrm{II}} R_{sq's'}^{\mathrm{II}} \right) \qquad \forall s' \tag{5.4}$$

By following Equation (5.1) – (5.4), the material balance of the biomass, intermediates and final products can be performed. Thus, an integrated biorefinery can be represented by using the developed superstructure.

The objective of this second stage of the optimisation approach is to determine the optimal conversion pathways that convert biomass into the optimal biochemical product identified in the first stage of the methodology. The optimality of the conversion pathways can be aimed to maximise the yield of the desired product, as shown in the following equation.

$$\text{Maximise} \quad T_{s'}^{\text{Prod}} \tag{5.5}$$

Other than maximising the yield of the desired product, maximum economic performance can also be aimed as one of the design goals during the configuration of an integrated biorefinery. Economic performance can be defined with the following equations.

$$\text{Maximise} \quad GP^{\text{Total}} \tag{5.6}$$

$$GP^{\text{Total}} = \sum_{s'} T_{s'}^{\text{Prod}} E_{s'}^{\text{Prod}} - \sum_{b} B_{b}^{\text{Bio}} E_{b}^{\text{Bio}} - TAC \tag{5.7}$$

$$TAC = TACC + TAOC \tag{5.8}$$

$$TACC = \sum_{q}\sum_{b} F_{bq}^{\text{I}} E_{bq}^{\text{Cap}} CRF + \sum_{q'}\sum_{s} F_{sq'}^{\text{II}} E_{sq'}^{\text{Cap}} CRF \tag{5.9}$$

$$TAOC = \sum_{q}\sum_{b} F_{bq}^{\text{I}} E_{bq}^{\text{Opr}} + \sum_{q'}\sum_{s} F_{sq'}^{\text{II}} E_{sq'}^{\text{Opr}} \tag{5.10}$$

In Equations (5.6) – (5.10), GP^{Total} is the gross profit of the overall integrated biorefinery configuration, TAC is the total annualised cost, $TACC$ is the total annualised capital cost, $TAOC$ is the total annualised operating cost, CRF is the capital recovery factor, $E_{s'}^{\text{Prod}}$ is the cost of product s’, E_{b}^{Bio} is the cost of biomass feedstock b, E_{bq}^{Cap} is the capital cost for the conversion of biomass feedstock *b*, $E_{sq'}^{\mathrm{Cap}}$ is the capital cost for the conversion of intermediate *s*, E_{bq}^{Opr} is the operating cost for the conversion of biomass feedstock *b*, $E_{sq'}^{\mathrm{Opr}}$ is the operating cost for the conversion of intermediate *s*. By solving the developed mathematical model based on different objective functions, the optimal conversion pathways that lead to the desired optimal biochemical product can be determined in this stage. For cases where the conversion pathways lead to the formation of products as mixtures of several components, separation processes are included. These separation processes are taken into account to refine and separate the final product from the other by-products based on the result obtained from the design of product in stage 1 of the methodology. With the available information, different production objectives (e.g. economic performance, environmental impact, process safety etc.) can be considered and included in the development of the superstructure as well.

For situations where the identified products cannot be produced in a feasible method (e.g. in terms of economic potential, product manufacturability etc.), an iterative identification of optimal product and its conversion pathways is required. In such situations, the overall design problem has to be repeated from Step 2 of the product design problem, where the target property and target property ranges are re-evaluated. Other than identifying the optimal product and feasible optimal conversion pathways, the iterative process also provides comparison and trade-off between multiple options of the products and conversion pathways. Alternative pathways can be generated based on different design goals such as manufacturability of the product and economic feasibility of the processing routes. For instance, when the optimal product in terms of customer requirements cannot be produced economically, iteration of the design problem can be applied to identify the best product which can be manufactured in a cost effective manner.

The developed methodology decomposes the integrated product and process design problem into two design problems and solves them sequentially in two stages. This approach offers the identification of optimal biochemical products in terms of target product properties as well as optimal conversion pathways that convert the biomass into the biochemical products. Although iteration(s) might be required for the identification of solution(s), the computational complexity of this developed approach is lower compared with solving the product and process design problem simultaneously. An algebraic approach for the simultaneous solution of process and molecular design problems developed by Bommareddy et al. (2010) can be utilised to solve the product and process design simultaneously. However, simultaneous solution is not considered in this work. Furthermore, as explained in Figure 5.1 and the discussion, recycle streams are not considered in the design and synthesis of the integrated biorefineries. The recycle of material streams can be taken into account by including additional equations for the flow rate of recycle streams to the existing material balance of the biomass, intermediates and final products as shown in Equations (5.1) – (5.4). In addition, it is aware that the composition of biomass is complex, and the conversion reactions involved are difficult to be defined straightforwardly. Please note that this approach serves as a general representation and idea to integrate the synthesis of integrated biorefinery with product design. Hence, for ease of illustration, side reactions, additional reactants required and intermediate products with complex chemical structure are not considered in the presented approach.

5.3. Case Study

A product design problem of producing bio-based fuel from biomass is solved to illustrate the proposed two-stage optimisation approach. In the first stage, signature based molecular design techniques are used to represent different classes of property prediction models in designing a bio-based fuel with optimal target properties. In the second stage, the optimum conversion pathways in terms of different production objectives that convert the biomass into the designed bio-based fuel are identified. In order to demonstrate the efficacy of the approach, the conversion pathways of an integrated biorefinery are synthesised for two scenarios: conversion pathways for maximum product yield and conversion pathways for maximum economic potential. For the ease of illustration, the bio-based fuel is targeted and designed as a single component bio-based fuel in this case study. In order to differentiate the case study with the case study presented in Chapter 4, the bio-based fuel is designed to fulfil different product needs from the ones presented in Chapter 4.

5.3.1. Design of Optimal Product

The bio-based fuel is designed in terms of different product needs. The first is engine efficiency, which can be measured as octane rating. Octane rating is a measure of a fuel’s ability to resist auto-ignition and knock in a spark-ignited engine conditions. Higher octane rating helps vehicles to run smoothly and keep the vehicles' fuel system clean for optimal performance. In addition, antiknock quality is the main property that set the price of bio-based fuel. In this case study, research octane number (*RON*) is used as the indication of antiknock quality of the fuel. Furthermore, it is very important for a bio-based fuel to be safe to use. Therefore, the flammability characteristics and toxicity of the bio-based fuel are also taken into consideration, which are measured as flash point (T_f) and lethal concentration (LC_{50}) respectively. Meanwhile, heat of vaporisation (H_v) and viscosity (η) of the bio-based fuel are the other target properties that are considered during the product design stage to ensure the consistency of the fuel flow as well as the stability of the bio-based fuel. Since higher *RON* bio-based fuel is desirable as it enables improved engine efficiency, the objective of this case study is to design a bio-based fuel with maximised *RON*. Hence, *RON* is target property to be optimised while T_f, LC_{50}, H_v and η are the target properties to be fulfilled. The target property ranges for each of the target property are shown in Table 5.1 as follows.

Table 5.1: Upper and lower limits for bio-based fuel design problem

Property	**Target property range**	
	v_p^{L}	v_p^{U}
T_f (K)	230.00	350.00
LC_{50}	10.00	100.00
H_v (kJ/mol)	25.00	55.00
η (cP)	0.10	3.00

After identifying the target properties for the product, property prediction models for each target properties are identified. In order to illustrate the ability of the methodology to utilise different classes of property prediction models in a design problem, property prediction models based on group contribution (GC) methods and connectivity index (CI) are chosen the estimate the target properties. For *RON*, a reliable group contribution is available (Albahri, 2003b).

$$\begin{aligned} f(p) = w^{\mathrm{I}} + w^{\mathrm{II}}\left(\sum_i N_i C_i\right) - w^{\mathrm{III}}\left(\sum_i N_i C_i\right)^2 + \\ w^{\mathrm{IV}}\left(\sum_i N_i C_i\right)^3 + w^{\mathrm{V}}\left(\sum_i N_i C_i\right)^4 + w^{\mathrm{VI}} / \left(\sum_i N_i C_i\right) \end{aligned} \tag{5.11}$$

In Equation (5.11), w^{I}, w^{II}, w^{III}, w^{IV}, w^{V} and w^{VI} are the correlation constants. Since the values of the constant w^{III}, w^{IV}, w^{V} and w^{VI} are relatively insignificant, only the first two terms of Equation (5.11) will be considered for this case study.

Valence CI of order zero is available for the prediction of T_f (Patel et al., 2009) and LC_{50} (Jurić et al., 1992) as shown in as shown in Equations (5.12) and (5.13) respectively.

$$T_f = 33.638\left({}^0\chi^v\right) + 164.386 \tag{5.12}$$

$$\log_{10}(LC_{50}) = 4.115 - 0.762\left({}^0\chi^v\right) \tag{5.13}$$

where ${}^0\chi$ is the zeroth order CI while ${}^0\chi^v$ is the zeroth order valence CI. GC model developed by Marrero and Gani (2001) is utilised to predict H_v while

GC model developed by Conte et al. (2008) is used for the estimation of η. These can be shown in Equations (5.14) and (5.15) respectively. H_{v0} in Equation (5.14) is an adjustable parameter.

$$H_v = H_{v0} + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \tag{5.14}$$

$$\ln \eta = \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{I}} \sum_k N_k C_k \tag{5.15}$$

With the identification of property prediction models, the next step is to select the suitable molecular building blocks for the design problem. As the objective of this design problem is to design a bio-based fuel, the target molecule category is identified as alkanes. Therefore, only carbon (C) and hydrogen (H) atoms are considered. As molecular signature descriptor is utilised in solving the chemical product design problem, only signatures with single bond are considered in this design problem to design the bio-based fuel. In addition, signatures of height one is required since property prediction models of zeroth order CI are utilised. The generated signatures can be classified into first order groups of carbon with zero (C-), one (CH-), two (CH_2-) and three (CH_3-) hydrogen atoms. The generated signatures for the design problem are shown in Table 5.2. The next step is to transform the property prediction models into their respective normalised property operators. Property prediction models as shown in Equations (5.11) – (5.15) are written as normalised property operators. Normalised property operators and the normalised target property ranges are shown in Table 5.3.

Table 5.2: List of signatures

No.	**Signature**
1.	C(C)
2.	C(CC)
3.	C(CCC)
4.	C(CCCC)

Table 5.3: Normalised property operators and normalised target property ranges for the bio-based fuel design problem

Property	$\boldsymbol{\Omega_p}$	**Normalised target property range**	
		$\boldsymbol{\Omega_p^{\mathrm{L}}}$	$\boldsymbol{\Omega_p^{\mathrm{U}}}$
RON	$\frac{RON - 103.6}{0.231}$	To be maximised	
T_f	$\frac{T_f - 164.386}{33.638}$	1.95	5.52
LC_{50}	$\frac{4.115 - \log_{10}(LC_{50})}{0.762}$	2.78	4.09
H_v	$H_v - 11.733$	13.27	43.27
η	$\ln \eta$	-2.30	1.10

Now, the molecular design problem can be written as a mixed-integer linear programming (MILP) model. As the objective of this case study is to design a bio-based fuel with maximised *RON*, the objective function for the case study can be written as shown in Equation (5.16).

$$\text{Maximise} \quad \Omega_{RON} \tag{5.16}$$

To ensure the formation of a complete molecule with no free bonds in the final molecular structure, structural constraints as shown in Equations (4.4) and (4.5) are employed. The objective function Equation (5.16) can now be solved together with property constraints and structural constraints to generate the optimal bio-based fuel in terms of highest *RON*. Commercial optimisation software LINGO version 13, in Asus N56V with Intel Core i5-3210M (2.50 GHz) processor and 4 GB DDR3 RAM is used to solve the MILP model. The average central processing unit (CPU) time for the generation of solutions is 0.1 s. The solution obtained is the bio-based fuel with maximised *RON* which fulfils other target properties. Additional solutions can be generated by using integer cuts. The list of possible solutions in terms of combination of signatures is shown in Table 5.4.

Table 5.4: List of solutions in terms of signatures

Solutions	**Signature**	**Number of occurrence**
A	C(C)	6
	C(CC)	0
	C(CCC)	0
	C(CCCC)	2
B	C(C)	6
	C(CC)	1
	C(CCC)	0
	C(CCCC)	2
C	C(C)	5
	C(CC)	0
	C(CCC)	1
	C(CCCC)	1
D	C(C)	5
	C(CC)	1
	C(CCC)	1
	C(CCCC)	1
E	C(C)	5
	C(CC)	0
	C(CCC)	3
	C(CCCC)	0

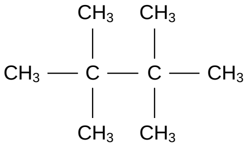
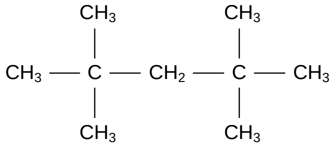
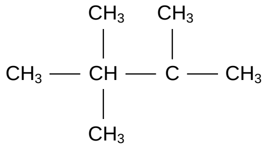
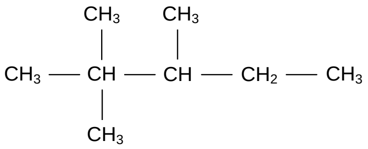
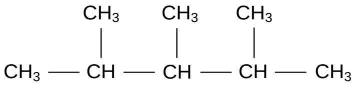
Molecular structures for the bio-based fuels can be generated from the signatures based on the graph signature enumeration algorithm developed by Chemmangattuvalappil and Eden (2013). Enumeration of molecules is performed on all five solutions obtained as shown in Table 5.4. The list of solutions for the design of bio-based fuel in terms of product specifications is given in Table 5.5 while the bio-based fuel design solutions in terms of molecular structures are shown in Table 5.6.

Table 5.5: List of solutions in terms of product specifications

Sol.	**Name**	**Property**				
		RON	T_f **(K)**	LC_{50}	H_v **(kJ/mol)**	η **(cP)**
A	2,2,3,3-tetramethylbutane	105.91	282.12	28.18	33.19	0.58
B	2,2,4,4-tetramethylpentane	103.96	294.01	15.14	38.10	0.72
C	2,2,3-trimethylbutane	103.64	266.60	63.10	30.43	0.37
D	2,2,3-trimethylpentane	101.69	278.49	33.88	35.34	0.45
E	2,3,4-trimethylpentane	100.80	277.61	35.48	36.85	0.31

In this case study, the bio-based fuel is designed to possess maximised *RON* while having other properties fall within the preferred target property ranges. It should be noted that these target ranges represent the product specifications that customers desire and prefer. From Table 5.5, it can be seen

Table 5.6: List of solutions in terms of molecular structure

Sol.	Name	Molecular structure
A	2,2,3,3-tetramethylbutane	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$
B	2,2,4,4-tetramethylpentane	 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$
C	2,2,3-trimethylbutane	 $CH_3-\underset{CH_3}{\overset{CH_3}{CH}}-\overset{CH_3}{C}-CH_3$
D	2,2,3-trimethylpentane	 $CH_3-\underset{CH_3}{\overset{CH_3}{CH}}-\overset{CH_3}{CH}-CH_2-CH_3$
E	2,3,4-trimethylpentane	 $CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$

that the solutions are arranged with decreasing *RON*. The optimal bio-based fuel designed for the case study is 2,2,3,3-tetramethylbutane with *RON* of 105.91 while the fifth best bio-based fuel is 2,3,4-trimethylpentne with *RON* of 100.80. In addition, it can be seen from Table 5.5 that all of the bio-based fuel properties fall within the target property ranges as shown in Table 5.1.

5.3.2. Selection of Optimal Conversion Pathway

With the identification of optimal bio-based fuel in the first stage of the approach, the optimal conversion pathways that convert the biomass into the bio-based fuel can now be identified in the second stage of the optimisation approach. In this case study, palm-based biomass known as empty fruit bunch (EFB) is chosen as feedstock of the integrated biorefinery. The lignocellulosic composition of the EFB is shown in Table 5.7.

Table 5.7: Lignocellulosic composition of EFB

Components	**Composition (% of dry matter)**
Lignin	39.00
Cellulose	22.00
Hemicellulose	29.00

From the first stage of the methodology, the optimal product in terms of highest *RON* is identified as 2,2,3,3-tetramethylbutane, which is an alkane with carbon number 8 (Alkane C_8). Hence, it is known that the end product of the integrated biorefinery is Alkane C_8. For illustration purpose, the end products alkanes of the integrated biorefinery are represented as straight-chain products without considering the formation of isomers. For example, the optimal bio-based fuel, 2,3,3,4-tetramethylpentane is represented as straight-chain alkane with carbon number of 8 in this case study. Possible conversion pathways that produce alkanes from biomass are compiled and shown in Table 5.8. Figure 5.2 shows the superstructure developed based on the conversion pathways in Table 5.8. As shown in Table 5.8, the identified conversion pathways consist of reactions from physical, thermochemical, chemical as well as biochemical platforms. It is noted that the developed superstructure can be revised to include more conversion pathways and technologies in synthesising an integrated biorefinery.

Table 5.8: List of conversions and selectivities for conversion pathways

Pathway	**Process**	**Product**	**Conversion (%)**	**Selectivity (%)**
1	Ammonia explosion	Sugars, Lignin	98.0	-
2	Steam explosion	Sugars, Lignin	49.2	-
3	Organosolv separation	Lignin	79.0[a]	-
4	Organosolv separation	Sugars	97.0[a]	-
5	Autohydrolysis	HMF	90.9	-
6	Dehydration of sugars	Furfural	40.9	-
7	Yeast fermentation	Ethanol	61.9	-
8	Bacterial fermentation	Ethanol	41.0	-
9	Hydrogenation of furfural	THFA	98.2	-
10	Hydrogenation of THFA 1	Pentanediol	99.0	95.0
		Pentanol		4.0
11	Hydrogenation of THFA 2	Pentanediol	60.0	51.0
		Pentanol		22.0
12	Pyrolysis	Syngas	94.0	-
13	Gasification	Syngas	90.0	-
14	Anaerobic digestion	Methane	40.0	-
15	Water gas shift reaction	Syngas	100.0	-
16	Fischer-Tropsch process 1	Hydrocarbon C_2-C_4	40.0	16.0
		Hydrocarbon C_5-C_9		27.0
		Hydrocarbon C_{10}		26.0
17	Fischer-Tropsch process 2	Hydrocarbon C_2-C_4	75.0	23.0
		Hydrocarbon C_5-C_9		19.0
		Hydrocarbon C_{10}		9.7
18	Conversion of syngas 1	Methanol	25.1	2.6
		Ethanol		61.4

Table 5.8: (continued) List of conversions and selectivities for conversion pathways

19	Conversion of syngas 2	Methanol	24.6	3.9
		Ethanol		56.1
20	Hydrogenation of CO	Methanol	28.8	20.7
		Ethanol		23.8
		Propanol		14.1
		Butanol		7.5
21	Monsanto process	Ethanoic Acid	99.0	-
22	Dehydration of alcohols 1	Hydrocarbon C_2	67.0	-
23	Dehydration of alcohols 2	Hydrocarbon C_3	59.0	28.8
		Hydrocarbon C_4		37.3
24	Dehydration of alcohols 3	Hydrocarbon C_5	64.0	15.2
		Hydrocarbon C_6		5.5
		Hydrocarbon C_7		5.6
		Hydrocarbon C_8		4.2
25	Decarboxylation of acids	Hydrocarbon C_2	62.0	21.3
26	Fractional distillation of alkanes	Hydrocarbon C_8	99.0[a]	-
		Hydrocarbon C_2-C_7, C_9- C_{10}	99.0[a]	-

[a] Separation efficiency.

In order to demonstrate the efficacy of the developed methodology, two scenarios of different production objectives are considered in synthesising the integrated biorefinery:

1. Design for maximum product yield

2. Design for maximum economic potential

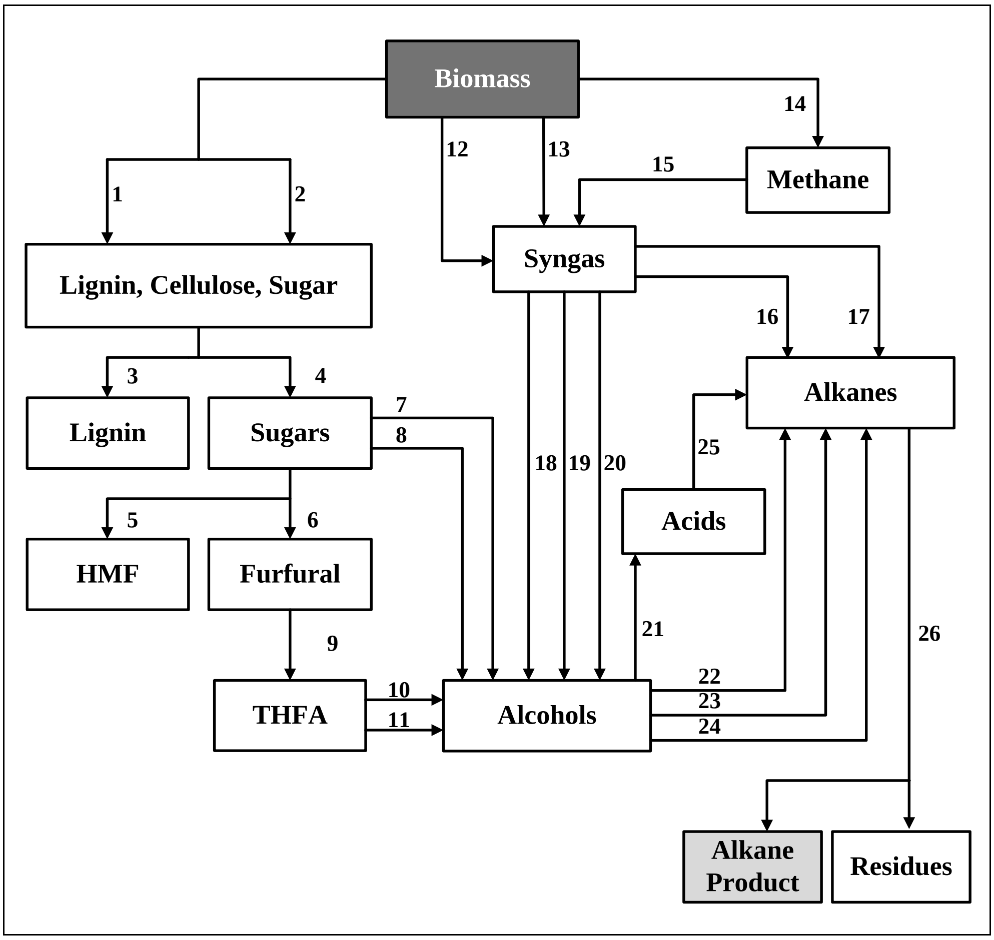


Figure 5.2: General representation of integrated biorefinery

In this case study, other than the revenue generated by producing the bio-based fuel, the revenue obtained from the generation of by-products is included in the overall economic potential of the integrated biorefinery as well. Table 5.9 shows the market prices of the products and biomass feedstock while Table 5.10 shows the capital and operating costs for each conversion pathway. Please note that the capital costs provided in Table 5.10 are the capital costs for nominal capacity of each conversion technology available in the market. Hence, the flow rate determined by the mathematical model is the

Table 5.9: List of market prices of products and raw material

Final product	**Revenue from final product (U.S.$) per tonne**
Ethane	424
Propane	670
Butane	900
Pentane	1200
Hexane	1600
Heptane	1800
Octane	2000
Nonane	2510
Decane	2750
Methanol	450
Ethanol	770
Propanol	950
Butanol	1120
Pentanol	1770
Pentanediol	3000
Raw material	**Cost of raw material (U.S.$) per tonne**
Biomass (EFB)	170

operating flow rate into the selected conversion technology with a fixed nominal capacity. It should be noted that the prices of the products, feedstock as well as the capital and operating costs for each conversion pathway can be revised according to the market prices to produce an up-to-date economic analysis. With a feed of 50000 tonnes per year of EFB, the optimisation problem is formulated as a linear programming (LP) model and solved for both of the scenarios. In this case study, alcohols produced from the synthesised integrated biorefinery are sold as by-products together with the main product Alkane C_8 and other alkane by-products.

Table 5.10: List of capital and operating costs for conversion pathways

Pathway	**Process**	**Capital cost (U.S.$)**	**Operating cost (U.S.$) per annual tonne**
1	Ammonia explosion	7.47×10^6	11.30
2	Steam explosion	5.29×10^6	7.97
3	Organosolv separation	1.55×10^7	23.30
4	Organosolv separation	1.55×10^7	23.30
5	Autohydrolysis	2.41×10^7	36.40
6	Dehydration of sugars	1.05×10^7	15.80
7	Yeast fermentation	1.54×10^7	22.00
8	Bacterial fermentation	1.20×10^7	18.00
9	Hydrogenation of furfural	1.15×10^7	17.30
10	Hydrogenation of THFA 1	1.65×10^7	24.90
11	Hydrogenation of THFA 2	1.73×10^7	26.00
12	Pyrolysis	2.39×10^7	36.00
13	Gasification	3.29×10^7	55.00
14	Anaerobic digestion	9.98×10^6	15.00
15	Water gas shift reaction	5.57×10^6	8.66
16	Fischer-Tropsch process 1	7.36×10^7	111.00
17	Fischer-Tropsch process 2	6.92×10^7	104.00
18	Conversion of syngas 1	1.47×10^7	22.10
19	Conversion of syngas 2	1.56×10^7	23.60
20	Hydrogenation of CO	1.53×10^7	23.00
21	Monsanto process	1.55×10^7	23.30
22	Dehydration of alcohols 1	1.54×10^7	23.20
23	Dehydration of alcohols 2	1.43×10^7	21.50
24	Dehydration of alcohols 3	1.31×10^7	19.70
25	Decarboxylation of acids	1.75×10^7	26.30
26	Fractional distillation of alkanes	6.52×10^7	98.20

5.3.2.1.Scenario 1: Design for Maximum Product Yield

In this scenario, an integrated biorefinery is synthesised by solving the optimisation model using the optimisation objective in Equation (5.17). Note that the optimum bio-based fuel 2,2,3,3-tetramethylbutane is represented as

Alkane C_8 in the case study. Similar commercial optimisation software with similar software and hardware specification is utilised in solving the mathematical model for both scenario 1 and 2. The average CPU time for the generation of solutions is 0.1 s for both scenarios.

$$\text{Maximise} \quad T^{\text{Prod}}_{\text{AlkaneC}_8} \tag{5.17}$$

Based on the result, the maximum yield for Alkane C_8 is 1979.75 t/y. Along with Alkane C_8, Alkanes with different carbon number are produced as by-products in the integrated biorefinery. The GP^{Total} for the scenario is U.S. $11.44 million per annum. The conversion pathways selected for the scenario is illustrated in the synthesised integrated biorefinery as shown in Figure 5.3.

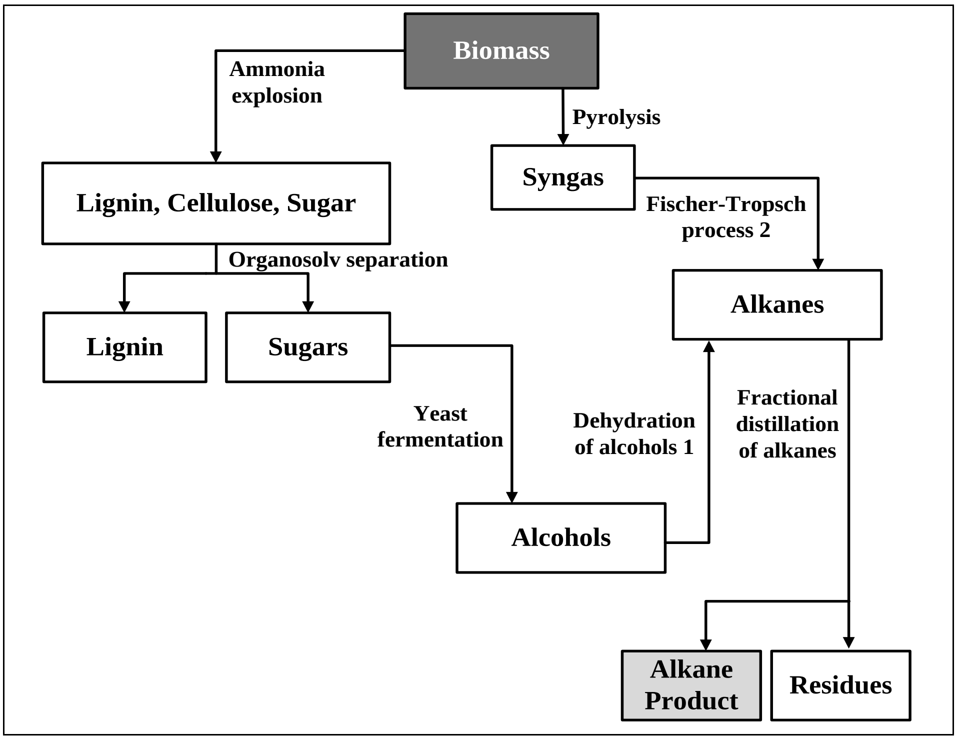


Figure 5.3: Flow diagram of synthesised integrated biorefinery (maximum product yield)

In order to produce Alkane C_8, a portion of biomass is first converted into lignin cellulose and sugar via ammonia explosion while the other portion of biomass is converted into syngas via pyrolysis, as seen from Figure 5.3. Conversion pathways of Organosolv separation, yeast fermentation and dehydration of alcohols 1 are selected to convert lignin, cellulose and sugar into alkanes. On the other hand, syngas produced from biomass is further converted into alkanes via Fischer-Tropsch process 2. Then, Alkane C_8 is produced from fractional distillation of alkanes. It is worth mentioning that specific separation processes that suit the identified product can be chosen and included in the integrated biorefinery to refine and separate the final product from the other generated by-products. Hence, separation processes for alkanes are chosen based on the results of the product design identified in stage 1 of the methodology. The performance of the separation processes are then taken into consideration in identifying the product yield and economic potential of the overall conversion pathway.

5.3.2.2.Scenario 2: Design for maximum economic potential

In this scenario, an integrated biorefinery configuration with maximum economic potential is determined by solving the optimisation objective as shown in Equation (5.18).

$$\text{Maximise} \quad GP^{\text{Total}} \tag{5.18}$$

Based on the result, the maximum GP^{Total} for the scenario is identified to be U.S. $24.04 million (per annum) with the annual production for Alkane C_8 of

1374.03 t. The conversion pathways chosen for the scenario is presented in the synthesised integrated biorefinery as shown in Figure 5.4.

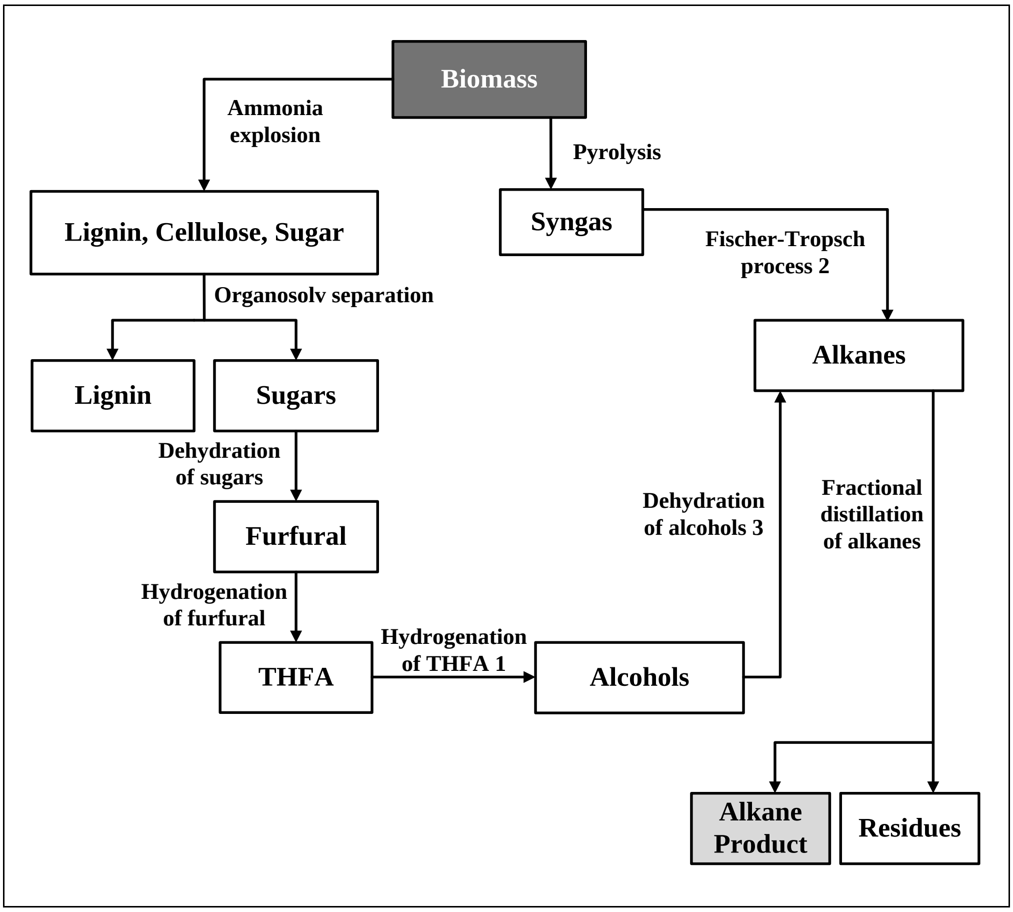


Figure 5.4: Flow diagram of synthesised integrated biorefinery (maximum economic potential)

Similar to the previous scenario, in order to produce Alkane C_8, a portion of biomass is first converted into lignin cellulose and sugar via ammonia explosion while the other portion of biomass is converted into syngas via pyrolysis. From Figure 5.4, it can be seen the conversion pathway sequence of ammonia explosion, Organosolv separation, dehydration of sugars, hydrogenation of furfural and hydrogenation of THFA 1 and dehydration of alcohols 3 are selected to convert lignin, cellulose and sugar into alkane. Meanwhile, Fischer-Tropsch process 2 is chosen to produce alkane from syngas. Alkane C_8 is then produced from fractional distillation of alkanes. The comparison of the results generated for scenario 1 and 2 are summarised in Table 5.11.

Table 5.11: Comparison of results for scenario 1 and 2

Scenario	**1**	**2**
GP^{Total} (U.S $/y)	11.44×10^6	24.04×10^6
Alkane C_8 production rate (t/y)	1979.75	1374.03
Alkane by-product production rate (t/y)	16979.38	10707.98
Alcohol production rate (t/y)	12588.26 (ethanol)	9486.92 (pentanol and pentanediol)

From Table 5.11, it can be seen that the production rate of Alkane C_8 in scenario 1 is higher compared to scenario 2. This is because the objective of scenario 1 is to identify the conversion pathways which produce maximum yield of Alkane C_8. Although the production rate of Alkane C_8 in scenario 2 is lower compared with scenario 1, the GP^{Total} generated is higher as the objective of scenario 2 is to synthesise an integrated biorefinery with maximum economic potential. As shown in Table 5.9, the market prices for alcohols are higher than the market prices of alkanes. In addition, the market price for both pentanol and pentanediol are higher than the market price of ethanol. Therefore, although the production rate of alcohol in scenario 1 is higher compared with scenario 2, the GP^{Total} for scenario 2 is higher as the alcohol produced in scenario 1 is ethanol while pentanol and pentanediol are produced in scenario 2. The mathematical formulations and results for this case study are provided in Appendix C of this thesis.

5.4. Conclusion

This chapter introduces a systematic two-stage optimisation approach to convert biomass into valuable biochemical products which meet the product needs. This is achieved by integrating the synthesis and design of integrated biorefinery with molecular product design techniques. In the first stage, signature based molecular design technique has been employed to determine the optimum biochemical products in terms of target properties. In the second stage of the optimisation approach, optimum conversion pathways that convert the biomass into the identified biochemical products have been determined via superstructural mathematical optimisation approach. Information such as new biomass conversion technologies, side reactions, reactants and intermediates with complex chemical structure can be included to extend the superstructure model. For the simplicity of illustration, the case study presented a bio-based fuel design problem based on the assumption that the targeted bio-based fuel is a single component bio-based fuel. The design problem can be formulated as mixture design problem where information such as properties of different components will be considered and analysed during the design process. This design consideration will be further discussed in Chapter 8.

CHAPTER 6

MULTI-OBJECTIVE OPTIMISATION APPROACH FOR OPTIMAL CHEMICAL PRODUCT DESIGN

6.1. Introduction

The integrated approaches for the design of optimal chemical product from biomass presented in Chapters 4 and 5 focus on the optimisation of a single product property while designing the chemical product. It is aware that in some situations, several important product properties are required to be considered and optimised simultaneously in order to design an optimal chemical product in terms of target product properties. In cases where more than one product property is to be considered and optimised, a multi-objective optimisation approach is needed to optimise all the important target properties simultaneously. In general, the target properties are normally optimised based on the weighting factors assigned by decision makers. This method tends to be biased as it depends heavily on the expert judgments or personal preferences. To address this problem, a systematic multi-objective optimisation approach for the design of chemical products with optimal properties is presented in this chapter. Fuzzy optimisation approach and signature based molecular design techniques are adapted to address the abovementioned chemical product design problem. Max-min aggregation and two-phase approaches are incorporated into fuzzy optimisation approach and the solutions generated from both approaches are compared. A case study on the design of a solvent used in gas sweetening process is presented to illustrate the developed approach.

6.2. Systematic Multi-objective Optimisation Approach

In order to solve multi-objective chemical product design problems under different fuzzy environments, a systematic multi-objective optimisation approach is presented. Signature based molecular design techniques incorporated with fuzzy optimisation approach are used to achieve this objective. In addition, for situations where the target property ranges are imprecise or unclear, bi-level optimisation approach is adapted for the identification of the target property ranges. The details of the developed systematic multi-objective optimisation approach are discussed in the following subsections.

6.2.1. Fuzzy Optimisation Approach

Fuzzy optimisation approach is incorporated in the presented approach to address the simultaneous consideration and optimisation of multiple target properties in a chemical product design problem. In order to trade-off multiple target properties, a degree of satisfaction, λ is introduced. To introduce λ, the target properties to be optimised are written as linear functions bounded by the target property ranges. This can be shown by Equations (6.1) and (6.2).

$$\lambda_p = \begin{cases} 1 & \text{if} \quad V_p \le v_p^{\mathrm{L}} \\ \dfrac{v_p^{\mathrm{U}} - V_p}{v_p^{\mathrm{U}} - v_p^{\mathrm{L}}} & \text{if} \quad v_p^{\mathrm{L}} \le V_p \le v_p^{\mathrm{U}} \qquad \forall p \in P \\ 0 & \text{if} \quad V_p \ge v_p^{\mathrm{U}} \end{cases} \tag{6.1}$$

$$\lambda_p = \begin{cases} 0 & \text{if} \quad V_p \le v_p^{\mathrm{L}} \\ \dfrac{V_p - v_p^{\mathrm{L}}}{v_p^{\mathrm{U}} - v_p^{\mathrm{L}}} & \text{if} \quad v_p^{\mathrm{L}} \le V_p \le v_p^{\mathrm{U}} \qquad \forall p \in P \\ 1 & \text{if} \quad V_p \ge v_p^{\mathrm{U}} \end{cases} \tag{6.2}$$

In Equations (6.1) and (6.2), λ_p is the degree of satisfaction for the target property p, V_p is the value for the property p, v_p^{L} and v_p^{U} are the lower and upper limits for the property p respectively. Values of 0 and 1 of λ_p denote the levels of satisfaction of the target property value V_p within the target property range. Higher λ_p indicates higher satisfaction of each target property. For property to be minimised, as lower values are desired, when the property approaches the lower limit, the value of λ_p approaches 1; when the property approaches the upper limit, the value of λ_p approaches 0, as shown in Figure 6.1 (a). Opposite trend is observed when the target property is maximised as higher values are desired, as shown in Figure 6.1 (b). Equation (6.1) is used for property to be minimised while Equation (6.2) is used for property to be maximised. A pictorial representation is shown in Figure 6.1. Note that the degree of satisfaction in Figure 6.1 can be split into below satisfactory, satisfactory and above satisfactory regions. In order to ensure a non-negative degree of satisfaction, the values of λ_p are set to be more than 0. This can be shown in Equation (6.3).

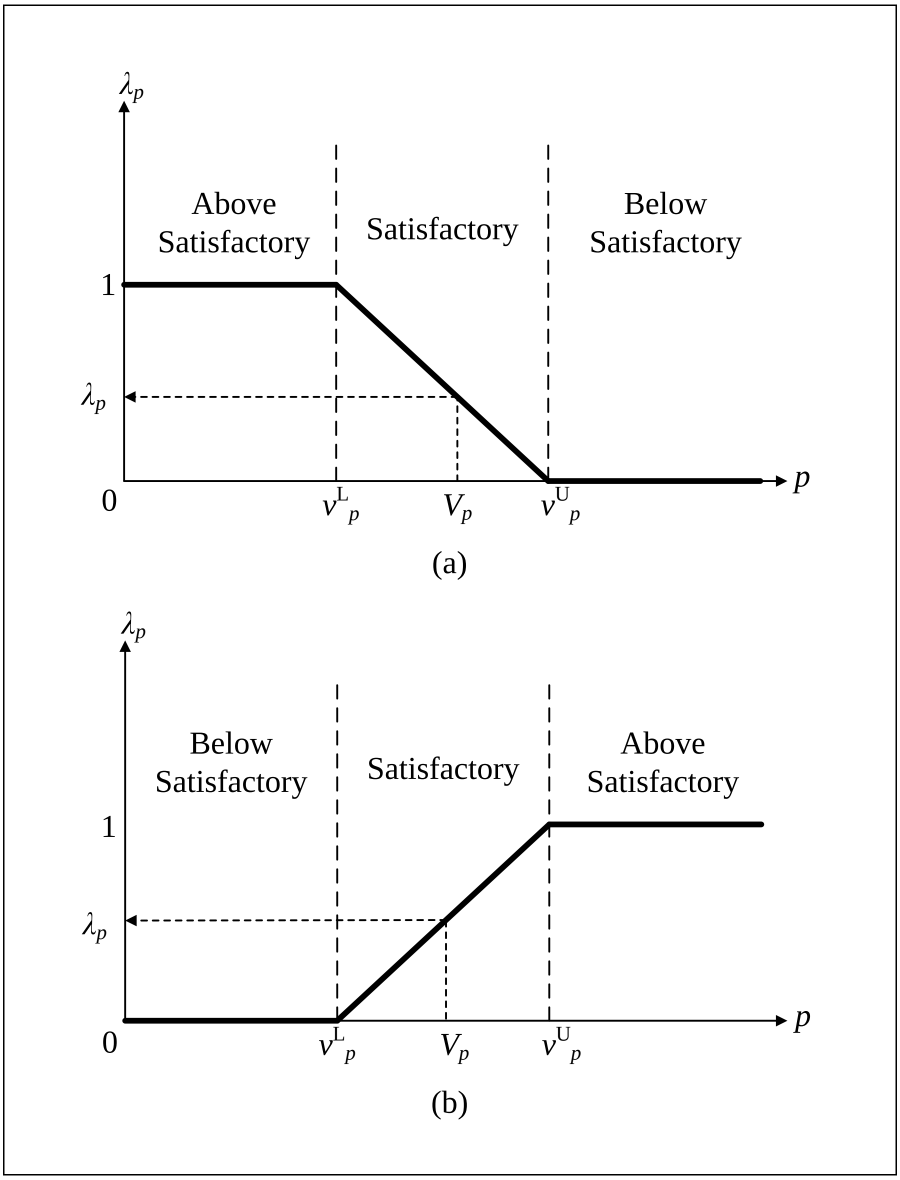


Figure 6.1: Fuzzy degree of satisfaction (λ) of the inequalities:

(a) property to be minimised; (b) property to be maximised

$$\lambda_p \geq 0 \qquad \forall p \in P \tag{6.3}$$

Hence, the target properties to be optimised will always fall within or above satisfactory region, but not in under satisfactory region.

6.2.2. Bi-level Optimisation Approach

In chemical product design problems, there are times where some of the product target property ranges are unknown. Besides, there are also situations where a product property is only bounded by either upper or lower limit as only one of them is significant. For instance, lethal concentration/toxicity (LC_{50}/LD_{50}) is one of the properties where only the lower limit is important. In this case, as long as the LC_{50}/LD_{50} is above the safety limit, it is non-hazardous. Hence, the upper limit for LC_{50}/LD_{50} becomes insignificant. However, in order to utilise fuzzy optimisation approach, both upper and lower limits for the target property are required.

As discussed in Section 6.2.1, the satisfactory level for each property to be optimised is defined by a linear membership function consisting of upper and lower limits of the target property range. The situation where the information of the target property ranges is incomplete is modelled as a bi-level optimisation problem. As discussed in Chapter 2, the concept of bi-level optimisation is to obtain an optimised solution for the upper-level objective while independently optimising the lower-level objective(s). To apply this in chemical product design problems where some of the product target property ranges are unknown, the overall objective of the multi-objective chemical product design problem is modelled as the upper-level objective. The lower-level objectives would be the identification of target properties with incomplete target property ranges. In other words, in order to optimise the upper-level objective (overall objective of the multi-objective chemical product design problem), the lower-level objectives (target properties with incomplete target property ranges) have to be optimised beforehand. In order to obtain the lower and/or upper limit(s) for target properties which are required for the formulation of fuzzy optimisation model, bi-level optimisation approach is adapted to determine the product target property ranges which are not well defined and do not have exact values. Target properties where the target property ranges are indefinite are modelled as the lower-level objectives in the bi-level optimisation problem, as shown in Equations (6.4) – (6.6).

$$\text{Maximise } V_{p*} \tag{6.4}$$

$$\text{Minimise } V_{p*} \tag{6.5}$$

Subject to

$$v_p^{\mathrm{L}} \leq V_p \leq v_p^{\mathrm{U}} \tag{6.6}$$

While setting the property with known target property ranges V_p as constraints, Equations (6.4) and (6.5) are solved for the target property with unknown target property ranges V_{p*}. The solution attained from Equations (6.4) would serve as the upper limit for the respective target property while the solution obtained from Equation (6.5) would serve as the lower limit. With the identification of all target property ranges, the leader's objective, which is the optimisation of multiple objectives of the chemical product design problem, can now be solved. This is modelled as a fuzzy optimisation problem, as discussed in the following section.

6.2.3. Approaches in Fuzzy Optimisation

In this proposed multi-objective optimisation approach, two different fuzzy optimisation approaches are utilised for their advantages and suitability in the chemical product design problems. These two approaches are discussed in detail in the following sections.

6.2.3.1.Max-min Aggregation Approach

The objective of max-min aggregation approach is to make sure that every individual objective will be satisfied partially to at least the degree λ. Therefore, each individual objective has an associated fuzzy membership function and the optimum overall objective is obtained by maximising the least satisfied objective (Zimmermann, 1983, 1978). The objective here is to optimise the least satisfied property among all target properties to be optimised. Hence, the difference between the individual objectives can be minimised. This approach is suitable for multi-objective chemical product design problems where each target product property to be optimised is treated with equal importance. Max-min aggregation approach makes sure that the objectives in a multi-objective optimisation approach will not be over-improved while neglecting the importance of the other objectives. Therefore, by utilising max-min aggregation approach, a chemical product with multiple important target properties can be designed without overlooking the significance of any of the target properties to be optimised. The mathematical formulation for max-min aggregation approach is shown as follows:

$$\text{Maximise} \quad \lambda \tag{6.7}$$

$$\lambda \leq \lambda_p \qquad \forall p \in P \tag{6.8}$$

In Equation (6.8), λ_p is the degree of satisfaction for the target property p determined from Equations (6.1) and (6.2) depending on whether the target property is to be minimised or maximised. In order to optimise the least satisfied property among all target properties to be optimised λ_p, the least satisfied degree of satisfaction λ is maximised, as shown in Equations (6.7) and (6.8). In order to generate different feasible solutions for a multi-objective optimisation problem, integer cuts are utilised.

Max-min aggregation approach aims to maximise the least satisfied property so that the disparity in degrees satisfaction among all target properties to be optimised would be lessen. However, it is noted that this approach is unable to discriminate between solutions that vary in attained levels of satisfaction other than the least satisfied goal (Dubois and Fortemps, 1999; Dubois et al., 1996). While the least satisfied goal is maximised, since the other goals might be overly curtailed or relaxed, there is still room to search for better solutions in terms of degree of satisfaction. Thus, other than max-min aggregation approach, two-phase approach proposed by Guu and Wu (1999, 1997) is adapted into the proposed multi-objective optimisation approach.

6.2.3.2.Two-phase Approach

In order to utilise the two-phase approach, the multi-objective optimisation problem is solved sequentially in two phases. In the first phase of the optimisation problem, the problem is solved by using the max-min aggregation approach to obtain the degree of satisfaction of the least satisfied property. In the second phase of the optimisation problem, two-phase approach is utilised to solve the problem. The overall objective for two-phase approach is maximising the summation of all degrees of satisfaction. This means that all of the individual objectives for the chemical product design problem are optimised as a whole. Hence, the optimisation objective of two-phase approach is set as the maximisation of the summation of all degrees of satisfaction for every target properties to be maximised. This can be described by Equation (6.9).

$$\text{Maximise} \quad \sum_{p} \lambda_p^* \tag{6.9}$$

In Equation (6.9), λ_p^* is the degree of satisfaction determined from the second phase by using two-phase approach. The main purpose of utilising two-phase approach is to distinguish the solutions with identical least satisfied objectives and search for improved solution if there is any. In order to achieve the goal in differentiating the solutions with similar least satisfied goal and identifying the better solution, it is required to ensure that the solution obtained in the second phase will not be of any worse than the solutions initially obtained in the first phase. Hence, the degree of satisfaction obtained by using two-phase approach should not be lower than the degree of satisfaction of the least satisfied goal determined by using max-min approach. This is achieved by adding Equation (6.10) to the mathematical model.

$$\lambda_p^* \geq \lambda_p \qquad \forall p \in P \tag{6.10}$$

In Equation (6.10), λ_p is the degree of satisfaction of the least satisfied property obtained by using the max-min aggregation approach. As shown in Equation (6.10), the degrees of satisfaction of the target properties identified in the second stage λ_p^* will not be lower than the least satisfied property obtained in the first stage, λ_p. For its ability to distinguish solutions with similar least satisfied degree of satisfaction and search for better solution, two-phase approach is utilised in the proposed multi-objective optimisation approach.

6.2.4. Solution Procedure

This chapter presents a systematic multi-objective product design approach that identifies the optimal product that fulfils product needs by considering and optimising multiple target product properties. Figure 6.2 is a flowchart that shows the systematic procedure to design a chemical product by incorporating bi-level and fuzzy optimisation approaches into signature based molecular design techniques. The procedure is designed specifically for chemical product design problems where different classes of property prediction models are used and multiple product properties are optimised.

Step 1: Define the objective for the chemical product design problem, which can be done by identifying the required product needs.

Step 2: Identify and analyse target properties for the design problem. Based on the product specifications, these properties can be optimised or utilised as constraints during the design stage.

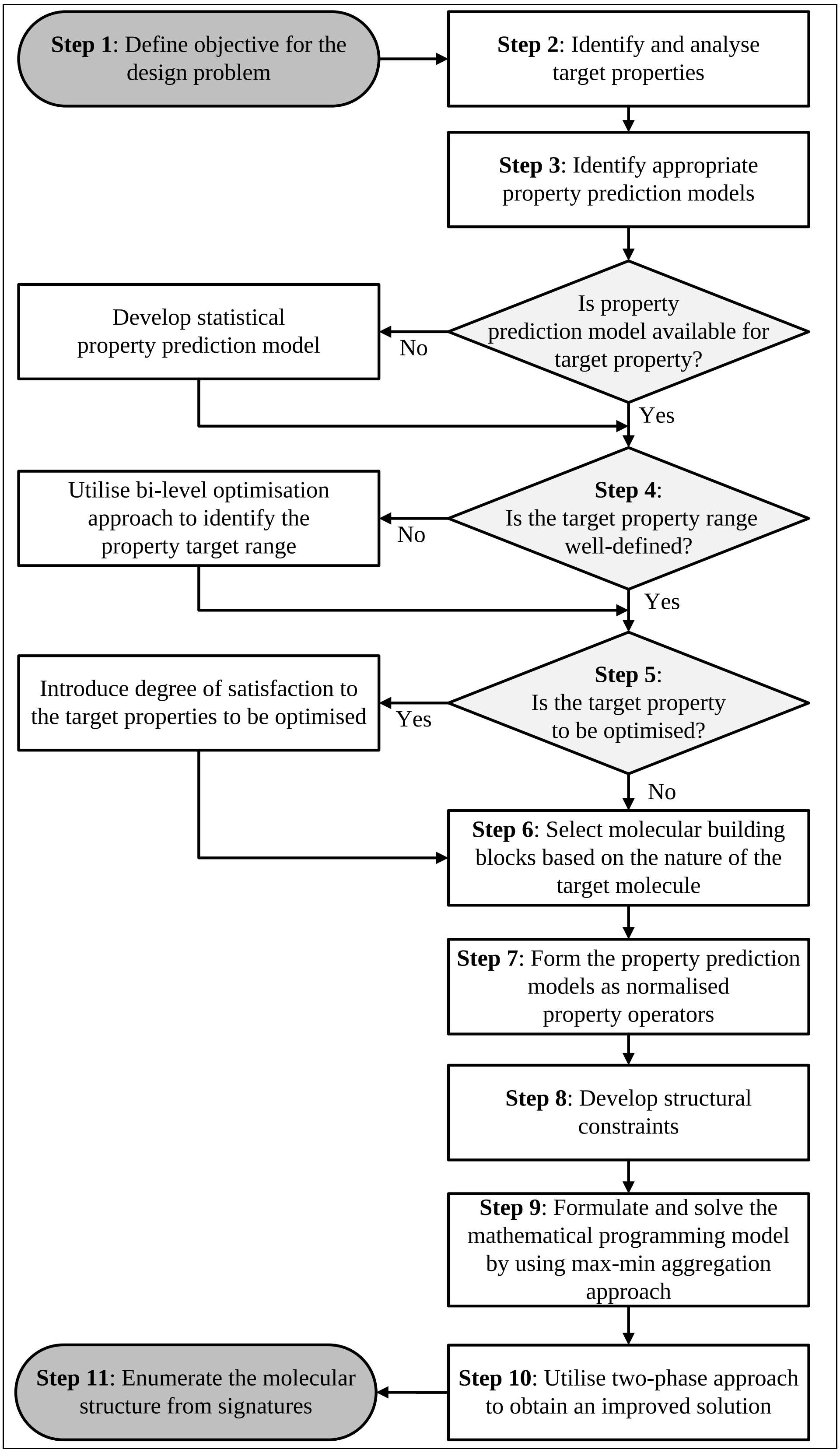


Figure 6.2: Procedure for solving a multi-objective chemical product design problem

Step 3: Identify appropriate property prediction models that can be used to estimate the target properties. The property prediction models chosen can be developed based on group contribution (GC) methods or different topological indices (TIs). For target properties where property prediction models are unavailable, models which combine experimental data and available property prediction models can be developed to estimate the respective property.

Step 4: Determine the target property ranges based on the product specifications, which can be obtained from product needs or process requirements. For target properties where the target property ranges are unknown, utilise bi-level optimisation approach as discussed in Section 6.2.2 to identify the particular target property ranges.

Step 5: Introduce degree of satisfaction, λ to target properties to be optimised by expressing the properties as fuzzy linear functions, as shown in Equations (6.1) and (6.2).

Step 6: Based on the nature of the chemical product target molecule, select the appropriate molecular building blocks (possible functional groups, types of bonds and atoms) and generate the molecular signatures.

Step 7: Form the property prediction models as normalised property operators, which are expressed as linear combinations of atomic signatures.

Step 8: Develop structural constraints from Equations (4.4) and (4.5) to ensure the formation of a complete molecular structure.

Step 9: Formulate and solve the mathematical programming model by using the max-min aggregation approach as discussed in Section 6.2.3.1 to obtain an initial solution with least satisfied fuzzy goal. Integer cuts are utilised to generate different alternatives.

Step 10: Utilise the two-phase approach as discussed in Section 6.2.3.2 to search for an improved solution.

Step 11: Enumerate the molecular structure from the list of signatures obtained from the design problem by using the graph signature enumeration algorithm developed by Chemmangattuvalappil and Eden (2013).

6.3. Case Study

To illustrate the proposed methodology, a solvent design problem for gas sweetening process taken from Kazantzi et al. (2007) is solved.

6.3.1. Problem Description and Problem Statement

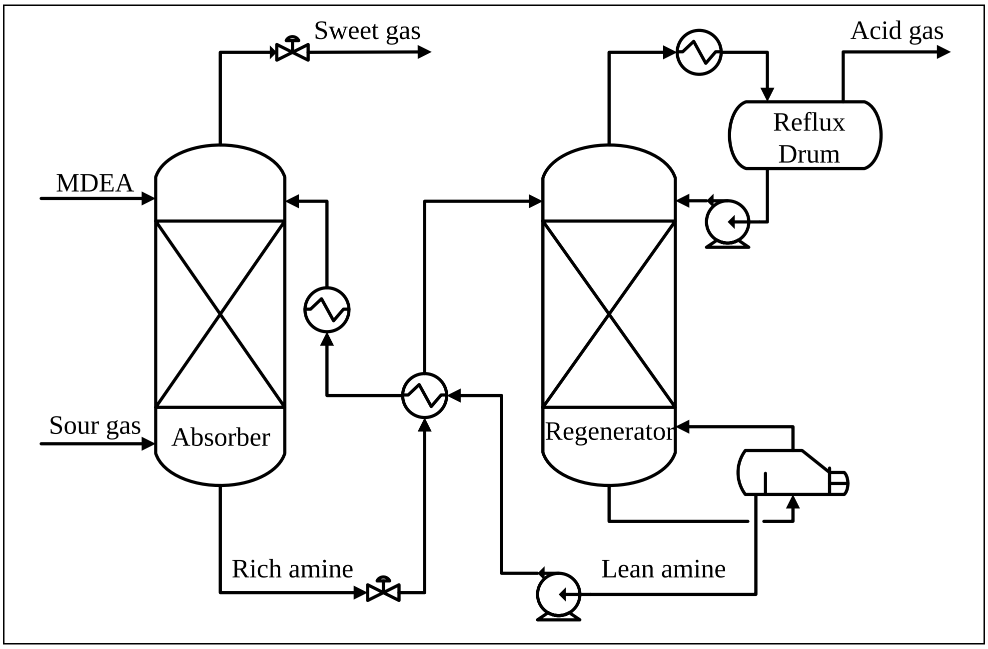


Figure 6.3: Process flow sheet of gas sweetening process

Figure 6.3 shows the gas sweetening process for the solvent design problem. Gas sweetening process aims to remove acid gases (hydrogen sulfide, H_2S and carbon dioxide, CO_2) from a gas stream. It is commonly used in refineries, petrochemical and natural gas processing plants. A typical gas sweetening process consists of mainly an absorber and a regenerator as well as other accessory equipment. In the absorber, amine solution removes the acid gases via counter-current absorption process. The gas stream free of acid gases (sweet gas) exits from the absorber as the top product while the amine solution rich in absorbed acid gases (rich amine) exits as the bottom product. The “rich amine” stream is then sent into a regenerator for regeneration process. The resultant bottom product, regenerated amine (lean amine) is recycled to the absorber, while the concentrated acid gases (H_2S and CO_2) exits as the stripped overhead gas. Typically, gas sweetening process uses methyl diethanolamine (MDEA) as the absorbent in the acid gas removal unit. The design goal is to identify a solvent that will replace MDEA as the absorbent that will reduce the usage of amine solution. Hence, the new solvent must be designed to possess similar functions of MDEA so that it can be used in the existing gas sweetening process without changing and rectifying the process.

Previously, Eljack et al. (2008) solved the same design problem via property clustering technique. As shown in Eljack et al. (2008), the targeted solution meets the required properties within the given target property ranges. The proposed technique solves the design problem as a property matching problem without performing property optimisation. Without optimising any property that can contribute to the design goal of reducing the usage of amine solution, it cannot be guaranteed that the designed product is the optimal product. The same design problem is solved by Chemmangattuvalappil and Eden (2013) as a single objective optimisation problem. In the work presented by Chemmangattuvalappil and Eden (2013), only one of the product properties is optimised during the design stage while matching the other product properties within the predefined target property ranges. Other than targeting only one property, there are other properties which play an equally important part in the overall design goal to be considered. Hence, in this case study, the solvent design problem is solved as multi-objective optimisation problem by addressing and optimising a number of important target properties simultaneously during the product design stage.

6.3.2. Solution of Design Problem

As the main objective of the design problem is to reduce the losses of MDEA, properties that contribute in attaining the overall design objective are chosen as the target properties of the design problem. In order to reduce the losses of MDEA, the designed solvent should possess high heat of vaporisation (H_v) and low vapour pressure (VP) to reduce evaporation losses of solvent. Furthermore, to encourage efficient removal of acid gases, the molar volume (V_m) of the solvent should be low so that there will be more solvent present in a fixed volume. Other than the properties which contribute to reducing the usage of MDEA, the designed solvent should have minimum soil sorption coefficient (K_{oc}), which is a measure of the tendency of a chemical to bind to soils to avoid accumulation of the escaping solvent in one place. Instead of estimating aqueous solubility of the solvent, K_{oc} is chosen as the measure of solubility to demonstrate the flexibility of the developed approach in utilising different classes of property models in a product design problem. This is further discussed in the next paragraph. Other than the abovementioned properties, the designed solvent should also be safe to use. Thus, the toxic limit concentration (*TLC*) for the solvent should be high. Note that based on the description, more than one target property has to be considered and optimised while designing the new solvent. Hence, this problem should be formulated as a multi-objective optimisation problem to design an optimal solvent which fulfils the design goals. In this case study, K_{oc}, *VP* and V_m are optimised simultaneously while designing the new solvent as they quantify the performance of the solvent. Meanwhile, H_v and *TLC* are target properties which are used as constraints to be fulfilled. The values of these properties are made sure to fall within the target property ranges without optimising the target properties. This solvent design problem is formulated as a fuzzy multi-objective optimisation problem.

Following the proposed procedure, after identifying the target properties for the solvent, property prediction models for each target property are identified. In order to demonstrate the ability of the developed approach in utilising different classes of property models in a product design problem, property models of GC methods and different TIs are chosen to estimate the target properties. Hence, log(K_{oc}) which can be estimated by using a TI model (Bahnick and Doucette, 1988) consists of different classes and heights of connectivity indices (CIs) is chosen over aqueous solubility, which can be estimated by GC method (Marrero and Gani, 2002) and CI (Siddhaye et al., 2004). Equation (6.11) shows the TI model that makes use of different classes and heights of CIs such as CI of order 1, valence CIs of order 0 and 1 as well as delta CI. As this property prediction model considers the polarity between different atoms, the difference between polar and non-polar molecular structure is addressed.

$$\log_{10}(K_{oc}) = 0.53\left({}^1\chi\right) - 1.25\left(\Delta^1\chi^v\right) - 0.72\left(\Delta^0\chi^v\right) + 0.66 \tag{6.11}$$

$$\Delta\chi = \chi_{np} - \chi \tag{6.12}$$

In Equations (6.11) and (6.12), ${}^1\chi$ is CI of order 1, ${}^0\chi^v$ and ${}^1\chi^v$ are the valence CIs of order 0 and 1 respectively; $\Delta\chi$ is the delta connectivity index while χ_{np} is the molecular CI of molecular non-polar structure.

For H_v, a reliable GC model is available as given in Equation (6.13) (Marrero and Gani, 2001). H_{v0} is an adjustable parameter, z^{I} and z^{II} are binary coefficients, N_i, N_j, N_k are the number of occurrence of first, second and third order molecular groups correspondingly and C_i, C_j, C_k are contribution of first, second and third order molecular groups respectively.

$$H_v = H_{v0} + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \tag{6.13}$$

As there is no CI or GC relationship available for the prediction of *VP*, an empirical relationship presented in Equation (6.14) is used to calculate VP from boiling point (Sinha et al., 2003). In Equation (6.14), *T* is the temperature where *VP* is evaluated at and T_b is the boiling point of the liquid, which can be expressed by using GC model developed by Marrero and Gani (2001).

$$\log_{10}(VP) = 5.58 - 2.7\left(\frac{T_b}{T}\right)^{1.7} \tag{6.14}$$

To demonstrate the ability of signature based inverse design technique in handling different classes of property prediction models, property prediction model based on edge adjacency index is utilised in this case study as well. Edge adjacency index is a TI developed by considering the interaction between the bonds (edges) in a molecule. In this case study, edge adjacency index developed by Dai et al. (1998) will be used to estimate the V_m of the solvent, as shown in Equation (6.15).

$$V_m = 33.52\varepsilon + 30.67 \tag{6.15}$$

In Equation (6.15), ε is the edge adjacency index. For *TLC*, a valence CI of order two developed by Koch (1982) will be utilised.

$$\log_{10}(TLC) = 34.204 - 1.385\left({}^{2}\chi^{v}\right) \tag{6.16}$$

With the identification of property prediction models, the next step is to determine the target property ranges for the target properties of solvent to be designed. The upper and lower limits of the target properties have been identified in the previous steps. Property prediction models and target property ranges for each of the target property are transformed into their respective normalised property operators. The target property ranges and their normalised target property ranges are shown in Table 6.1.

Table 6.1: Incomplete target property range and normalised target property ranges for the solvent design problem

Property	Ω_p	**Target property range**		**Normalised target property range**	
		v_p^{L}	v_p^{U}	Ω_p^{L}	Ω_p^{U}
K_{oc}	$\log_{10}(K_{oc}) - 0.66$	unknow	unknow	unknow	unknow
VP	$e^{\frac{T_b}{t_{b0}}}$	0.07 mm Hg	515.00 mm Hg	4.50	12.00
V_m	$\frac{V_m - 30.67}{33.52}$	60 cm3/m	216 cm^3/mol	0.89	5.50
H_v	$H_v - 11.733$	28 kJ/mol	66 kJ/mol	16.81	53.46
TLC	$\frac{4.204 - \log_{10}(TLC)}{1.385}$	10 ppm	-	-	2.31

As shown in Table 6.1, the target property range for K_{oc} is unknown at this stage. In order to determine the lower and upper bounds for K_{oc}, bi-level optimisation approach is utilised. The design problem is formulated as a single objective optimisation problem at this stage where only K_{oc} is optimised while the other properties are made sure to fall within the identified target property ranges. Since the target property ranges for VP, V_m, H_v and TLC are known, these properties are taken constraints while K_{oc} is optimised. The objective function is shown in Equation (6.17).

$$\text{Maximise/Minimise} \quad \Omega_{K_{oc}} \tag{6.17}$$

Together with structural constraints, the design problem is formulated and solved as a single objective mixed-integer linear programming (MILP) model. K_{oc} is minimised and maximised to obtain the lowest and highest values achievable for K_{oc} while satisfying other property and structural constraints as shown in Table 6.1. These values can be used as an indication for the identification of the lower and upper limits for K_{oc}. As shown in Table 6.2, the identified lower and upper limit for K_{oc} is 100 and 1000 respectively. These values are then transformed into the normalised property operators, with the value of 1.34 and 2.34 as shown in Table 6.2.

Table 6.2: Complete target property ranges and normalised target property ranges for the solvent design problem

Property	$\boldsymbol{\Omega_p}$	**Target property range**		**Normalised target property range**	
		$\boldsymbol{v_p^{\mathrm{L}}}$	$\boldsymbol{v_p^{\mathrm{U}}}$	$\boldsymbol{\Omega_p^{\mathrm{L}}}$	$\boldsymbol{\Omega_p^{\mathrm{U}}}$
K_{oc}	$\log_{10}(K_{oc}) - 0.66$	100	1000	1.34	2.34
VP	$e^{\frac{T_b}{t_{b0}}}$	0.07 mm Hg	515.00 mm Hg	4.50	12.00
V_m	$\frac{V_m - 30.67}{33.52}$	60 cm3/m	216 $\mathrm{cm^3/mol}$	0.89	5.50
H_v	$H_v - 11.733$	28 kJ/mol	66 kJ/mol	16.81	53.46
TLC	$\frac{4.204 - \log_{10}(TLC)}{1.385}$	10 ppm	-	-	2.31

Note that bi-level optimisation approach can be applied to identify the target property ranges even when the target property ranges for all properties of interest are unknown. This is because other than the property constraints, the objective function of the design problem is solved together with the structural constraints. Hence, without the presence of any target property ranges, bi-level optimisation approach identifies the lower and upper limits for each target properties that satisfy the structural constraints.

Following the procedure, the properties to be optimised are written as linear membership functions as shown in Equations (6.18) – (6.20) for K_{oc}, *VP* and V_m respectively. For target properties which are not optimised but used as constraints to fulfil, this step is unnecessary. The property constraints for such properties will remain the same, bounded by lower and upper limits.

$$\lambda_{K_{oc}} = \frac{2.34 - \Omega_{K_{oc}}}{2.34 - 1.34} \tag{6.18}$$

$$\lambda_{VP} = \frac{\Omega_{VP} - 4.50}{12.00 - 4.50} \tag{6.19}$$

$$\lambda_{V_m} = \frac{5.50 - \Omega_{V_m}}{5.50 - 0.89} \tag{6.20}$$

Note that K_{oc}, *VP* and V_m are to be minimised in this case study. From Equation (6.14) where Ω_{VP} is expressed in term of T_b, it is known that higher T_b values lead to lower values of *VP*. Hence, Ω_{VP} (expressed in terms of T_b) is maximised in order to obtain minimum *VP* as shown in Equation (6.18).

Next, molecular building blocks which are suitable for the design problem are determined. The molecular building blocks have to be selected such that the properties and molecular structure of the new solvent are similar to the available amine solutions. Absorbents which are available in the market and widely used industrially for gas sweetening process are identified as follow.

Monoethanolamine	$NH_2CH_2CH_2OH$
Diethanolamine	$OHCH_2CH_2NHCH_2CH_2OH$
Methyl diethanolamine	$OHCH_2CH_2NCH_3CH_2CH_2OH$
Diisopropylamine	$CH_3CH_3CHNHCHCH_3CH_3$

Based on the chemical formula of these existing amine solutions, molecular groups were chosen as the building blocks for the design of the new absorbent. These potential molecular groups are:

- OH
- CH_3
- CH_2
- CH_3N
- CH_2NH2
- CH_2NH
- $NHCH$

It is assumed that by designing a new absorbent with the chosen molecular groups as building blocks, the designed product will possess the functionalities of an amine solution capable of removing the acid gases. Signatures corresponding to these molecular groups are then generated so that only those which can form identical structures to the existing absorbents are selected.

6.3.3. Results and Discussions

6.3.3.1. Max-min Aggregation Approach

First the design problem is solved with max-min aggregation approach. The optimisation objective is to maximise the least satisfied property among K_{oc}, VP and V_m. The multi-objective MILP model is showed as below.

$$\text{Maximise} \quad \lambda \tag{6.21}$$

subject to

$$\lambda \le \frac{2.34 - \Omega_{K_{oc}}}{2.34 - 1.34} \tag{6.22}$$

$$\lambda \le \frac{\Omega_{VP} - 4.50}{12.00 - 4.50} \tag{6.23}$$

$$\lambda \le \frac{5.50 - \Omega_{V_m}}{5.50 - 0.89} \tag{6.24}$$

$$16.81 \le \Omega_{H_v} \le 53.46 \tag{6.25}$$

$$\Omega_{TLC} \le 2.31 \tag{6.26}$$

Together with the structural constraints, the design problem is solved and the optimum solution is obtained in terms of signatures. By utilising integer cuts, the best five solutions are obtained in terms of signatures and summarised in Table 6.3.

Table 6.3: List of solutions in terms of signatures

Solution	Signature	Occurrence
A	C1(C2(C1(C)C2(CC)))	1
	C2(C1(C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C1(C)C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)C2(CO)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)O2(CC)))	1
	C2(C2(C2(CC)C2(OC))O2(C1(O)C2(CO)))	1
	O2(C1(O2(CC))C2(C2(CC)O2(CC)))	1
	C1(O2(C1(O)C2(CO)))	1
B	C1(C2(C1(C)C2(CC)))	1
	C2(C1(C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C1(C)C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)C2(CO)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)O2(CC)))	1
	C2(C2(C2(CC)C2(OC))O2(C2(CO)C2(CO)))	1
	O2(C2(C1(C)O2(CC))C2(C2(CC)O2(CC)))	1
	C2(C1(C2(OC))O2(C2(CO)C2(CO)))	1
	C1(C2(C1(C)O2(CC)))	1
C	C1(C2(C1(C)C2(CC)))	1
	C2(C1(C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C1(C)C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)C2(CC)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(OC)C2(CC)))	1
	C2(C2(C2(CC)C2(CC))C2(C2(CC)O2(CC)))	1
	C2(C2(C2(CC)C2(OC))O2(C2(CO)C2(CO)))	1
	O2(C2(C1(C)O2(CC))C2(C2(CC)O2(CC)))	1
	C2(C1(C2(CO))O2(C2(CO)C2(CO)))	1
	C1(C2(C1(C)O2(CC)))	1
D	C1(C2(C1(C)C2(CC))	2
	C2(C1(C2(CC))C2(C2(CC)C2(CC)))	2
	C2(C2(C1(C)(2(CC))C2(C2(CC)C2(CC)))	2
	C2(C2(C2(CC)C2(CC))C2(C2(CC)C2(CC)))	1
E	C1(C2(C1(C)C2(CC))	2
	C2(C1(C2(CC))C2(C2(CC)C2(CC)))	2
	C2(C2(C1(C)(2(CC))C2(C2(CC)C2(CC)))	2

With the signatures obtained by solving the design problem, molecular graph can now be generated based on the graph signature enumeration algorithm developed by Chemmangattuvalappil and Eden (2013). By using the graph enumeration algorithm, molecular structure is generated from the list of signatures, and the name of the new solvent is identified. The best five solutions are summarised in Table 6.4. The enumerated molecular structures of the solutions are shown in Table 6.5.

Table 6.4: List of solutions in terms of product specifications

Sol.	**Solvent**	K_{oc}	***VP*** **(mm Hg)**	V_m **(cm^3/mol)**	H_v **(kJ/mol)**	***TLC*** **(ppm)**
A	Heptyl methyl ether	139	22.82	169	47	14
B	Ethyl hexyl ether	108	22.82	171	47	58
C	Ethyl heptyl ether	198	9.13	188	52	19
D	Heptane	295	151.85	128	37	22
E	Hexane	160	470.01	112	32	69

From Table 6.4, it can be seen that all of the solvent properties fall between the target property ranges that represent the customer requirements (see Table 6.2). Note that these molecules are targeted based on the given properties and structural constraints. Therefore, these molecules are capable in replacing MDEA as the solvent for gas sweetening process. Compared to MDEA, most of the generated solvents possess better performance of K_{oc} while having comparable values with MDEA for V_m and H_v. However, *VP*

Table 6.5: List of solutions in terms of molecular structure

Sol.	Name and molecular structure
A	Heptyl methyl ether $CH_3 - O - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
B	Ethyl hexyl ether $CH_3 - CH_2 - O - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
C	Ethyl heptyl ether $CH_3 - CH_2 - O - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
D	Heptane $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$
E	Hexane $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

and *TLC* for the generated solvents are not as good as those possessed by MDEA as *VP* for most of the generated solvents are higher than MDEA's while *TLC* for most of designed solvents are lower than MDEA's.

In order to compare the solutions with the solutions generated by solving the design problem as single objective optimisation problem, the MILP model is solved as single objective optimisation problem to generate solutions with single optimised property. Equations (6.27) – (6.29) are solved separately subject to the corresponding property and structural constraints.

$$\text{Minimise} \quad \Omega_{K_{oc}} \tag{6.27}$$

$$\text{Maximise} \quad \Omega_{VP} \tag{6.28}$$

$$\text{Minimise} \quad \Omega_{V_m} \tag{6.29}$$

Table 6.6 shows the solutions with minimised K_{oc}, minimised *VP* and minimised V_m.

Table 6.6: List of solutions with single optimised target property

Optimised property	**Solution**	K_{oc}	***VP*** **(mm Hg)**	V_m **(cm^3/mol)**	H_v **(kJ/mol)**	***TLC*** **(ppm)**
Minimised K_{oc}	B	108	22.82	171	47	58
Minimised *VP*	C	198	9.13	188	52	19
Minimised V_m	E	160	470.01	112	32	69

From Table 6.6, the solution with minimised K_{oc} is solution B (ethyl hexyl ether), the solution with minimised *VP* is solution C (ethyl heptyl ether) while the solution with minimised V_m is solution E (hexane). Although the generated solutions with single optimised property are within the solutions generated by using the developed multi-objective optimisation approach, it is very difficult to ensure that the generated solutions are Pareto optimal solutions. As single objective optimisation approach identifies solutions by optimising only one of the target properties, there is a possibility that the other properties of interest can be improved to produce a better solution. Hence, Pareto optimal solutions cannot be guaranteed while solving the product design problem with multiple target properties by using single objective optimisation approach. Table 6.7 shows the comparison of degrees of satisfaction between the solutions generated by using max-min aggregation approach. The relative importance of each properties of interest, a_p shown in Table 6.7 can be determined by using Equation (6.30).

Table 6.7: Comparison of λ_p between different solutions

Solution	**Solvent**	$\lambda_{K_{oc}}$	λ_{VP}	λ_{V_m}	$a_{K_{oc}}$	a_{VP}	a_{V_m}
A	Heptyl methyl ether	0.8572	0.2807	0.2983	0.60	0.19	0.21
B	Ethyl hexyl ether	0.9680	0.2807	0.2863	0.63	0.18	0.19
C	Ethyl heptyl ether	0.7030	0.3759	0.1779	0.56	0.30	0.14
D	Heptane	0.5304	0.1025	0.5606	0.44	0.09	0.47
E	Hexane	0.7954	0.0073	0.6690	0.54	0.01	0.45

$$a_p = \frac{\lambda_p}{\sum \lambda_p} \tag{6.30}$$

In Equation (6.30), a_p denotes the weighting factors that a decision maker has to assign to each target property if the design problem is solved by using the conventional weighted sum method. As shown in Table 6.7, the property with highest weighting factors is not always the same for the generated solutions. Since the relative importance for each target property is different for each solution, it is very difficult in identifying the optimal solutions by using the conventional weighted sum method.

From Table 6.7, it can be seen that each of the property of the solvent is treated justly as solutions are ranked accordingly to their least satisfied property. It is shown that the least satisfied property is not always the same property for all the five generated solutions. This indicates that the developed approach identifies the relative importance of each property to be optimised without the presence of a decision maker. As long as the degree of satisfaction for the least satisfied property is maximised, the generated solution is a feasible molecule capable of replacing the available solvent. However, it can also be noticed from Table 6.7 that the least satisfied property for Solution A and Solution B are the same, where *VP* for both solutions are having the same value of 0.2807. Therefore, it is not possible to distinguish which solution is more superior at this stage by solely referring to the least satisfied property. This is the limitation of max-min aggregation approach. As discussed earlier, the primary weakness of max-min aggregation approach is its lack of discriminatory power to distinguish between solutions which have different levels of satisfaction other than the least satisfied goal. It is noted that the max-min aggregation approach models flexible constraints rather than objective functions. Some of the objectives might be overly relaxed or curtailed in order to maximise the least satisfied objective. Due to this limitation, max-min aggregation approach does not guarantee to yield a Pareto optimal solution (Clark and Westerberg, 1983; Jiménez and Bilbao, 2009). In order to discriminate these solutions to refine the order of solutions and at the same time ensure the generation of a Pareto optimal solution, two-phase approach is utilised.

6.3.3.2.Two-phase Approach

The aim of two-phase approach is to maximise all the properties as a whole, as shown in Equation (6.31). As the degree of satisfaction for the least satisfied property identified by using the max-min aggregation approach is 0.2807, the degree of satisfaction for the second stage should be equal or higher than this value to ensure that the solution obtain in the second stage is not worse than the solution obtained in the first stage. Hence, Equation (6.32) is included in the optimisation model.

$$\text{Maximise} \quad \sum_{p} \lambda_{p}^{*} \tag{6.31}$$

subject to

$$\lambda_{p}^{*} \geq 0.2807 \tag{6.32}$$

$$\lambda_{K_{oc}}^{*} = \frac{2.34 - \Omega_{K_{oc}}}{2.34 - 1.34} \tag{6.33}$$

$$\lambda_{VP}^{*} = \frac{\Omega_{VP} - 4.50}{12.00 - 4.50} \tag{6.34}$$

$$\lambda_{V_{m}}^{*} = \frac{5.50 - \Omega_{V_{m}}}{5.50 - 0.89} \tag{6.35}$$

$$16.81 \leq \Omega_{H_{v}} \leq 53.46 \tag{6.36}$$

$$\Omega_{TLC} \leq 2.31 \tag{6.37}$$

The mathematical model above is solved and the best five solutions are obtained and showed in Table 6.8. The solutions are ranked according to their summation of all degrees of satisfaction.

From Table 6.8, it is noted that the ranking changes significantly compared to that obtained in the first stage (see Table 6.4). More importantly, the solutions with similar least satisfied property are distinguished. According

Table 6.8: Comparison of $\sum \lambda_p^*$ between different solutions

Solution	**Solvent**	$\lambda_{K_{oc}}^*$	λ_{VP}^*	$\lambda_{V_m}^*$	$\sum \lambda_p^*$
B	Ethyl hexyl ether	0.9680	0.2807	0.2863	1.5350
E	Hexane	0.7954	0.0073	0.6690	1.4716
A	Heptyl methyl ether	0.8572	0.2807	0.2983	1.4362
C	Ethyl heptyl ether	0.7030	0.3759	0.1779	1.2568
D	Heptane	0.5304	0.1025	0.5606	1.1934

to their summation of all levels of satisfaction, although both heptyl methyl ether (Solution A) and ethyl hexyl ether (Solution B) have the same least satisfied property, heptyl methyl ether is now ranked third, while ethyl hexyl ether is now ranked first among all the solutions. The degree of satisfaction in terms of least satisfied property is still the highest for Solution 1 by using two-phase approach. This indicates that even though two-phase approach is able to discriminate the solutions with similar least satisfied property, the approach does not compromise the degree of satisfaction of that property. Hence, utilisation of two-phase approach after max-min aggregation approach ensure the generation of optimal results without worsening any property in terms of degree of satisfaction. This can be further confirmed by illustrating all possible optimal solutions via Pareto frontier as shown in Figure 6.4.

Figure 6.4 shows the Pareto frontier for the solvent design problem. The optimisation objective used to generate the Pareto frontier is given in Equation (6.38) as shown below.

$$\text{Maximise} \quad a_{K_{oc}} \Omega_{K_{oc}} + a_{VP} \Omega_{VP} + a_{V_m} \Omega_{V_m} \tag{6.38}$$

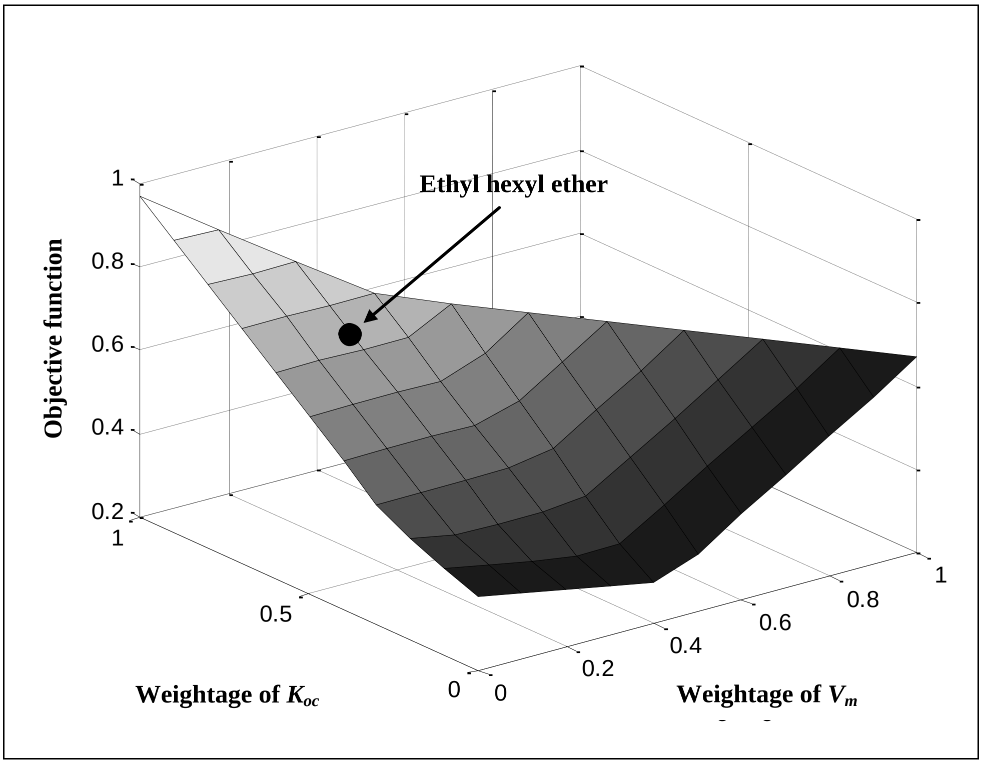


Figure 6.4: Pareto frontier for the solvent design problem

In Equation (6.38), $a_{K_{oc}}$, a_{VP} and a_{V_m} are the weighting factors manually assigned to K_{oc}, VP and V_m to represent the property contributions decided by a decision maker. Figure 6.4 is constructed with the list of solutions obtained by altering the values of $a_{K_{oc}}$, a_{VP} and a_{V_m} in Equation (6.38) and solving the objective function together with other property and structural constraints. From Figure 6.4, it can be seen that ethyl hexyl ether (Solution B) is on the Pareto frontier. This shows although max-min aggregation approach maximises the least satisfied property, it does not guarantee to yield a Pareto optimal solution. However, by utilising two-phase approach after max-min approach, a Pareto optimal solution can be obtained. By seeking for maximum utilisation of each product properties, this guarantees a Pareto optimal product while optimising multiple product properties. The mathematical formulations and results generated by using bi-level optimisation approach, max-min aggregation approach and two-phase approach in this case study can be found in Appendix D of this thesis.

6.4. Conclusion

This chapter introduces a systematic multi-objective optimisation approach for chemical product design problems by incorporating fuzzy and bi-level optimisation approaches into molecular design techniques. By utilising signature based molecular design techniques, different classes of property prediction models are expressed in terms of molecular signatures and utilised in a chemical product design problem. By incorporating fuzzy optimisation approach into the methodology, property weighting factors in a multi-objective optimisation problem are able to be addressed systematically without bias and optimal product can be identified. Bi-level optimisation approach has been utilised to determine the target property ranges which are undefined. The product properties are first maximised based on max-min aggregation approach. Two-phase approach is then employed to discriminate the products with similar least satisfied property. The developed multi-objective optimisation approach is able to design chemical product by considering and optimising multiple target properties simultaneously without any bias.

CHAPTER 7

ROBUST CHEMICAL PRODUCT DESIGN VIA FUZZY OPTIMISATION APPROACH

7.1. Introduction

While utilising CAMD techniques for chemical product design problems, optimal chemical products are designed by identifying the molecules with the best properties that correspond with the target functionalities of the products. In general, the optimality of the product property(s) is the only factor considered while designing the optimal products by using CAMD techniques. However, it is noted that property prediction models are developed with certain accuracy and uncertainty. According to Vose (2008), uncertainty of a model reflects the lack of knowledge during the development of the model. As the accuracy of property prediction models affect the effectiveness of CAMD techniques in predicting the product property, the effects of the property prediction model accuracy have to be considered while applying CAMD techniques. This chapter presents a robust chemical product design approach for the optimum chemical product design by optimising property superiority while considering property robustness.

According to Gregory et al. (2011), robust optimisation is a modelling methodology that seeks to minimise the negative impact of future events when the variable and their distributions are uncertain, and the values of model parameters are unknown. Model robustness can be defined in many different ways. In general, robustness can be viewed as a performance guarantee. In order words, a model can be defined as robust if it guarantees, with high probability, that the solution will be feasible, and the optimal objective will be achieved for all possible realisations of each unknown parameter (Gregory et al., 2011). Sensitivity analysis can be used to test the robustness of the results generated by a model in the presence of uncertainty (Chau et al., 2009). According to Komorowski et al. (2011), sensitivity analysis is generally done to illustrate the effect of changes in parameters and factors on a model performance. Hence, model robustness can be analysed. For process system engineering applications, robustness can be understood as the stability of the system behaviour under simultaneous changes in the model parameters (Komorowski et al., 2011). In this developed optimisation approach, the approach is defined as robust if it can identify, with high probability, the chemical product by using property prediction models.

In order to design an optimal chemical product, both property superiority and property robustness are taken into consideration in this systematic robust chemical product design approach. Property superiority is quantified by the property optimality. Meanwhile, property robustness is expressed by the standard deviation of the property prediction model, which is a measure of the average variation between the experimental data and the estimated values of product properties by using the property prediction models. Signature based molecular design techniques are utilised to identify the optimal molecular structure which satisfies the product needs. In addition, fuzzy optimisation approach is adapted to address and trade off both property superiority and robustness simultaneously. To illustrate the presented approach, a case study is presented where the optimal solution is selected based on how much the solution satisfied the criteria of property superiority and robustness.

7.2. Robust Chemical Product Design Approach

In order to design optimal products with optimised product properties subject to property prediction model accuracy, a systematic robust chemical product design approach is presented. The goal of the chemical product design problem is to determine the optimal chemical product where multiple target properties are optimised simultaneously while considering both property superiority and robustness. As proven to be effective in solving multi-objective optimisation problems, different fuzzy optimisation approaches are adapted in developing the robust chemical product design approach. Max-min aggregation approach (discussed in Section 6.2.3.1) and two-phase approach (discussed in Section 6.2.3.2) are utilised to address the simultaneous consideration and optimisation of property superiority and robustness during the product design stage. The details of the developed robust chemical product design approach are discussed in the following sections.

7.2.1. Fuzzy Optimisation based Molecular Design Techniques under Uncertainty of Property Prediction Models

The presented approach designs optimal chemical products where multiple target properties are optimised simultaneously while considering both property superiority and robustness. To maximise the optimality of product properties (property superiority), target properties to be optimised are first identified and expressed as target property ranges bounded by upper and lower limits. Then, the comparison and trade-off between the target properties to be optimised are done by introducing a degree of satisfaction for property superiority, λ^{s} to each of the properties. This can be achieved through writing λ^{s} as a linear membership function bounded by lower and upper limits of the target property. The mathematical representation of the relationship between the target property and λ^{s} is shown by Equations (7.1) and (7.2). Note that Equation (7.1) is used for property to be minimised while Equation (7.2) is used for property to be maximised.

$$\lambda_p^{\mathrm{s}} = \begin{cases} 1 & \text{if} \quad V_p \le v_p^{\mathrm{L}} \\ \dfrac{v_p^{\mathrm{U}} - V_p}{v_p^{\mathrm{U}} - v_p^{\mathrm{L}}} & \text{if} \quad v_p^{\mathrm{L}} \le V_p \le v_p^{\mathrm{U}} \\ 0 & \text{if} \quad V_p \ge v_p^{\mathrm{U}} \end{cases} \qquad \forall p \in P \qquad (7.1)$$

$$\lambda_p^{\mathrm{s}} = \begin{cases} 0 & \text{if} \quad V_p \le v_p^{\mathrm{L}} \\ \dfrac{V_p - v_p^{\mathrm{L}}}{v_p^{\mathrm{U}} - v_p^{\mathrm{L}}} & \text{if} \quad v_p^{\mathrm{L}} \le V_p \le v_p^{\mathrm{U}} \\ 1 & \text{if} \quad V_p \ge v_p^{\mathrm{U}} \end{cases} \qquad \forall p \in P \qquad (7.2)$$

$$0 \le \lambda_p^{\mathrm{s}} \le 1 \qquad \forall p \in P \qquad (7.3)$$

In Equations (7.1) and (7.2), λ_p^{s} is the degree of satisfaction for property superiority. As shown in Equation (7.3), λ_p^{s} is bounded within the interval of 0 to 1, which represents the level of satisfaction of the target property value V_p within the predefined target property range (v_p^{L} and v_p^{U}). The higher the λ_p^{s}, the better the product is in terms of property superiority. For property to be minimised, as lower value is preferred, when the property approaches the lower limit, the λ_p^{s} approaches 1; when the property approaches the upper limit, the λ_p^{s} approaches 0. Vice versa applies to property to be maximised as higher value is desired. This can be explained graphically in Figure 6.1, which has been discussed in Chapter 6.

As target properties of the product are estimated by using property prediction models, the predefined target property ranges are highly dependent on the accuracy of the property prediction model. Hence, the optimal solution for a design problem might differ accordingly to the accuracy of the property prediction models. To maximise the property robustness, the effect of property prediction model accuracy (property robustness) in the form of standard deviation of the property prediction model for the target property p, σ_p is considered. σ_p is chosen as it is the measure of the average variation between the measured and estimated values in regression analysis. After taking the allowance of the property prediction model accuracy, the target property ranges are shifted and divided into three different regions to improve the estimation of the target properties. An example to estimate a molecule with target property range for boiling point (T_b), 80 ℃ < T_b < 100 ℃ by utilising a property prediction model with σ_p of 10 ℃ is shown here. In order to take the allowance of property prediction model accuracy in terms of σ_p into consideration, the target property range is revised as 70 ℃ < T_b < 110 ℃. This allows the effect of property prediction model accuracy to be considered during the generation of the molecule. Hence, together with the optimality of product property, the effects of the accuracy of property prediction models are taken into consideration while identifying the optimal product. The three regions after shifting and dividing the target property ranges are certain region (CR) and uncertain region (UR) which consists of lower uncertain region (LUR) and upper uncertain region (UUR). Figure 7.1 shows the graphical representation and comparison of fuzzy linear functions for property superiority and robustness after the shifting and diving of the target property ranges.

In Figure 7.1 (a), LUR is the region below the CR while UUR is the region above it. Depending on the accuracy of the property prediction model provided from the source literature of the property prediction model, the confidence level that the predicted target property will fall within the CR is higher compared to the confidence level that the predicted target property will fall within the LUR or UUR. The lower and upper limits for these regions are obtained by adding and subtracting σ_p for the respective property prediction model from the v_p^{L} and v_p^{U} of the target property. LUR is bounded by lower

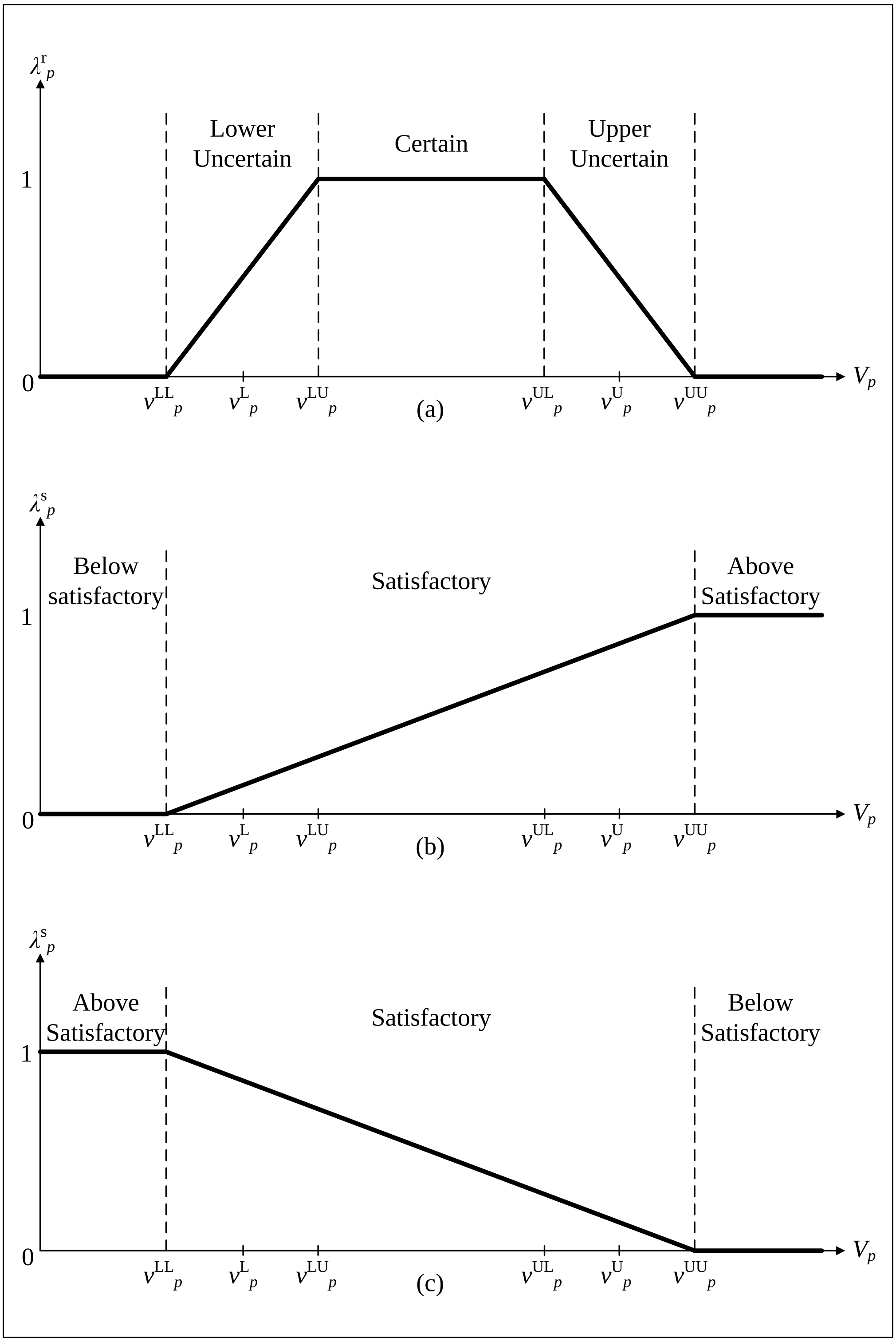


Figure 7.1: Fuzzy membership functions for: (a) property robustness;

(b) property superiority of property to be maximised;

(c) property superiority of property to be minimised lower limit (v_p^{LL}) and lower upper limit (v_p^{LU}); CR is bounded by lower upper limit (v_p^{LU}) and upper lower limit (v_p^{UL}); UUR is bounded by upper lower limit (v_p^{UL}) and upper upper limit (v_p^{UU}). This is summarised in Table 7.1.

Table 7.1: Lower and upper limits for regions with different certainty

Region	**Lower limit**	**Upper limit**
Lower uncertain region	$v_p^{\mathrm{LL}} = v_p^{\mathrm{L}} - \sigma_p$	$v_p^{\mathrm{LU}} = v_p^{\mathrm{L}} + \sigma_p$
Certain region	$v_p^{\mathrm{LU}} = v_p^{\mathrm{L}} + \sigma_p$	$v_p^{\mathrm{UL}} = v_p^{\mathrm{U}} - \sigma_p$
Upper uncertain region	$v_p^{\mathrm{UL}} = v_p^{\mathrm{U}} - \sigma_p$	$v_p^{\mathrm{UU}} = v_p^{\mathrm{U}} + \sigma_p$

For chemical product design problems, other than the target properties to be optimised, there are target properties which are used as property constraints to be fulfilled without optimising the target properties. It is worth noting that the shifting of target property ranges applies to these target properties which are not optimised as well. By taking the property prediction model accuracy into consideration for target properties which are not optimised, it is made sure that the developed approach is consistent towards every property prediction models utilised in the product design problem. From Figure 7.1 (b) and (c), it can be seen that the target property ranges are stretched. As the property prediction model accuracy is taken into account, the lower and upper limits of the product specification are shifted as well. This can be shown in Equation (7.4). Similarly, lower and upper limits in Equations (7.1) and (7.2) are modified as well. Equations (7.5) and (7.6) show the mathematical representation of λ^{s} after the shifting of target property ranges.

$$v_p^{\mathrm{LL}} \le V_p \le v_p^{\mathrm{UU}} \qquad \forall p \in P \tag{7.4}$$

$$\lambda_p^{\mathrm{s}} = \begin{array}{lll} 1 & if & V_p \le v_p^{\mathrm{LL}} \\ \dfrac{v_p^{\mathrm{UU}} - V_p}{v_p^{\mathrm{UU}} - v_p^{\mathrm{LL}}} & if & v_p^{\mathrm{LL}} \le V_p \le v_p^{\mathrm{UU}} \qquad \forall p \in P \\ 0 & if & V_p \ge v_p^{\mathrm{UU}} \end{array} \tag{7.5}$$

$$\lambda_p^{\mathrm{s}} = \begin{array}{lll} 0 & if & V_p \le v_p^{\mathrm{LL}} \\ \dfrac{V_p - v_p^{\mathrm{LL}}}{v_p^{\mathrm{UU}} - v_p^{\mathrm{LL}}} & if & v_p^{\mathrm{LL}} \le V_p \le v_p^{\mathrm{UU}} \qquad \forall p \in P \\ 1 & if & V_p \ge v_p^{\mathrm{UU}} \end{array} \tag{7.6}$$

In order to maximise property robustness for a chemical product design problem, trade-off between the target properties to be optimised is done by introducing a degree of satisfaction for property robustness, λ^{r} to each of the target properties. As mentioned earlier, after making allowances for the accuracy of property prediction models, the confidence level that the predicted target property will fall within the CR is higher compared with the confidence level that the predicted target property will fall within LUR or UUR. Thus, a value of 1 is given to λ^{r} when the target property falls within CR and 0 when it falls outside of the range bounded by LUR and UUR. Within LUR and UUR, the nearer the target property falls from the CR, the better it is in terms of property robustness. As CR, assigned with λ^{r} of 1 is bounded by two linear membership functions, which are λ^{r} in LUR and UUR, this forms an isosceles trapezoidal shape as shown in Figure 7.1 (a). Therefore, this can be modelled as a two-sided fuzzy optimisation problem by using the trapezoidal fuzzy membership function, as discussed in Chapter 2. This is described mathematically by using the following equations.

$$\lambda_p^{\mathrm{r}} = \begin{cases} 0 & \textit{if} \quad V_p \le v_p^{\mathrm{LL}} & \\ \dfrac{V_p - v_p^{\mathrm{LL}}}{v_p^{\mathrm{LU}} - v_p^{\mathrm{LL}}} & \textit{if} \quad v_p^{\mathrm{LL}} \le V_p \le v_p^{\mathrm{LU}} & \forall p \in P \\ 1 & \textit{if} \quad v_p^{\mathrm{LU}} \le V_p \le v_p^{\mathrm{UL}} & \forall p \in P \\ \dfrac{v_p^{\mathrm{UU}} - V_p}{v_p^{\mathrm{UU}} - v_p^{\mathrm{UL}}} & \textit{if} \quad v_p^{\mathrm{UL}} \le V_p \le v_p^{\mathrm{UU}} & \forall p \in P \\ 0 & \textit{if} \quad V_p \ge v_p^{\mathrm{UU}} & \end{cases} \tag{7.7}$$

$$0 \le \lambda_p^{\mathrm{r}} \le 1 \qquad \forall p \in P \tag{7.8}$$

In Equations (7.7) and (7.8), λ_p^{r} is the degree of satisfaction for property robustness for the target property *p*. When V_p falls within LUR, λ_p^{r} approaches 0 as V_p approaches v_p^{LL} and it approaches 1 when V_p approaches v_p^{LU}; when V_p falls within UUR, λ_p^{r} approaches 0 as V_p approaches v_p^{UU} and it approaches 1 when V_p approaches v_p^{UL}; when V_p falls within CR, λ_p^{r} remains as 1.

To obtain the optimal solution in terms of property superiority and property robustness, the multi-objective chemical product design problem is solved by utilising fuzzy optimisation approaches in two stages. In the first stage, max-min aggregation approach is adapted to obtain the least satisfied degree of satisfaction. The objective of max-min aggregation approach is to make sure that every individual objective will be satisfied partially to at least the degree λ. Therefore, each individual objective has an associated fuzzy function and the optimum overall objective is obtained by maximising the least satisfied objective (Zimmermann, 1978). The objective function of max-min aggregation approach is shown in Equation (7.9), subjected to constraint as shown in Equation (7.10).

$$\text{Maximise} \quad \lambda \tag{7.9}$$

$$\lambda \leq \lambda_p \qquad \forall p \in P \tag{7.10}$$

Note that the degree of satisfaction for target property p, λ_p applies to both property superiority and property robustness. By solving Equations (7.9) and (7.10), a solution with maximised least satisfied degree of satisfaction is generated. This solution is the optimal product in terms of property superiority and property robustness. Additional feasible solutions can be generated by using integer cuts. Max-min aggregation approach aims to maximise the least satisfied degree of satisfaction so that the difference among all degrees of satisfaction would be reduced. However, as discussed in Section 6.2.3.1, max-min aggregation approach is unable to distinguish between solutions that possess similar value of least satisfied degree of satisfaction. Hence, two-phase approach is adapted to address this limitation.

In the second stage, two-phase approach is applied to solve the optimisation problem. The overall objective for two-phase approach is to maximise the summation of all degrees of satisfaction. This means that all of the individual objectives are contributing to the objective function and optimised as a whole. The objective function of two-phase approach is shown in Equation (7.11).

$$\text{Maximise} \quad \sum_{p} \lambda_{p}^{*} \tag{7.11}$$

Moreover, to generate improved solutions and at the same time differentiate between solutions with identical least satisfied degree of satisfaction, it must be ensured that the solution obtained in the second stage will not be worse than the solution initially obtained in the first phase. In order to guarantee so, Equation (7.12) is introduced.

$$\lambda_{p}^{*} \geq \lambda_{p} \qquad \forall p \in P \tag{7.12}$$

In Equations (7.11) and (7.12), λ_{p}^{*} is the new degree of satisfaction identified in second stage and λ_p is the least satisfied degree of satisfaction identified in the first stage. As explained earlier, λ_{p}^{*} and λ_p apply to both property superiority and property robustness. From Equation (7.12), the individual degree of satisfaction obtained in the second stage must be equal or greater than the one obtained in the first stage in order to obtain a feasible solution. Thus, if two-phase approach does not generate a feasible solution in the second stage, the solution obtained in the first stage by using max-min aggregation approach is the optimal solution for the multi-objective product design problem.

7.2.2. Solution Procedure

This chapter presents a systematic robust chemical product design approach that identifies the optimal product in terms of property superiority and property robustness. Different fuzzy optimisation approaches are adapted to address and maximise both property superiority and property robustness of the target properties simultaneously. At the same time, signature-based molecular design techniques are utilised to identify the feasible molecular structure of the optimal product that fulfils the property and structural constraints. Figure 7.2 shows the procedure of the developed approach, which has been summarised in the following steps:

Step 1: Define the design goal and objective for the chemical product design problem. This can be done by identifying the required product needs.

Step 2: Identify and analyse target properties for the design problem. Based on the product specifications, these properties can be optimised or utilised as constraints during the product design stage.

Step 3: Identify the appropriate property prediction models that can estimate the target properties. The property prediction models chosen can be developed based on group contribution (GC) methods or different topological indices (TIs). For target properties where property prediction models are unavailable,

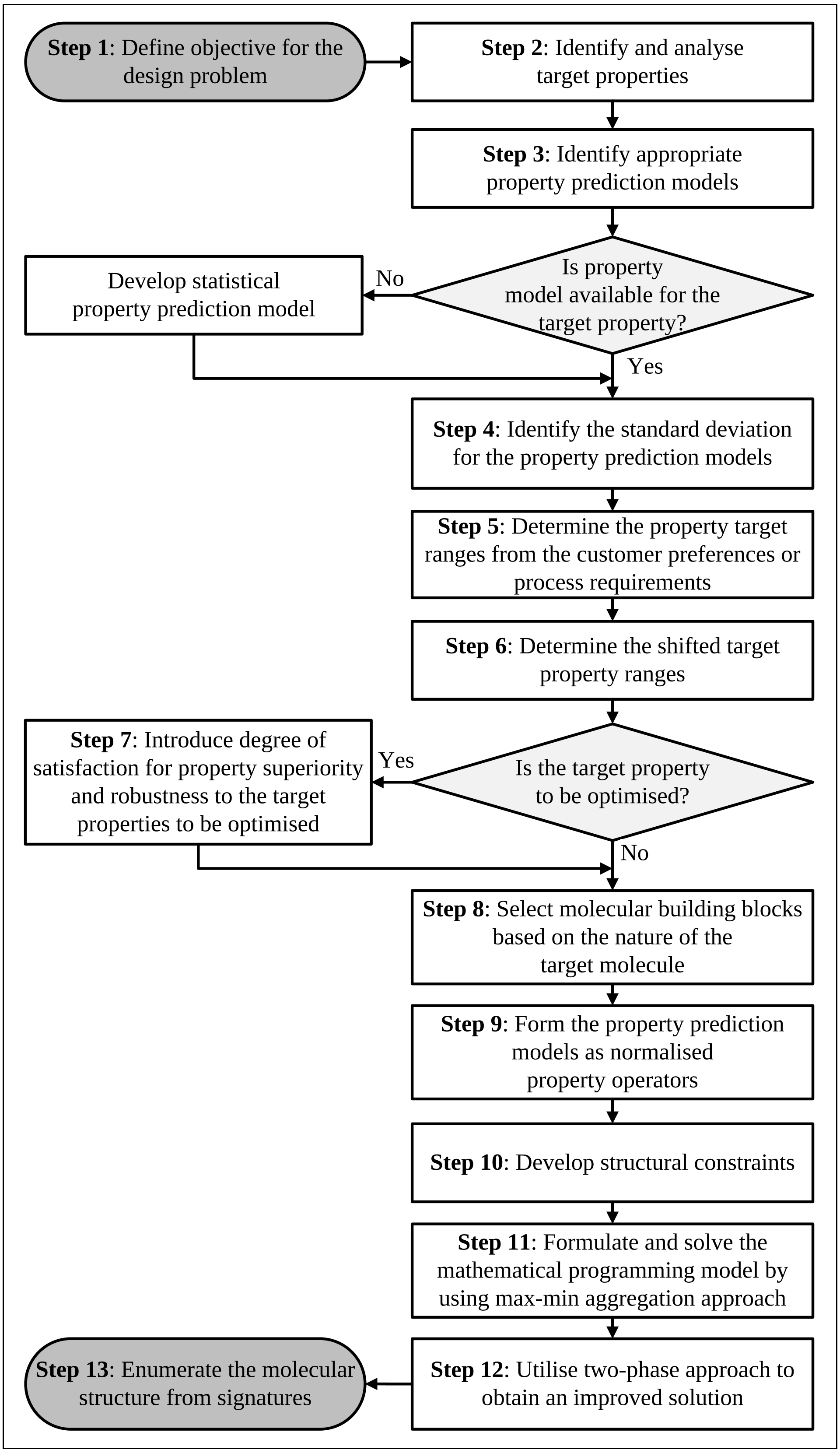


Figure 7.2: Procedure for solving a chemical product design problem with consideration of property prediction model uncertainty

models which combine experimental data and available property prediction models can be developed to estimate the respective target property.

Step 4: Identify the standard deviation, σ for each of the property prediction models identified in Step 3 from the source literature of the property prediction models.

Step 5: Determine the target property ranges based on the product specifications, which can be obtained from the product needs or process requirements.

Step 6: Based on the standard deviation of the property prediction model, identify the shifted target property ranges as discussed in Section 7.2.1.

Step 7: Introduce degree of satisfaction, λ_p to target properties to be optimised by expressing the properties as fuzzy linear functions. Utilise Equation (7.7) for optimisation of property robustness. Equations (7.5) and (7.6) are used for optimisation of property superiority.

Step 8: Based on the nature of the chemical product target molecule, select the appropriate molecular building blocks (possible functional groups, types of bonds and atoms) and express them as their signature equivalents by using molecular signature descriptor.

Step 9: Transform the property prediction models as normalised property operators, which are expressed as linear combinations of atomic signatures.

Step 10: Develop structural constraints to ensure the formation of a complete molecular structure.

Step 11: Define the objective function and solve the overall model by using max-min aggregation approach as discussed in Section 6.2.3.1 to determine the optimal solution with maximised least satisfied degree of satisfaction. The generated solution is obtained in terms of signatures. Integer cuts may be utilised to generate different alternatives.

Step 12: Utilise two-phase approach as discussed in Section 6.2.3.2 to search for an improved solution.

Step 13: Enumerate the molecular structures from the solutions which are obtained in terms of signatures by following the graph signature enumeration algorithm developed by Chemmangattuvalappil and Eden (2013).

7.3. Case Study: Optimal Design of Alkyl Substituent for Fungicide

The application of the proposed robust chemical product design approach is illustrated by reworking the alkyl substituent design problem for fungicide dialkyl dithiolanylidenemalonate (DD) taken from Uchida (1980). This chemical design problem was initially solved by Raman and Maranas (1998) as a single objective optimisation problem. The developed methodology incorporated different TIs as structural descriptors and solved the design problem while considering the effect of property prediction model uncertainty by using multivariate probability density distributions. Chemmangattuvalappil et al. (2010) later solved the design problem as a single objective optimisation problem. By writing the target properties described by property prediction models developed from GC methods and TIs in terms of molecular signatures, the developed approach utilised different classes of property prediction models in solving the design problem.

In this case study, the proposed robust chemical product design approach is applied to solve the design problem as a multi-objective optimisation problem. Signature based molecular design technique are used to represent different classes of property prediction models while property superiority and property robustness are considered and optimised by using different fuzzy optimisation approaches.

7.3.1. Problem Description

DD is a common fungicide used to protect rice plants from insect pests and diseases. The protective ability of the fungicide DD is measured by its ability to be transported, distributed and retained in the plant. Hence, the effect of DD to be designed is quantified in terms of affinity (V_E), mobility (μ) and retention (R). In this case study, an optimal fungicide is produced by designing alkyl substituent to replace R_1 and R_2 of DD, as shown in Figure 7.3.

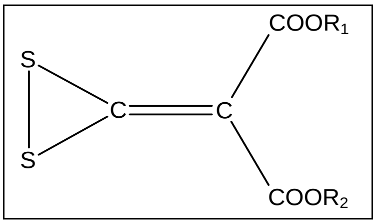


Figure 7.3: Chemical structure of DD

Uchida (1980) presented the correlation between these properties with hydrophobic factor (log*P*). Before this, Murray et al. (1975) developed a linear relation between log*P* and first order molecular connectivity index (CI), ${}^1\chi$. Thus, the correlation between V_E, μ and R with ${}^1\chi$ are utilised in this design problem, as shown by the following equations (Raman and Maranas, 1998).

$$\log(V_E) = 0.5751\left({}^1\chi\right) - 0.2942 \tag{7.13}$$

$$\log(\mu) = -0.6983\left({}^1\chi\right) + 2.0143 \tag{7.14}$$

$$\log\left(\frac{R}{1-R}\right) = 0.787\left({}^1\chi\right) - 2 \tag{7.15}$$

As the main objective of the design problem is to produce a fungicide with optimal ability to be transported, distributed and retained in the plant, the fungicide to be designed should possess high V_E, μ as well as R. Other than the abovementioned properties, toxicity of the DD is also a target property, which is expressed in terms of lethal concentration (LC_{50}) in this case study. Property prediction model of GC methods is used for this purpose, as shown in Equation (7.16) (Martin and Young, 2001).

$$\log_{10}(LC_{50}) = -\sum_{i=1}^{N} N_i C_i \tag{7.16}$$

In this case study, V_E, μ and R of the fungicide are the target properties to be optimised while LC_{50} is a constraint to be fulfilled without optimising the target property.

7.3.2. Problem Formulation

After the identification of target properties and property prediction models, target property ranges, standard deviation of the property prediction models and shifted target property ranges for each of the properties are identified. This can be shown in Table 7.2.

Table 7.2: Target property ranges and shifted target property ranges for the fungicide design problem

Property	**Standard deviation and target property range**			**Shifted target property range**			
	σ_p	v_p^{L}	v_p^{U}	v_p^{LL}	v_p^{LU}	v_p^{UL}	v_p^{UU}
Affinity: log(E)	0.10	1.10	1.42	1.00	1.20	1.32	1.52
Mobility: log(μ)	0.14	-0.30	0.10	-0.44	-0.16	-0.04	0.24
Retention: $\log\left(\frac{R}{1-R}\right)$	0.23	-0.10	0.50	-0.33	0.13	0.27	0.73
Toxicity: $-\log_{10}(LC_{50})$	0.37	-	3.00	-	-	-	3.37

With the target property ranges identified, the next step is to transform the property models in Equations (7.13) – (7.16) into their normalised property operators as shown in Equations (7.17) – (7.20).

$$\Omega_{V_E} = \frac{\log(V_E) + 0.2942}{0.5751} \tag{7.17}$$

$$\Omega_{\mu} = -\frac{\log(\mu) - 2.0143}{0.6983} \tag{7.18}$$

$$\Omega_R = \frac{\log\left(\frac{R}{1-R}\right) + 2}{0.787} \tag{7.19}$$

$$\Omega_{LC_{50}} = -\log_{10}(LC_{50}) \tag{7.20}$$

Once the normalised property operators for all target properties are identified, the next step is to formulate the product design problem as a multi-objective optimisation problem. In order to achieve so, property superiority (λ_p^{s}) and property robustness (λ_p^{r}) of the target properties to be optimised are written as fuzzy linear functions. A degree of satisfaction is then assigned to each of them, as shown in Table 7.3.

Table 7.3: Fuzzy membership functions of target properties

Property	**Interest**	**Fuzzy membership functions**		
		λ_p^{s}	λ_p^{r}	
			LUR	**UUR**
VE	Maximise	$\frac{\Omega_{V_E} - 2.25}{3.15 - 2.25}$	$\frac{\Omega_{V_E} - 2.25}{2.60 - 2.25}$	$\frac{3.15 - \Omega_{V_E}}{3.15 - 2.80}$
μ	Minimise	$\frac{3.51 - \Omega_{\mu}}{3.51 - 2.54}$	$\frac{\Omega_{\mu} - 2.54}{2.94 - 2.54}$	$\frac{3.51 - \Omega_{\mu}}{3.51 - 3.12}$
R	Maximise	$\frac{\Omega_R - 2.13}{3.46 - 2.13}$	$\frac{\Omega_R - 2.13}{2.70 - 2.13}$	$\frac{3.46 - \Omega_R}{3.46 - 2.89}$
LC_{50}	Constraint	-	-	-

After the identification of normalised property operators, the next step is to select the suitable molecular building blocks for the design problem. As the objective of this design problem is to identify an alkyl substituent, only carbon (C) and hydrogen (H) atoms are considered. As molecular signature descriptor is utilised in solving the chemical product design problem, only signatures with single bond are considered in this design problem to determine the alkyl substituent. Signatures of height two is required for this case study since property prediction models of first order CI are utilised. The generated signatures can be classified into first order groups of carbon with zero (C-), one (CH-), two (CH_2-) and three (CH_3-) hydrogen atoms. For this design problem, it is possible to generate a total of 65 signatures which consist of three signatures of group C-, nine signatures of group CH-, nineteen signatures of group CH_2- and thirty four signatures of group CH_3-, as shown in Table 7.4.

Table 7.4: List of generated height two signatures

No.	Signature
1	C1(C2(CC))
2	C1(C3(CCC))
3	C1(C4(CCCC))
4	C2(C2(CC)C1(C))
5	C2(C3(CCC)C1(C))
6	C2(C4(CCCC)C1(C))
7	C2(C2(CC)C2(CC))
8	C2(C3(CCC)C2(CC))
9	C2(C4(CCCC)C2(CC))
10	C2(C4(CCCC)C4(CCCC))
11	C2(C3(CCC)C3(CCC))
12	C2(C4(CCCC)C3(CCC))
13	C3(C4(CCCC)C4(CCCC)C4(CCCC))
14	C3(C4(CCCC)C4(CCCC)C3(CCC))
15	C3(C4(CCCC)C4(CCCC)C2(CC))
16	C3(C4(CCCC)C4(CCCC)C1(C))
17	C3(C4(CCCC)C3(CCC)C3(CCC))
18	C3(C4(CCCC)C3(CCC)C2(CC))
19	C3(C4(CCCC)C3(CCC)C1(C))
20	C3(C4(CCCC)C2(CC)C2(CC))
21	C3(C4(CCCC)C2(CC)C1(C))
22	C3(C4(CCCC)C1(C)C1(C))
23	C3(C3(CCC)C3(CCC)C3(CCC))
24	C3(C3(CCC)C3(CCC)C2(CC))
25	C3(C3(CCC)C3(CCC)C1(C))

Table 7.4: (continued) List of generated height two signatures

26	C3(C3(CCC)C2(CC)C2(CC))
27	C3(C3(CCC)C2(CC)C1(C))
28	C3(C3(CCC)C1(C)C1(C))
29	C3(C2(CC)C2(CC)C2(CC))
30	C3(C2(CC)C2(CC)C1(C))
31	C3(C2(CC)C1(C)C1(C))
32	C4(C4(CCCC)C4(CCCC)C4(CCCC)C4(CCCC))
33	C4(C4(CCCC)C4(CCCC)C4(CCCC)C3(CCC))
34	C4(C4(CCCC)C4(CCCC)C4(CCCC)C2(CC))
35	C4(C4(CCCC)C4(CCCC)C4(CCCC)C1(C))
36	C4(C4(CCCC)C4(CCCC)C3(CCC)C3(CCC))
37	C4(C4(CCCC)C4(CCCC)C3(CCC)C2(CC))
38	C4(C4(CCCC)C4(CCCC)C3(CCC)C1(C))
39	C4(C4(CCCC)C4(CCCC)C2(CC)C2(CC))
40	C4(C4(CCCC)C4(CCCC)C2(CC)C1(C))
41	C4(C4(CCCC)C4(CCCC)C1(C)C1(C))
42	C4(C4(CCCC)C3(CCC)C3(CCC)C3(CCC))
43	C4(C4(CCCC)C3(CCC)C3(CCC)C2(CC))
44	C4(C4(CCCC)C3(CCC)C3(CCC)C1(C))
45	C4(C4(CCCC)C3(CCC)C2(CCC)C2(CC))
46	C4(C4(CCCC)C3(CCC)C2(CCC)C1(C))
47	C4(C4(CCCC)C3(CCC)C1(C)C1(C))
48	C4(C4(CCCC)C2(CC)C2(CC)C2(CC))
49	C4(C4(CCCC)C2(CC)C2(CC)C1(C))
50	C4(C4(CCCC)C2(CC)C1(C)C1(C))
51	C4(C4(CCCC)C1(C)C1(C)C1(C))
52	C4(C3(CCC)C3(CCC)C3(CCC)C3(CCC))
53	C4(C3(CCC)C3(CCC)C3(CCC)C2(CC))
54	C4(C3(CCC)C3(CCC)C3(CCC)C1(C))
55	C4(C3(CCC)C3(CCC)C2(CC)C2(CC))
56	C4(C3(CCC)C3(CCC)C2(CC)C1(C))
57	C4(C3(CCC)C3(CCC)C1(C)C1(C))
58	C4(C3(CCC)C2(CC)C2(CC)C2(CC))
59	C4(C3(CCC)C2(CC)C2(CC)C1(C))
60	C4(C3(CCC)C2(CC)C1(C)C1(C))
61	C4(C3(CCC)C1(C)C1(C)C1(C))
62	C4(C2(CC)C2(CC)C2(CC)C2(CC))
63	C4(C2(CC)C2(CC)C2(CC)C1(C))
64	C4(C2(CC)C2(CC)C1(C)C1(C))
65	C4(C2(CC)C1(C)C1(C)C1(C))

Next, the property prediction models are expressed in terms of linear combinations of atomic signatures. By substituting the values of v_p^{LL} and v_p^{UU} into the normalised property operators as shown in Equations (7.17) – (7.20), the property specification for each target property can be written in terms of signatures as follows.

Affinity: $$2.25 \le \sum_{d=1}^{65} \alpha_d L_d \le 3.15 \tag{7.21}$$

Mobility: $$2.54 \le \sum_{d=1}^{65} \alpha_d L_d \le 3.51 \tag{7.22}$$

Retention: $$2.13 \le \sum_{d=1}^{65} \alpha_d L_d \le 3.46 \tag{7.23}$$

Toxicity: $$\sum_{d=1}^{3} \alpha_d c_{LC_{50}d} + \sum_{d=4}^{12} \alpha_d c_{LC_{50}d} + \sum_{d=13}^{31} \alpha_d c_{LC_{50}d} + \sum_{d=32}^{65} \alpha_d c_{LC_{50}d} \le 3.37 \tag{7.24}$$

Equations (7.21) – (7.23) can be rewritten using interval arithmetic, as shown in Equation (7.25).

$$2.54 \le \sum_{d=1}^{65} \alpha_d L_d \le 3.15 \tag{7.25}$$

7.3.3. Results and Discussions

7.3.3.1.Stage 1: Max-min Aggregation Approach

The alkyl substituent design problem can now be formulated as a mixed-integer linear programming (MILP) model. The objective function shown in Equation (7.26) and the constraint shown in Equation (7.27) are applied only in the first stage of optimisation by using max-min aggregation approach, where the objective is to maximise the least satisfied degree of satisfaction among all property superiority and robustness.

Objective functions:

$$\text{Maximise} \quad \lambda \tag{7.26}$$

Subject to:

$$\lambda \leq \lambda_p \qquad \forall p \in P \tag{7.27}$$

The mathematical model is solved together with Equations (7.24) and (7.25), structural constraints as well as fuzzy linear functions as shown in Table 7.3. Commercial optimisation software LINGO version 13, in Asus N56V with Intel Core i5-3210M (2.50 GHz) processor and 4 GB DDR3 RAM is used to solve the MILP model. The average central processing unit (CPU) time for the generation of solutions is 0.1 s. The solution is obtained in terms of molecular signatures. Integer cuts have been applied to generate different feasible alternatives for the design of alkyl substituent. With the generated solutions, molecular graphs can be generated based on the graph signature enumeration algorithm by Chemmangattuvalappil and Eden (2013). The molecular structure of the new DD can then be identified. Best five solutions are obtained in terms of signatures and summarised in Table 7.5. Table 7.6 shows the list of solutions arranged according to their least satisfied degree of satisfaction.

Table 7.5: List of solutions of alkyl substituents for DD in terms of signatures

Solution	**Signature**	**Occurrence**
A	C1(C3(CCC))	2
	C1(C4(CCCC))	3
	C3(C4(CCCC)C1(C)C1(C))	1
	C4(C3(CCC)C1(C)C1(C)C1(C))	1
B	C1(C2(CC))	2
	C2(C2(CC)C1(C))	2
	C2(C2(CC)C2(CC))	2
C	C1(C2(CC))	2
	C1(C3(CCC))	1
	C2(C3(CCC)C1(C))	2
	C3(C2(CC)C2(CC)C1(C))	1
D	C1(C2(CC))	1
	C1(C3(CCC))	2
	C2(C2(CC)C1(C))	1
	C2(C3(CCC)C2(CC))	1
	C3(C2(CC)C1(C)C1(C))	1
E	C1(C2(CC))	1
	C1(C4(CCCC))	3
	C2(C2(CC)C1(C))	1
	C2(C4(CCCC)C2(CC))	1
	C4(C2(CC)C1(C)C1(C)C1(C))	1

Table 7.6: List of solutions by using max-min aggregation approach

Sol.	V_E			μ			R			LC_{50}
	V_p	λ_p^s	λ_p^r	V_p	λ_p^s	λ_p^r	V_p	λ_p^s	λ_p^r	
A	1.40	0.77	0.61	-0.04	0.59	1.00	0.32	0.61	0.90	3.05
B	1.38	0.73	0.69	-0.02	0.62	0.94	0.29	0.59	0.96	3.02
C	1.32	0.62	1.00	0.05	0.73	0.67	0.21	0.51	1.00	2.90
D	1.30	0.57	1.00	0.08	0.77	0.57	0.18	0.48	1.00	2.90
E	1.47	0.90	0.27	-0.12	0.47	1.00	0.41	0.70	0.70	3.18

The solutions are named as solution A to solution E. It can be seen from Table 7.6 that all of the substituents properties fall between the target property ranges that represent the product needs (see Table 7.2). Note that these values are the optimised target properties subjected to the properties and structural constraints. These solutions are capable to replace R_1 and R_2 for optimal substituent selection for DD that has the protective and eradicating abilities to protect rice plants against insect pests and diseases.

As mentioned beforehand, this fungicide design problem was solved by Raman and Maranas (1998) as a single objective optimisation problem while considering the effect of property prediction model uncertainty by using multivariate probability density distributions. The same design problem was later attempted by Chemmangattuvalappil et al. (2010) as a single objective optimisation problem which utilised different classes of property prediction models. The optimal solutions obtained from both of the previous works are shown in Table 7.7 as follows.

Table 7.7: Optimal solutions obtained by works from other authors

	V_E	μ	R	LC_{50}
(Raman and Maranas, 1998)	1.61	-0.30	0.60	-
(Chemmangattuvalappil et al., 2010)	1.61	-0.30	0.60	0.92

In order to compare the solutions obtained by using the developed approach with the solutions generated by solving the design problem without the consideration of property robustness, the MILP model is solved again in three different scenarios:

1. Solved as single objective optimisation problems without the consideration of property robustness (optimisation of single target properties Ω_{V_E}, Ω_{μ} and Ω_R separately), with objective function shown in Equations (7.28) – (7.30).

$$\text{Maximise} \quad \Omega_{V_E} \tag{7.28}$$

$$\text{Maximise} \quad \Omega_{\mu} \tag{7.29}$$

$$\text{Maximise} \quad \Omega_{R} \tag{7.30}$$

2. Solved as a multi-objective optimisation problem without considering property robustness (optimisation of multiple target properties λ_p^s) with objective function Equation (7.31).

$$\text{Maximise} \quad \lambda, \qquad \lambda \le \lambda_p^s \tag{7.31}$$

3. Solved as multi-objective optimisation problems with consideration of property robustness (optimisation of single target properties λ_{V_E}, λ_{μ} and λ_R separately) with objective functions shown in Equations (7.32) – (7.34).

$$\text{Maximise} \quad \lambda_{V_E} \tag{7.32}$$

$$\text{Maximise} \quad \lambda_{\mu} \tag{7.33}$$

$$\text{Maximise} \quad \lambda_{R} \tag{7.34}$$

Note that the degree of satisfaction for target property p, λ_p for Equation (7.31) applies only to property superiority while degree of satisfaction for Equations (7.32) – (7.34) applies to both property superiority and property robustness for the respective target property. Equations (7.28) – (7.34) are solved separately subject to the corresponding property and structural constraints. The generated solutions are shown in Table 7.8.

Table 7.8: Designs of alkyl substituents for DD for different scenarios

Sol.	V_E			μ			R			LC_{50}
	V_p	λ_p^s	λ_p^r	V_p	λ_p^s	λ_p^r	V_p	λ_p^s	λ_p^r	
Scenario 1: Maximised Ω_{V_E}										
C	1.32	0.69	-	0.05	0.88	-	0.21	0.52	-	2.90
Scenario 1: Minimised Ω_{μ}										
D	1.30	0.63	-	0.08	0.95	-	0.18	0.47	-	2.90
Scenario 1: Maximised Ω_R										
C	1.32	0.69	-	0.05	0.88	-	0.21	0.52	-	2.90
Scenario 2: Maximised λ										
C	1.32	0.69	-	0.05	0.88	-	0.21	0.52	-	2.90
Scenario 3: Maximised λ_{V_E}										
B	1.38	0.73	0.69	-0.02	0.62	0.94	0.29	0.59	0.96	3.02
Scenario 3: Maximised λ_{μ}										
C	1.32	0.62	1.00	0.05	0.73	0.67	0.21	0.51	1.00	2.90
Scenario 3: Maximised λ_R										
E	1.47	0.90	0.27	-0.12	0.47	1.00	0.41	0.70	0.70	3.18

As shown in Table 7.8, for scenario 1, solution C is the solution with maximised V_E and maximised R while solution D is the solution with maximised μ. For scenario 2, solution C is the solution with maximised λ. For scenario 1 and 2, as the standard deviation of property prediction models are not taken into account, the target property ranges are not shifted. It can be seen in Table 7.8 that all of the substituents properties from scenario 1 and 2 fall between v_p^{L} and v_p^{U} that represent customer requirements without considering the property robustness. There is a possibility that improved solutions might be found outside the range bounded by v_p^{L} and v_p^{U} due to the effect of property prediction model accuracy on the generation of solutions. The design problem is solved again in scenario 3, where the property prediction model accuracy is taken into account in the form of property robustness. For solutions generated in scenario 3, all of the substituents properties now fall between v_p^{LL} and v_p^{UU} that represents customer requirements with consideration of property robustness. For scenario 3, solution B is the solution with maximised λ_{V_E}, solution C is the solution with maximised λ_{μ} while solution E is the solution with maximised λ_R. It can be seen from Table 7.8 that the optimal solution identified by optimising multiple product properties and considering both property superiority and robustness (solution A) is not among the solutions generated without considering property robustness. Therefore, without optimising multiple target properties and taking the allowance of property prediction model accuracy into consideration, there is a possibility that optimal solutions might not be identified.

From Table 7.6, it is noted that the level of satisfaction of property superiority is higher than that of property robustness for some solutions. The opposite case can be observed for some other solutions, where the level of satisfaction or property robustness is higher than that of property superiority. In addition, the least satisfied degree of satisfaction is not always from the same target property, and it is not restricted to only the property superiority or property robustness of a property. For example, the least satisfied fuzzy goal in solution A is the property superiority of mobility, $\lambda_{\mu}^{\mathrm{r}}$ with the value of 0.59, while the least satisfied fuzzy goal in solution E is the property robustness of affinity, $\lambda_{VE}^{\mathrm{r}}$ with the value of 0.27. This indicates that the developed algorithm identifies the priority of each goal to be optimised without the presence of a decision maker. As long as the degree of satisfaction for the least satisfied goal is maximised, the generated solution is a candidate for optimal alkyl substituent. The comparison of degrees of satisfaction between the solutions generated by using max-min aggregation approach can be shown in an alternate manner by using a column chart as shown in Figure 7.4.

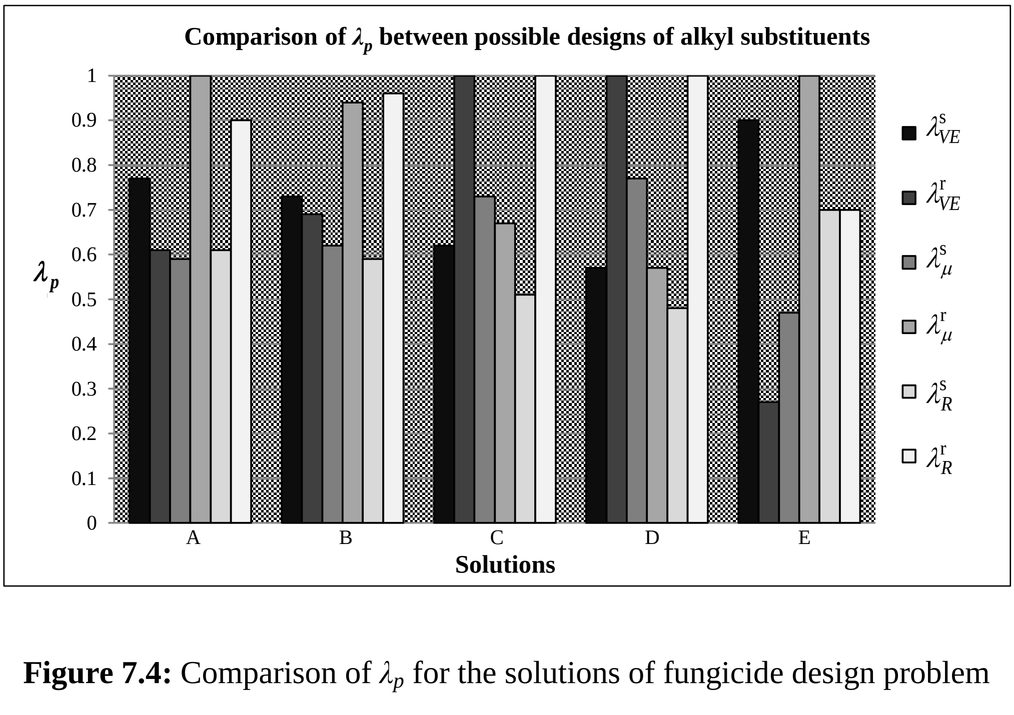


Figure 7.4: Comparison of λ_p for the solutions of fungicide design problem

Furthermore, as shown in Table 7.6, the least satisfied goal for solution A and solution B has the same value of 0.59. Although the least satisfied goal for solution A is property superiority of mobility λ_{μ}^{s} while the least satisfied goal for solution B is property superiority of retention λ_{R}^{s}, it is difficult and impossible to identify the better solution at this stage as they have similar values for least satisfied fuzzy goals. As mentioned earlier, the major drawback of max-min aggregation approach is its lack of discriminatory power to distinguish between solutions which have different levels of satisfaction other than the least satisfied goal. While the least satisfied goal is maximised, the other goals might be overly relaxed or curtained, thus leaving room for improvement to search for better solutions. Due to this limitation, max-min aggregation approach does not guarantee to yield a Pareto optimal solution (Jiménez and Bilbao, 2009). In order to discriminate these solutions to refine the order of solutions and at the same time to ensure Pareto optimal solution, two-phase approach is utilised.

7.3.3.2.Stage 2: Two-phase Approach

The optimisation model is solved again by using the two-phase approach. The aim is to maximise the summation of all degrees of satisfaction, as shown in Equation (7.35). As the least satisfied goal identified by using the max-min aggregation approach is 0.59, the degree of satisfaction for the second stage should at least be equal or higher than this value to ensure that the solution obtain in the second stage is not worse than the solution obtained in the first stage. Hence, Equation (7.36) is introduced.

Objective functions:

$$\text{Maximise} \quad \sum_{p} \lambda_p^* \tag{7.35}$$

Subject to:

$$0.59 \le \lambda_p^* \le 1 \tag{7.36}$$

The MILP model is solved by using the same computational software and hardware specification as mentioned above. The average CPU time required for the generation of solutions is 0.1 s. The top five solutions generated by using the two-phase approach are arranged accordingly to their summation of degrees of satisfaction as shown in Table 7.9.

Table 7.9: List of solutions by using by using two phase approach

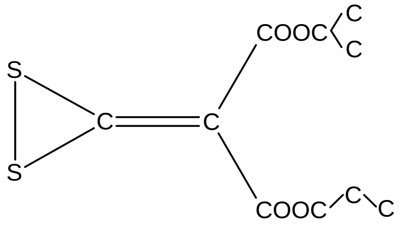
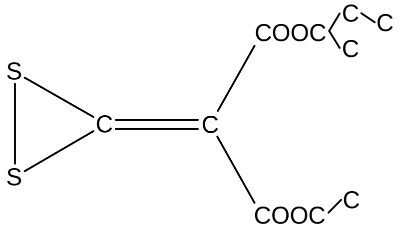
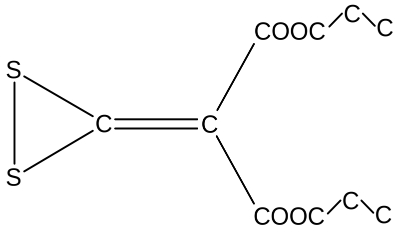
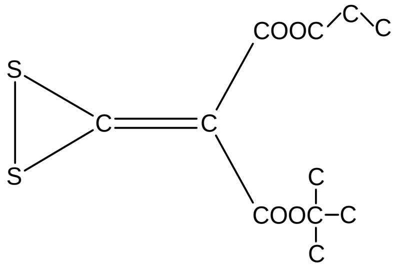
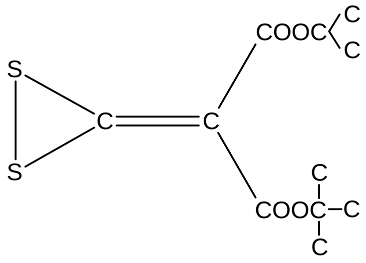
Sol.	V_E			μ			R			LC_{50}	$\sum \lambda_p^*$
	V_p	λ_p^{s*}	λ_p^{r*}	V_p	λ_p^{s*}	λ_p^{r*}	V_p	λ_p^{s*}	λ_p^{r*}		
B	1.38	0.73	0.69	-0.02	0.62	0.94	0.29	0.59	0.96	3.02	4.53
C	1.32	0.62	1.00	0.05	0.73	0.67	0.21	0.51	1.00	2.90	4.52
A	1.40	0.77	0.61	-0.04	0.59	1.00	0.32	0.61	0.90	3.05	4.48
D	1.30	0.57	1.00	0.08	0.77	0.57	0.18	0.48	1.00	2.90	4.40
E	1.47	0.90	0.27	-0.12	0.47	1.00	0.41	0.70	0.70	3.18	4.03

From Table 7.9, although the best five solutions remain the same as solution A to solution E, it can be seen that the ranking of solutions changes significantly compared with that obtained in the first stage. As two-phase approach identifies the best solution which cannot be worse than the solution identified earlier by using max-min aggregation, the least satisfied degree of satisfaction among all the best five solutions is still the property robustness of affinity,

λ_{VE}^{r*} of solution E, which has the value of 0.27. From Table 7.9, although both solution A and solution B have same value for least satisfied fuzzy goal, solution A is now the third best solution, while solution B is now the best solution. This is because the objective for two phase approach is the maximisation of the summation of degrees of satisfaction of all fuzzy goals. Thus, solutions with similar values of least satisfied goals are distinguished.

For this case study, the best product is solution B, with λ of 0.59 and $\sum \lambda_p^*$ of 4.53, while the other solution with λ of 0.59, solution A is now ranked third with its $\sum \lambda_p^*$ of 4.48 as shown in Table 7.9. Furthermore, it can be observed from Table 7.9 that by using two-phase approach, the least satisfied degree of satisfaction is still the highest for the best product (solution B). This proves that even though two-phase approach is able to discriminate the solutions with similar least satisfied fuzzy goal, the approach does not compromise the degree of satisfaction of that goal. Hence, utilisation of two-phase approach after max-min aggregation approach ensure the generation of optimal results without worsening any other goals. It is noted that in order to utilise two-phase approach, the problem must first be solved by using max-min aggregation approach to obtain the least satisfied degree of satisfaction. The least satisfied degree of satisfaction is then used as a constraint to make sure that two-phase approach seeks for improved solutions without worsening any of the degrees of satisfaction. Molecular structure for the possible designs of alkyl substituents for DD can now be enumerated by following the graph signature enumeration algorithm. This can be shown in Table 7.10.

Table 7.10: Molecular structures for the solutions of fungicide design problem

Sol.	Molecular structure
A	
B	
C	
D	
E	

From Table 7.10, it can be seen that R_1 and R_2 of DD as illustrated in Figure 7.4 are replaced by different length of straight or branched alkyl chains. This shows the ability of the developed approach in designing the optimal molecule by considering both property superiority and property robustness. The mathematical formulations and the results generated by using max-min aggregation approach as well as two-phase approach in this case study are provided in Appendix E of this thesis.

7.4. Conclusion

This chapter introduces a novel approach in chemical product design by incorporating fuzzy optimisation approaches into molecular design techniques. The proposed robust chemical product design approach designs optimal chemical product by considering both property superiority and robustness. By incorporating fuzzy optimisation approaches into the developed approach, the relative importance of property superiority and robustness of the target properties in multi-objective optimisation problems can be addressed systematically without bias and optimal product can be identified. Property superiority provides an indication of the product optimality in terms of product property while the accuracy of the estimated target property by using property prediction model is expressed in terms of property robustness. The effect of the accuracy of property prediction model is represented in terms of standard deviation of the model. Different regions with different confidence levels in terms of property robustness are divided by shifting the lower and upper limits of the target properties. Compared to the usual attempt of molecule generation followed by sensitivity analysis, this approach considers the effect of property prediction model accuracy during the molecule generation.

CHAPTER 8

SYSTEMATIC METHODOLOGY FOR OPTIMAL MIXTURE DESIGN IN INTEGRATED BIOREFINERIES

8.1. Introduction

Biomass is a sustainable source of energy which can be utilised to produce value-added products such as biomaterials and biochemical products. The concept of integrated biorefinery is utilised to produce a sustainable supply of such value-added products. As proposed and discussed in Chapters 4 and 5, during the synthesis of an integrated biorefinery, the process design of the integrated biorefinery is inter-linked with the product design as it is important to identify the required product prior to designing its production routes. In cases where the desired properties cannot be met by a single component product, the design of mixture of chemicals would be required. The mixture can be designed by identifying and mixing several chemical components, or by designing additive components for an existing main component to enhance the product properties. In this respect, product and process design decisions would be a challenging task for an integrated biorefinery as it is required to identify the optimal conversion pathways for the production of different chemical components in the integrated biorefinery. In this chapter, the two-stage optimisation approach presented in Chapter 5 is extended to identify the optimal conversion pathways in an integrated biorefinery to convert biomass into optimal mixture in terms of target product properties. In the first stage, the optimal mixture is designed via signature based molecular design techniques. The main component of the mixture is first identified from the target properties. Following this, the additive components are determined to form an optimal mixture with the main component based on the desired product properties. The multi-objective optimisation approach proposed in Chapter 6 is utilised for the design of optimal mixture while considering and optimising multiple product properties simultaneously. Once the optimal mixture is identified, the second stage determines the optimal conversion pathways via superstructural mathematical optimisation approach. With such approach, the optimal conversion pathways for the production of optimal mixture can be determined based on different optimisation objectives. To illustrate the proposed methodology, a case study on the design of bio-based fuel additives as a mixture of different molecules from palm-based biomass is presented.

8.2. Two-stage Optimisation Approach for Optimal Mixture Design

In order to identify the optimal product in terms of mixture of several individual components as well as the optimal conversion pathways for the production of the mixture, a two-stage optimisation approach is developed. In the first stage of the optimisation approach, signature based molecular design techniques are employed to design the optimal mixture in terms of several target product properties. In the second stage of the optimisation approach, an integrated biorefinery is synthesised based on the components designed for the optimal mixture in the first stage. Superstructural mathematical optimisation approach is utilised for the identification of the optimal conversion pathways that lead to the designed optimal mixture. The proposed two-stage optimisation approach for the design of optimal mixture can be shown by using a general representation as shown in Figure 8.1.

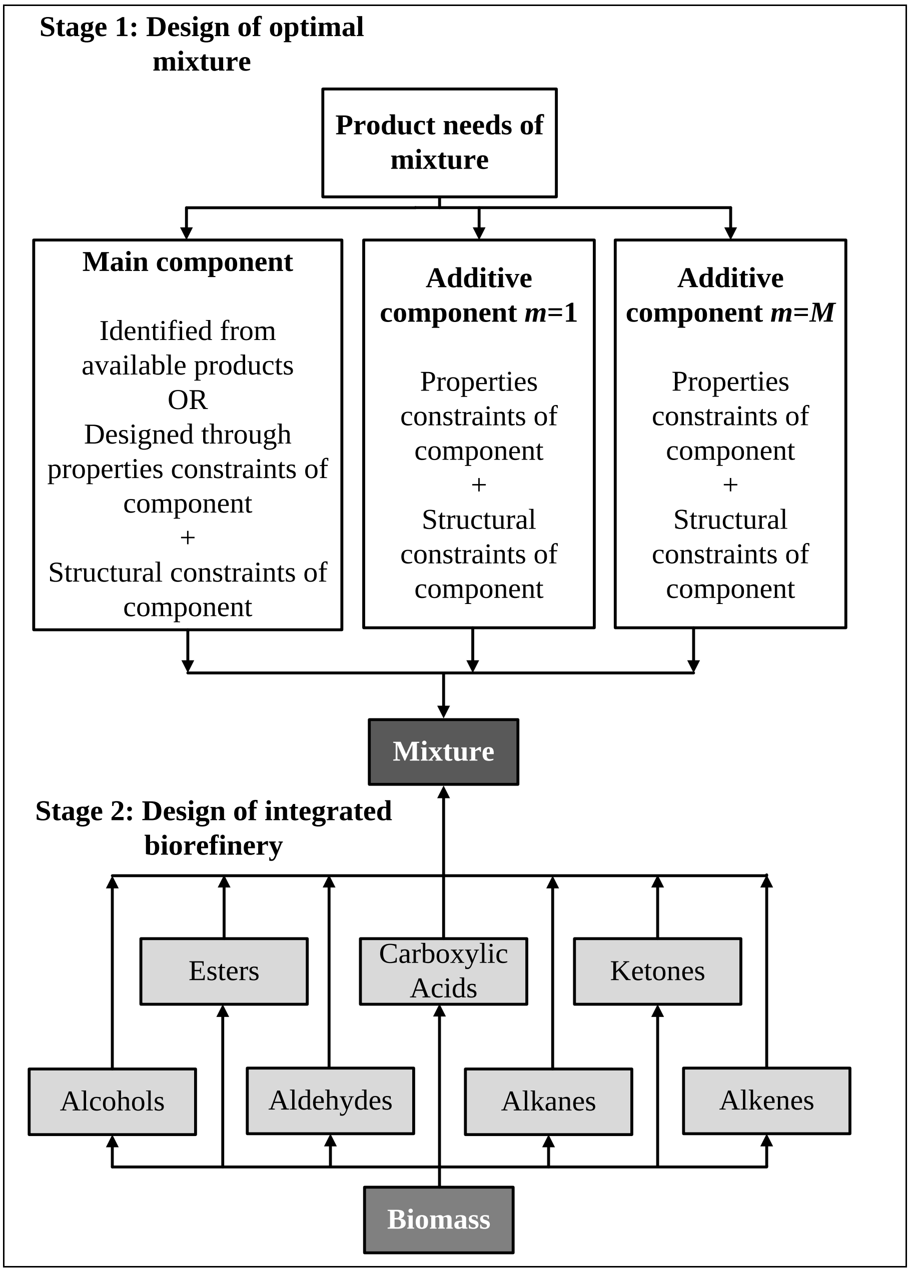


Figure 8.1: Two-stage optimisation approach to produce optimal mixture from biomass

As shown in Figure 8.1, optimum mixture that fulfils the product needs is first identified in the first stage. Based on the product needs, the number of components in designing the product is identified. A mixture is necessary to be designed if the number of components required to design the product that fulfils the target properties exceeds one. The mixture can then be designed as binary, ternary or multi-component mixture by mixing different number of individual components. The component which performs the main functionality of the mixture is referred as the main component while the components which enhance the performance of the mixture are represented as the additive components. These individual components that contribute to the design of mixture are identified by utilising the signature based molecular design techniques developed by Chemmangattuvalappil et al. (2010). Once the potential individual components that form an optimal product are determined, the optimal mixture is identified by mixing the components.

After the identification of optimal mixture, the optimal conversion pathways that convert biomass into the mixture are identified in the second stage of the optimisation approach. As presented in Figure 8.1, based on the result from the design of the optimal mixture, biomass can be converted into the identified chemical components represented as different chemical products (alcohol, alkane, carboxylic acid etc.) in an integrated biorefinery. Based on the available conversion pathways and technologies, a superstructure is constructed as a representation of an integrated biorefinery. By using the superstructural mathematical optimisation approach, optimal conversion pathways based on different design goals such as economic potential, production yield, environmental impact etc. can be determined in this stage. By integrating mixture design with the synthesis of integrated biorefinery, the proposed two-stage optimisation approach is able to determine the optimum conversion pathways to convert biomass into the optimal mixture that meets the product needs. The following subsections further elaborate the proposed two-stage optimisation approach.

8.2.1. Stage 1: Mixture Design

In this stage, the optimal mixture is designed by utilising the signature based molecular design techniques. The steps involved in the optimal mixture design are represented by using a flowchart as shown in Figure 8.2. Note that the procedure is designed specifically for mixture design problems where different classes of property prediction models are used and the molecular structure of the product is represented by using molecular signature descriptor. The details of each step are discussed as follows.

8.2.1.1. Define Objective for the Mixture Design Problem

The objective for the mixture design problem is determined by identifying the product needs. These product needs can be extracted from the operating conditions of an industrial process or from the customer requirements. The product needs cover the physical properties which are responsible for a particular functionality of the product. Properties that make sure that the product fulfils the environmental and safety regulations can be considered as well.

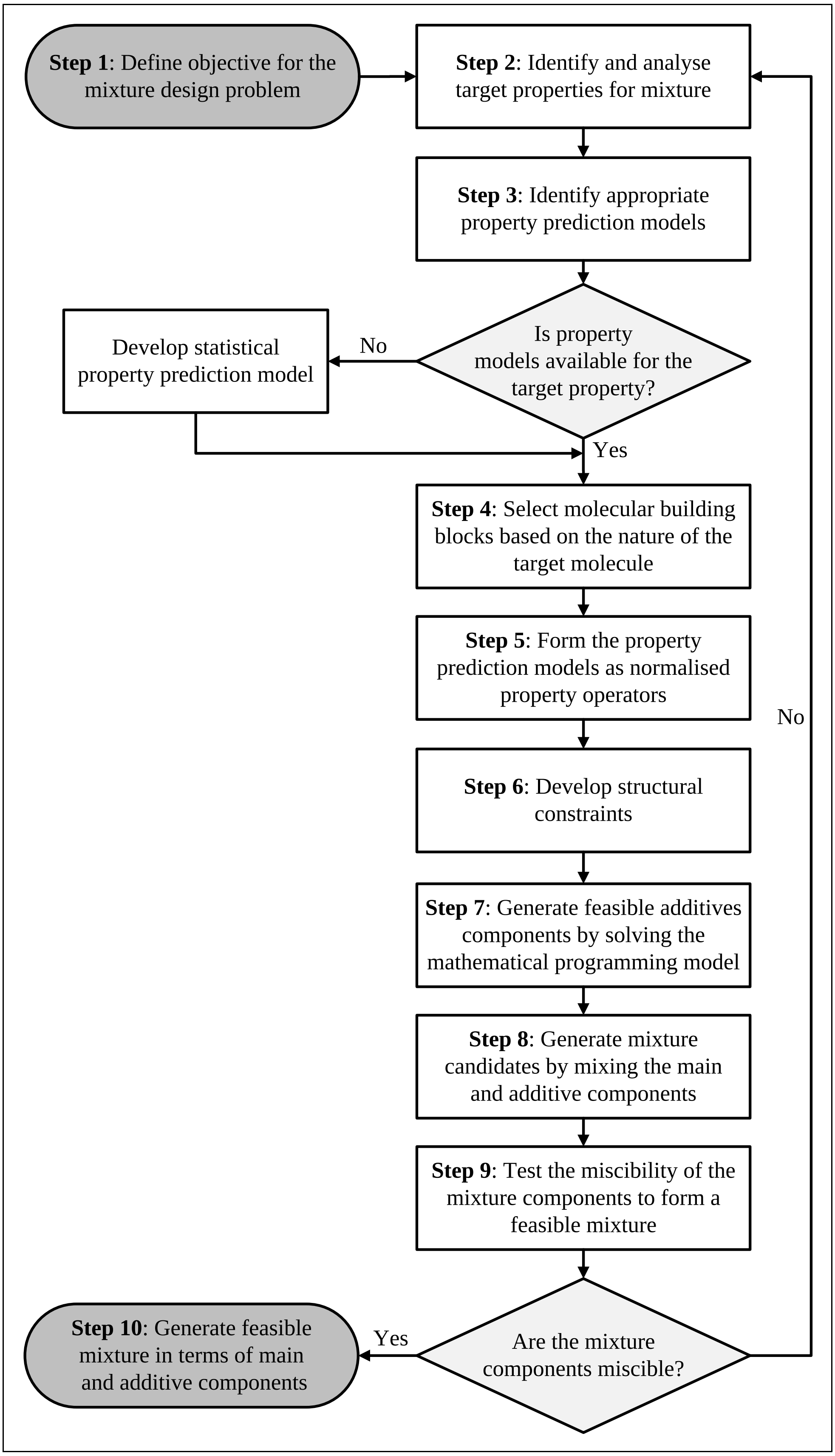


Figure 8.2: Procedure for solving a mixture design problem

8.2.1.2.Identify and Analyse Target Properties

Once the product needs and the objective of the mixture design problem have been identified, the identified descriptive product needs are translated into measurable quantitative target properties. These target properties are then expressed as property specifications, which can be written as a set of property constraints bounded by upper and lower limits, as shown in Equation (8.1).

$$v_p^{\mathrm{MIX,\,L}} \le V_p^{\mathrm{MIX}} \le v_p^{\mathrm{MIX,\,U}} \qquad \forall p \in P \tag{8.1}$$

In Equation (8.1), V_p^{MIX} is the value of target property p for the mixture, bounded by lower ($v_p^{\mathrm{MIX,\,L}}$) and upper ($v_p^{\mathrm{MIX,\,U}}$) limits of the mixture product specification. Once the target properties and target property ranges have been identified, the number of components for the design of the mixture is determined. The main component of the mixture is first identified from the available products or designed based on the target properties. The additive components required for the mixture are then designed such that when mixed with the main component, the properties of the mixture will fall within the target property ranges. Hence, mixture design problem can be described as the enhancement of main component by designing the additive components for the main component to produce a mixture which fulfils the product specifications.

8.2.1.3.Identify Appropriate Property Prediction Models

After the identification of target property ranges, suitable property prediction models which estimate the target properties of the mixture are determined. Different classes of property prediction models such as property prediction models developed from group contribution (GC) method or topological indices (TIs) are utilised for the prediction of target properties. For target properties where property prediction models are unavailable, models which combine experimental data and available property prediction models can be developed to estimate the respective product property.

8.2.1.4.Select Molecular Building Blocks

Suitable molecular building blocks for the mixture design problem are determined in this step. The molecular building blocks have to be selected such that the properties and molecular structure of the new product are similar to the available product from where the molecular building blocks are chosen. It is assumed that by designing a new molecule with the chosen molecular groups as the building blocks, the designed product will possess the properties and functionalities of the desired product. As the mixture design methodology employs signature based molecular design techniques, signatures corresponding to the selected molecular groups are then generated.

8.2.1.5.Form Property Prediction Models as Normalised Property Operators

Once the suitable molecular building blocks are selected, the identified property prediction models are expressed and formed as normalised property operators. Property specifications for the mixture in Equation (8.1) can be written as normalised property operators as shown in Equation (8.2).

$$\Omega_p^{\mathrm{MIX,\,L}} \le \Omega_p^{\mathrm{MIX}} \le \Omega_p^{\mathrm{MIX,\,U}} \qquad \forall p \in P \tag{8.2}$$

In Equation (8.2), Ω_p^{MIX} is the normalised property operator for the mixture for the target property *p*, $\Omega_p^{\mathrm{MIX,\,L}}$ is the lower limit for the normalised property operator and $\Omega_p^{\mathrm{MIX,\,U}}$ is the upper limit for the normalised property operator. As signature based molecular design techniques are employed in this developed methodology, normalised property operators are used to express molecules as linear combinations of atomic signatures.

8.2.1.6.Develop Structural Constraints

In mixture design problems, property constraints developed from the product needs make sure that the designed mixture possesses target properties which satisfy the product needs. Other than property constraints, structural constraints are required to ensure that the designed mixture has a feasible and stable chemical structure (Chemmangattuvalappil et al., 2010). In order to form a complete molecule, structural constraints are employed to make sure that the generated molecule is complete without any free bond in the structure. In addition, it must be ensured that the signatures in the solution set must be consistent. The details of the development and applications of structural constraints have been discussed earlier, which can be found in Chapter 4.

8.2.1.7.Generate Feasible Additive Components

Based on the objective of the design problem determined earlier, the optimisation model is formulated from the objective function together with the developed property and structural constraints. The optimisation model is formulated as a mixed-integer linear programming (MILP) problem and solved to identify the optimal candidates of additive components. Integer cuts are utilised to generate different alternatives for the additive components.

8.2.1.8.Generate and Rank Potential Mixture Candidates

As discussed beforehand, the main purpose in designing mixtures is its potential for giving a good mix of target properties which are difficult to achieve by individual chemical components. Therefore, multiple target properties are needed to be considered and optimised simultaneously to design an optimal mixture in terms of product properties. Once the main and additive components have been identified, the mixture design problem is formulated as a multi-objective optimisation problem. The optimal mixture is obtained by mixing the main component with the additive components. In order to identify the mixture property values by mixing the main and additive components, mixing rules are required. As property prediction models are expressed in terms of normalised property operators, Equation (8.3) can be utilised in predicting the mixture target properties from the composition and properties values of the chemical components.

$$\Omega_p^{\mathrm{MIX}} = \sum_m x_m \Omega_{mp} \tag{8.3}$$

$$\sum_m x_m = 1 \tag{8.4}$$

Here, x_m is the fraction of the chemical component m while Ω_{mp} is the value of normalised property operator of the target property p for the chemical component *m*. However, as linear mixing models may result in significant errors for non-ideal mixtures, rigorous property models are required for property prediction for non-ideal mixtures. By combining Equations (8.2) and (8.3), Equation (8.5) can be used to predict the target property of the chemical components *m* in the mixture.

$$\Omega_p^{\text{MIX, L}} \leq \sum_m x_m \Omega_{mp} \leq \Omega_p^{\text{MIX, U}} \qquad \forall p \in P \tag{8.5}$$

As mentioned beforehand, in order to design an optimal mixture in terms of product properties by mixing different chemical components, multiple mixture target properties are needed to be considered and optimised simultaneously. Thus, the mixture design problem is formulated and solved as a multi-objective optimisation design problem where multiple target properties are optimised during the design of the mixture. Fuzzy optimisation approach is applied to trade off different target properties simultaneously. To trade off multiple target properties by using fuzzy optimisation approach, a degree of satisfaction, λ is introduced. This is achieved by writing λ as a linear membership function bounded by the lower and upper limits of the target properties. The mathematical representation of the λ is shown by Equations (8.6) and (8.7). In Equations (8.6) and (8.7), λ_p is the degree of satisfaction for the target property *p*. λ_p is a continuous variable between 0 to 1. For target property to be minimised, since lower values are desired, the value of λ_p approaches 1 when the property approaches the lower limit; when the property approaches the upper limit, the value of λ_p approaches 0. The opposite trend can be observed for target property to be maximised. Equation (8.6) is used for property to be minimised while Equation (8.7) is used for property to be maximised.

$$\lambda_p = \begin{cases} 1 & \text{if} \quad V_p^{\text{MIX}} \le v_p^{\text{MIX, L}} \\ \dfrac{v_p^{\text{MIX, U}} - V_p^{\text{MIX}}}{v_p^{\text{MIX, U}} - v_p^{\text{MIX, L}}} & \text{if} \quad v_p^{\text{MIX, L}} \le V_p^{\text{MIX}} \le v_p^{\text{MIX, U}} \qquad \forall p \in P \\ 0 & \text{if} \quad V_p^{\text{MIX}} \ge v_p^{\text{MIX, U}} \end{cases} \tag{8.6}$$

$$\lambda_p = \begin{cases} 0 & \text{if} \quad V_p^{\text{MIX}} \le v_p^{\text{MIX, L}} \\ \dfrac{V_p^{\text{MIX}} - v_p^{\text{MIX, L}}}{v_p^{\text{MIX, U}} - v_p^{\text{MIX, L}}} & \text{if} \quad v_p^{\text{MIX, L}} \le V_p^{\text{MIX}} \le v_p^{\text{MIX, U}} \qquad \forall p \in P \\ 1 & \text{if} \quad V_p^{\text{MIX}} \ge v_p^{\text{MIX, U}} \end{cases} \tag{8.7}$$

The objective of the fuzzy optimisation approach applied in this presented approach is max-min aggregation approach (Zimmermann, 1983, 1978). By following the max-min aggregation approach, each objective (target property) will be satisfied partially to at least the degree λ. Therefore, each objective has an associated fuzzy membership function and the optimum overall objective is obtained by maximising the least satisfied objective. This can be shown in Equations (8.8) and (8.9).

$$\text{Maximise} \quad \lambda \tag{8.8}$$

$$\lambda \le \lambda_p \qquad \forall p \in P \tag{8.9}$$

Here, λ_p is the degree of satisfaction for the target property p determined from Equations (8.6) and (8.7) depending on whether the target property is to be minimised or maximised. Integer cuts are utilised to generate alternative designs of mixture. As the multi-objective mixture design problem is solved by using max-min aggregation approach, all the generated mixture alternatives are ranked according to the least satisfied target property. In this developed methodology, the optimal mixture in terms of target product properties is obtained by mixing the main component with the identified optimal additive components. Although this approach does not guarantee the generation of Pareto optimal solution, the complexity of this approach is low because the mathematical formulations are written and solved as a linear programming model. In addition, by mixing the main component with optimal additive components in terms of target product properties, mixtures which are close to Pareto optimal solution can be generated.

8.2.1.9.Test the Miscibility of Mixture Components

In order to design a feasible mixture, the main and additive components are required to form a feasible mixture with each other. Therefore, after the identification of potential mixture candidates by mixing the main and additive components, the miscibility of the mixture components is examined in this step. The miscibility of the mixture components is determined by measuring the Hildebrand solubility parameter (δ) of the components. According to Vandenburg et al. (1999), δ provides a numerical estimate of the degree of interaction between materials, which can be used as a good indication of the solubility of materials. δ of the mixture components can be predicted by using a property prediction model of GC method developed by Hukkerikar et al. (2012b), as shown in Equation (8.10).

$$\delta = \delta_0 + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \tag{8.10}$$

In Equation (8.10), δ_0 is a universal constant for the prediction of δ. If the mixture components can produce a miscible mixture with each other, a feasible mixture can be generated. On the other hand, if the mixture components are not miscible with each other, the combination of the main and additive components cannot produce a feasible mixture. In this case, the mixture design problem has to be repeated from Step 2 of the mixture design procedure, where the target property ranges, potential main component and the number of mixture components are re-evaluated.

This step acts as a screening tool to select the feasible mixtures from the generated mixture candidates. In addition to the miscibility test, other methods for the verification of mixture feasibility can be applied in this step.

8.2.1.10. Generate Feasible Mixtures in terms of Main and Additive Components

With the verification of the miscibility of mixture components, the generated mixtures which have passed through the verification process are the feasible mixtures in terms of main and additive components. These mixtures are the optimal mixtures in terms of target properties that satisfy the required product needs.

8.2.2. Stage 2: Integrated biorefinery design

In the first stage of the propose two-stage optimisation approach, optimal mixture in terms of target product properties are identified. The second stage determines the optimal biomass conversion pathway to produce the identified optimal mixture by utilising superstructural mathematical optimisation approach. A superstructure which includes all the possible conversion pathways and technologies that process the biomass into the intermediates, and convert the intermediates into the final products is constructed as the representation of an integrated biorefinery. The superstructural mathematical optimisation approach adapted in identifying the optimal conversion pathways is similar to the approach proposed in Chapter 5. Therefore, the details of the approach will not be discussed in this section. The information and procedure involved in the identification of optimal conversion pathways can be found in Section 5.2.2. By identifying different potential conversion pathways for the production of the final product, comparison and trade-off between different combinations of optimal conversion pathways and optimal mixtures can be made. For instance, when the optimal mixture in terms of product needs cannot be manufactured economically, iterations are required to identify the alternative candidates which can be produced in a cost effective manner.

The developed optimisation approach provides the identification of optimal mixture product as well as the optimal conversion pathways that convert the biomass into the mixture product. This approach decomposes the overall product and process design problem into two design problems and solves them sequentially in two stages. Compared with solving the product and process design problem simultaneously, the computational complexity of this developed approach is lower. An algebraic approach for the simultaneous solution of process and molecular design problems developed by Bommareddy et al. (2010) can be utilised to solve the product and process design simultaneously. To illustrate the application and efficacy of this two-stage optimisation approach, a case study on the design of fuel additives as a mixture of different molecules from palm-based biomass is presented.

8.3. Case Study: Mixture design for bio-based fuel additives

A mixture design problem of producing fuel additives from biomass is solved to illustrate the proposed methodology. In the first stage, fuel additives with optimal target properties are designed. A mixture of different types of hydrocarbons is chosen as the main component of the fuel mixture. Fuel additives are then designed such that when mixed with the main component, the target properties of the mixture are within the predetermined target property ranges. For the simplicity of illustration, the additive components are designed based on the assumption that the targeted additives are single component products. In the second stage, the optimal conversion pathways in terms of different production objectives that convert biomass into the designed fuel additives are identified. In order to demonstrate the efficacy of the methodology, the conversion pathways of an integrated biorefinery are synthesised for two scenarios: conversion pathways for maximum product yield and conversion pathways for maximum economic potential. Please note that the proposed approach is a generic approach developed for the identification of the optimal mixture in terms of target product properties as well as the optimal conversion pathway in an integrated biorefinery. Therefore, the application of the proposed approach is not limited to the mixture design problem as shown in this case study.

8.3.1. Design of Optimal Mixture

8.3.1.1. Define Objective, Identify and Analyse Target Properties

In this case study, the fuel is designed in terms of different product needs. The first is engine efficiency, which is measured as energy content in terms of higher heating value (*HHV*). As the energy of a fuel is determined by the heat content of the compounds, *HHV* is identified as the measurement of energy content of the fuel mixture. In order to increase the engine efficiency, the *HHV* of the fuel should be high so that the energy content of the fuel is high. Other than engine efficiency, oxygen content (*OC*) of the fuel is another target property to be considered during the design of fuel mixture. According to American Petroleum Institute, the presence of oxygen encourages oxidation during fuel combustion. Thus, this results in a more efficient and complete fuel combustion (API, 2008). In addition, the fuel should be less toxic. The toxicity of the fuel is considered during the design stage to make sure the fuel is safe to be utilised. The toxicity of the fuel is measured as lethal concentration (LC_{50}) in this case study. The *OC* and LC_{50} of the fuel are designed to be as high as possible within the specification ranges. Meanwhile, heat of vaporisation (H_v) and viscosity (η) of the fuel are the other target properties that are considered during the mixture design to ensure the stability and consistency of the fuel flow. The target property range for each property are shown in Table 8.1.

Table 8.1: Target property ranges for the mixture design

Target property	**Lower limit**	**Upper limit**
HHV (kJ/mol)	3500	5500
OC (wt %)	2.00	6.70
LC_{50}	700	1400
H_v (kJ/mol)	35	45
η (cP)	0.30	0.90

In this case study, the design of the optimal fuel is solved by designing multiple additive components for a pre-identified main component which acts as the conventional fuel. A pseudo-component which consists of different hydrocarbons is selected as the main component for the case study. The components and composition of the main component is shown in Table 8.2.

Table 8.2: Components and composition of the main component

Component	**Composition (wt %)**
butane	6.58
heptane	12.60
iso-octane	53.99
methylclclopentane	3.63
toluene	14.73

Based on the basis of the description, more than one target property is optimised while designing the fuel mixture. Hence, this design problem is formulated as a multi-objective optimisation problem to design the optimal fuel which fulfils the design goals.

8.3.1.2. Identify Appropriate Property Prediction Models

Following the proposed procedure, after identifying the target properties for the mixture, property prediction model for each target property is identified. In order to illustrate the ability of the proposed methodology to utilise different classes of property prediction models in a design problem, property prediction models based on GC methods and TIs are chosen the estimate the target properties. For the prediction of *HHV*, a GC model developed by Yunus (2014) as shown in Equation (8.11) is utilised.

$$HHV = HHV_0 + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \tag{8.11}$$

In Equation (8.11), HHV_0 is an adjustable parameter for the prediction of *HHV*. For the prediction of LC_{50}, a valence connectivity index (CI) of order two developed by Koch (1982) as shown in Equation (8.12) will be utilised.

$$\log_{10} LC_{50} = 4.865 - 0.899({}^{1}\chi^{v}) \tag{8.12}$$

For H_v and η, reliable GC models are available as given in Equation (8.13) (Marrero and Gani, 2001) and Equation (8.14) (Conte et al., 2008) respectively.

$$H_v = H_{v0} + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k \tag{8.13}$$

$$\ln \eta = \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{I}} \sum_k N_k C_k \tag{8.14}$$

In Equation (8.13), H_{v0} is the adjustable parameter for the prediction of H_v. As there is no property prediction model available for *OC,* a relationship presented in Equation (8.15) is used to calculate the *OC* of the fuel mixture.

$$OC = \frac{MW^{\mathrm{O}}}{MW^{\mathrm{MIX}}} \tag{8.15}$$

In Equation (8.15), MW^{O} is the molecular weight of the oxygen atom in the mixture and MW^{MIX} is the molecular weight of the mixture.

8.3.1.3.Select molecular building blocks

With the identification of property prediction models, the next step is to select the molecular building blocks which are suitable for the mixture design problem. As the main objective of the mixture design problem is to increase the *HHV* and *OC* of the fuel, carbon (C), hydrogen (H) and oxygen (O) atoms are considered during the design of fuel additives. As molecular signature descriptor is utilised in identifying the additives molecule, only signatures with single bonds are considered. Signatures of height two are required for the mixture problem since property prediction model of first order CI is utilised. The selected molecular building blocks are carbon with three hydrogen atoms (-CH_3), carbon with two hydrogen atoms (-CH_2), carbon with a hydrogen atom (-CH), carbon with zero hydrogen atom (-C) and oxygen with a hydrogen atom (-OH).

8.3.1.4. Form Property Prediction Models as Normalised Property Operators

In this step, the property prediction models are transformed into their respective normalised property operators. Property prediction models as shown in Equations (8.11) – (8.15) are written as normalised property operators as shown below.

$$\Omega_{HHV} = HHV - HHV_0 \quad (8.16)$$

$$\Omega_{LC_{50}} = \frac{4.865 - \log LC_{50}}{0.899} \quad (8.17)$$

$$\Omega_{H_v} = H_v - H_{v0} \quad (8.18)$$

$$\Omega_{\eta} = \ln \eta \quad (8.19)$$

$$\Omega_{OC} = \frac{MW^{\mathrm{O}}}{MW^{\mathrm{MIX}}} \quad (8.20)$$

8.3.1.5. Develop structural constraints and generate feasible additive components

The additives for the fuel are designed in this step. As the main objective of the mixture design problem is to increase the *HHV* and *OC* of the fuel, alkane is identified as the additive to increase the *HHV* of the fuel while alcohol is selected as the additive to improve the *OC* of the fuel. By taking the specifications of the existing products as reference, alkane with carbon number 5 – 10 and alcohol with carbon number 2 – 5 are identified as the additives to be designed for the fuel mixture. The target property ranges and target property operator ranges for the design of alkane and alcohol are shown in Table 8.3 and Table 8.4 respectively.

In order to design an additive made from alkane with maximised *HHV*, the additive design problem is formulated as a MILP model. Equation (8.21) is solved with structural constraints and other property constraints as shown in Table 8.3.

$$\text{Maximise} \quad \Omega_{HHV} \tag{8.21}$$

Table 8.3: Target property ranges and target operator ranges for the design of additive made from alkane

Target property	**Target property range**		**Target property operator range**	
	$\boldsymbol{v_p^{\mathrm{L}}}$	$\boldsymbol{v_p^{\mathrm{U}}}$	$\boldsymbol{\Omega_p^{\mathrm{L}}}$	$\boldsymbol{\Omega_p^{\mathrm{U}}}$
HHV	6000 kJ/mol	7000 kJ/mol	5853	6853
OC	0.00 wt %	0.00 wt %	0.00	0.00
LC_{50}	5.00	26.00	3.85	4.63
H_v	40.00 kJ/mol	50.00 kJ/mol	28.27	38.27
η	0.40 cP	1.10 cP	-0.92	0.10

Likewise, Equation (8.22) is solved with structural constraints and other property constraints as shown in Table 8.4 in order to design an additive made from alcohol with maximised *OC*.

$$\text{Maximise} \quad \Omega_{OC} \tag{8.22}$$

Table 8.4: Target property ranges and target operator ranges for the design of additive made from alcohol

Target property	**Target property range**		**Target property operator range**	
	$\boldsymbol{v}_p^{\mathbf{L}}$	$\boldsymbol{v}_p^{\mathbf{U}}$	$\boldsymbol{\Omega}_p^{\mathbf{L}}$	$\boldsymbol{\Omega}_p^{\mathbf{U}}$
HHV	2000 kJ/mol	4000 kJ/mol	1853	3853
OC	15.00 wt %	35.00 wt %	15.00	35.00
LC_{50}	200.00	2000.00	1.74	2.85
H_v	47.00 kJ/mol	57.00 kJ/mol	35.27	45.27
η	2.00 cP	3.20 cP	0.69	1.16

Optimum solution is obtained in terms of signatures. By utilising integer cuts, the best five solutions are obtained and summarised in Table 8.5 for the design of additives made from alkane and Table 8.6 for the design of additives made from alcohol. Molecular graph and the name of the generated molecule can be generated for the solutions based on the graph signature algorithm developed by Chemmangattuvalappil and Eden (2013).

Table 8.5: List of solutions of additive made from alkane

Sol.	**Name**	**Target property**				
		HHV **(kJ/mol)**	***OC*** **(wt %)**	$\boldsymbol{LC_{50}}$	$\boldsymbol{H_v}$ **(kJ/mol)**	$\boldsymbol{\eta}$ **(cP)**
Alk. A	2,2,5,5-tetramethylhexane	6767	0.00	12.02	44.32	0.89
Alk. B	2,2,5-trimethylheptane	6765	0.00	7.24	46.24	0.69
Alk. C	2,3,4,4-tetramethylhexane	6751	0.00	7.94	44.60	0.60
Alk. D	4,4-dimethylheptane	6126	0.00	14.45	42.97	0.64
Alk. E	3-ethyl-2,2-dimethylpentane	6112	0.00	17.78	41.33	0.56

Table 8.6: List of solutions of additive made from alcohol

Sol.	**Name**	**Target property**				
		HHV **(kJ/mol)**	***OC*** **(wt %)**	LC_{50}	H_v **(kJ/mol)**	η **(cP)**
Alc. A	butan-1-ol	2683	21.62	1122.02	50.90	2.50
Alc. B	butan-2-ol	2669	21.62	1288.25	49.25	2.18
Alc. C	pentan-1-ol	3335	18.18	398.11	55.80	3.09
Alc. D	pentan-3-ol	3321	18.18	426.58	54.16	2.70
Alc. E	3-methylbutan-2-ol	3307	18.18	602.56	52.52	2.36

From Table 8.5, the optimal additive is 2,2,5,5-tetramethylhexane (Alk. A), with a *HHV* of 6767 kJ/mol. It can be seen from Table 8.5 that all of the additive properties fall within the target property ranges, as shown in Table 8.3. These solutions are targeted based on the properties of the existing products and the structural constraints. Therefore, these additives are capable of improving the performance of the fuel in terms of *HHV*. Since additive made from alkane is designed, it is noted that the value of *OC* are zeros for all of the generated solutions. Meanwhile, Table 8.6 shows the list of generated solution for the design of additive made from alcohol, arranged in terms of *OC*. As seen from Table 8.6, the optimal additive in terms of *OC* is butan-1-ol (Alc. A), with a value of *OC* of 21.62 wt %. It can be observed from Table 8.6 that all of the additive properties fall within the target property ranges, as shown in Table 8.4. As these solutions are designed based on the properties of the existing product and structural constraints, they are capable of improving the performance of the fuel in terms of *OC*. It is worth pointing out that some of the generated solutions as shown in Tables 8.5 and 8.6 are among the commonly used additives in the current market. For example, according to

United States Environmental Protection Agency, 3-ethyl-2,2-dimethylpentane (Alk. E) and butan-1-ol (Alc. A) are used as antiknock agent and oxygenate respectively to improve the quality of the fuel (EPA, 2015). Hence, the identified solutions as shown in Tables 8.5 and 8.6 have the potential to be accepted and utilised as fuel additives by the current market.

8.3.1.6.Generate and rank potential mixture candidates

With the identification of the optimal additives, the optimal mixture in terms of multiple target properties is designed in this step. In this case study, linear mixing rule is applied to estimate HHV, $\log_{10}LC_{50}$, OC and H_v of the mixture. The linear mixing rule is shown in the following equation.

$$V_p^{\mathrm{MIX}} = \sum_m x_m V_{mp} \qquad \forall p \in P \tag{8.23}$$

In Equation (8.23), V_p^{MIX} is the value for the target property p for the mixture, x_m is the fraction for the chemical component m and V_{mp} is the value for the target property p for the chemical component m. For η, a mixing rule developed based on property integration as proposed by Qin et al. (2004) is utilised. This is shown in Equation (8.24).

$$\log \eta^{\mathrm{MIX}} = \sum_m x_m \log \eta_m \tag{8.24}$$

In Equation (8.24), η^{MIX} is the η for the mixture while η_m is the η for the chemical component m. Table 8.7 shows the target property ranges for the design of optimal mixture.

Table 8.7: Lower and upper limits for the mixing of target properties

Target property	**Lower limit**	**Upper limit**
HHV	3500 kJ/mol	5500 kJ/mol
OC	2.00 wt %	6.70 wt %
$\log_{10}LC_{50}$	2.85	3.15
H_v	35 kJ/mol	45 kJ/mol
$\log_{10}\eta$	-0.52	-0.05

As the mixture design problem is solved as a multi-objective optimisation problem, target properties to be optimised are written as linear membership functions as shown by Equations (8.25) – (8.27) for HHV, OC and LC_{50}. This step is unnecessary for H_v and η, which are not optimised but used as constraints.

$$\lambda_{HHV} = \frac{V_{HHV}^{\mathrm{MIX}} - 3500}{5500 - 3500} \tag{8.25}$$

$$\lambda_{OC} = \frac{V_{OC}^{\mathrm{MIX}} - 2.00}{6.70 - 2.00} \tag{8.26}$$

$$\lambda_{LC_{50}} = \frac{V_{\log_{10}LC_{50}}^{\mathrm{MIX}} - 2.85}{3.15 - 2.85} \tag{8.27}$$

The mixture design problem is solved by using the max-min aggregation approach. The optimisation objective is to maximise the least satisfied target property among the target properties to be optimised while keeping all the target properties within the target property ranges. The formulated multi-objective MILP model is shown as below.

$$\text{Maximise} \quad \lambda \tag{8.28}$$

$$\lambda \leq \frac{V_{HHV}^{\text{MIX}} - 3500}{5500 - 3500} \tag{8.29}$$

$$\lambda \leq \frac{V_{OC}^{\text{MIX}} - 2.00}{6.70 - 2.00} \tag{8.30}$$

$$\lambda \leq \frac{V_{\log_{10} LC_{50}}^{\text{MIX}} - 2.85}{3.15 - 2.85} \tag{8.31}$$

$$v_p^{\text{MIX, L}} \leq \sum_m x_m V_{mp} \leq v_p^{\text{MIX, U}} \qquad \forall p \in P \tag{8.32}$$

$$\sum_m x_m = 1 \tag{8.33}$$

Together with the structural constraints, the mixture design problem is solved and an optimum solution is obtained in terms of composition of main and additive components. By utilising integer cuts, the best five solutions are generated and summarised in Table 8.8. From Table 8.8, it can be seen that all of the mixture properties fall between the boundaries that represent the product needs as specified in Table 8.1. The optimal mixture, mixture A is produced by mixing 54.53 wt% of main component, 21.40 wt% of 2,2,5,5-tetramethylhexane (Alk. A) and 24.07 wt% of pentan-1-ol (Alc. C). It is noticed that the mixing ratio for additives alkane and alcohol varies for different solutions. For mixtures A, B and C, the amount of additive alcohol is more than the amount of additive alkane required; for mixtures D and E, the opposite trend is observed. In addition, it can be seen from Table 8.8 that 2,2,5,5-tetramethylhexane (Alk. A) and pentan-1-ol (Alc. C) are the preferred additives to improve the *HHV* and *OC* of the fuel as they are both selected as

Table 8.8: List of solutions of fuel mixture

Sol.		**Mix. A**	**Mix. B**	**Mix. C**	**Mix. D**	**Mix. D**
Composition (wt%)	Main component	54.53	56.33	53.78	53.90	53.87
	Alkane	Alk. A 21.40	Alk. B 19.78	Alk. D 22.47	Alk. A 26.37	Alk. C 26.45
	Alcohol	Alc. C 24.07	Alc. C 23.89	Alc. D 23.75	Alc. A 19.73	Alc. B 19.68
Target property	*HHV* (kJ/mol)	4542	4519	4455	4455	4451
	OC (wt %)	4.42	4.34	4.32	4.27	4.25
	LC_{50}	1060	1075	989	1189	1142
	H_v (kJ/mol)	39.98	40.00	39.42	38.78	38.02
	η (cP)	0.82	0.78	0.75	0.77	0.69

the additives in two out of five best mixtures. The mixtures are arranged in terms of the least satisfied degree of satisfaction between *HHV*, *OC* and LC_{50}. Table 8.9 shows the comparison of degrees of satisfaction between the generated mixtures.

Table 8.9: Comparison of λ_p between different designs of mixture

Sol.	λ_{HHV}	λ_{OC}	$\lambda_{LC_{50}}$
Mix. A	0.5212	0.5150	0.5847
Mix. B	0.5094	0.4987	0.6043
Mix. C	0.4960	0.4933	0.4840
Mix. D	0.4775	0.4822	0.7500
Mix. E	0.4754	0.4797	0.6920

From Table 8.9, it can be seen that the least satisfied property is not always the same property for all of the five generated solutions. For example, the least satisfied property for mixture A is OC with λ of 0.5150, the least satisfied property for mixture C is LC_{50} with λ of 0.4840 while the least satisfied property for mixture E is HHV with λ of 0.4754. This indicates that the developed methodology identifies the relative importance of each property to be optimised without the presence of a decision maker. As long as the degree of satisfaction for the least satisfied property is maximised, the generated solution is a feasible mixture that fulfils the product needs.

8.3.1.7. Test the miscibility of mixture components and generate feasible mixtures

In order to design a feasible mixture, the main and additive components are required to form a feasible mixture with each other. Therefore, after the identification of the potential mixture candidates, the miscibility of the mixture components is examined in this step. In this case study, the miscibility of the mixture components is determined by measuring the δ of the components. The GC model developed by Hukkerikar et al. (2012b) as shown in Equation (8.10) is utilised for the prediction of δ. δ is determined for the main component as well as the designed additive components from both alkane and alcohol as shown in Tables 8.5 and 8.6. The δ identified for the main and additive components are tabulated in Table 8.10.

Table 8.10: Hildebrand solubility parameters determined for main and additive components

Main/additive components	**δ (MPa$^{1/2}$)**
Main component	17.0908
Alk. A	12.6488
Alk. B	13.7564
Alk. C	13.0757
Alk. D	14.5911
Alk. E	13.9104
Alc. A	19.6131
Alc. B	20.8824
Alc. C	21.4091
Alc. D	20.7284
Alc. E	20.0477

As shown in Table 8.10, the δ for the main component is 17.0908 MPa$^{1/2}$, the range of δ for additive alkanes is between 12.6488 MPa$^{1/2}$ and 14.5911 MPa$^{1/2}$ while the range of δ for additive alcohols is between 19.6131 MPa$^{1/2}$ and 21.4091 MPa$^{1/2}$. It can be seen that the difference in values of δ for all the mixture components are small. This indicates that the identified additive components are miscible with the main component to form feasible mixtures. Hence, by mixing the main components with the identified additive components, feasible mixtures with optimal target product properties can be produced. Since the mixture components are miscible, a feasible mixture can be produced. Thus, the mixture design problem can be carried on into the second stage of the methodology. Please be noted that this step acts as a screening tool to select the feasible mixtures from the generated mixture candidates. In addition to the miscibility test, other methods for the verification of mixture feasibility can be applied in this step.

8.3.2. Selection of Optimal Conversion Pathway

In this second stage of the methodology, optimal conversion pathways that convert the biomass into the additive components are identified in an integrated biorefinery. In this case study, palm-based biomass known as empty fruit bunch (EFB) is chosen as the feedstock of the integrated biorefinery. The composition of the EFB is shown in Table 8.11.

Table 8.11: Lignocellulosic composition of EFB

Components	**Composition (% of dry matter)**
Lignin	39.00
Cellulose	22.00
Hemicellulose	29.00

From the first stage of the two-stage optimisation approach, it is known that the end products of the integrated biorefinery are alkanes and alcohols. A list of possible conversion pathways that produce alkanes and alcohols from biomass are shown in Table 8.12. These conversion pathways include the conversion pathways from physical, thermochemical, chemical as well as biochemical platforms. For illustration purpose, the end products alkanes and alcohols of the integrated biorefinery are represented as straight-chain products without considering the formation of isomers. For example, the optimal additive made from alkane, 2,2,5,5-tetramethylhexane is represented as alkane with carbon number 10 (Alkane C_{10}) while the optimal additive made from alcohol, butan-1-ol is represented as alcohol with carbon number 4 (Alcohol C_4) in this case study. For cases where the conversion pathways lead

Table 8.12: List of conversions and selectivities for conversion pathways

Pathway	Process	Product	Conversion (%)	Selectivity (%)
1	Ammonia explosion	Sugars, Lignin	98.0	-
2	Steam explosion	Sugars, Lignin	49.2	-
3	Organosolv separation	Lignin	79.0[a]	-
4	Organosolv separation	Sugars	97.0[a]	-
5	Autohydrolysis	HMF	90.9	-
6	Dehydration of sugars	Furfural	40.9	-
7	Yeast fermentation	Ethanol	61.9	-
8	Bacterial fermentation	Ethanol	41.0	-
9	Hydrogenation of furfural	THFA	98.2	-
10	Hydrogenation of THFA 1	Pentanediol	99.0	95.0
		Pentanol		4.0
11	Hydrogenation of THFA 2	Pentanediol	60.0	51.0
		Pentanol		22.0
12	Pyrolysis	Syngas	94.0	-
13	Gasification	Syngas	90.0	-
14	Anaerobic digestion	Methane	40.0	-
15	Water gas shift reaction	Syngas	100.0	-
16	Fischer-Tropsch process 1	Hydrocarbon C_2-C_4	40.0	16.0
		Hydrocarbon C_5-C_9		27.0
		Hydrocarbon C_{10}		26.0
17	Fischer-Tropsch process 2	Hydrocarbon C_2-C_4	75.0	23.0
		Hydrocarbon C_5-C_9		19.0
		Hydrocarbon C_{10}		9.7
18	Conversion of syngas 1	Methanol	25.1	2.6
		Ethanol		61.4

Table 8.12: (continued) List of conversions and selectivities for conversion pathways

19	Conversion of syngas 2	Methanol	24.6	3.9
		Ethanol		56.1
20	Hydrogenation of CO	Methanol	28.8	20.7
		Ethanol		23.8
		Propanol		14.1
		Butanol		7.5
21	Monsanto process	Ethanoic Acid	99.0	-
22	Dehydration of alcohols 1	Hydrocarbon C_2	67.0	-
23	Dehydration of alcohols 2	Hydrocarbon C_3	59.0	28.8
		Hydrocarbon C_4		37.3
24	Dehydration of alcohols 3	Hydrocarbon C_5	64.0	15.2
		Hydrocarbon C_6		5.5
		Hydrocarbon C_7		5.6
		Hydrocarbon C_8		4.2
25	Decarboxylation of acids	Hydrocarbon C_2	62.0	21.3
26	Fractional distillation of alcohols	Pentane	97.0[a]	-
		Pentanediol	97.0[a]	-
27	Fractional distillation of alkanes	Hydrocarbon C_{10}	99.0[a]	-
		Hydrocarbon C_2-C_9	99.0[a]	-

[a] Separation efficiency.

to the formation of product as a mixture of several components, separation processes are included. These separation processes are taken into account to refine and separate the final product from the other by-products based on the results obtained from the design of product in stage 1 of the two-stage optimisation approach. In Table 8.12, conversion pathways 26 and 27 are two separation processes which are utilised to refine and separate the final product alcohol and alkane from their by-products respectively. Figure 8.3 presents a superstructure developed based on the conversion pathways in Table 8.12. It is noted that the developed superstructure can be revised to include more conversion pathways and technologies in synthesising an integrated biorefinery.

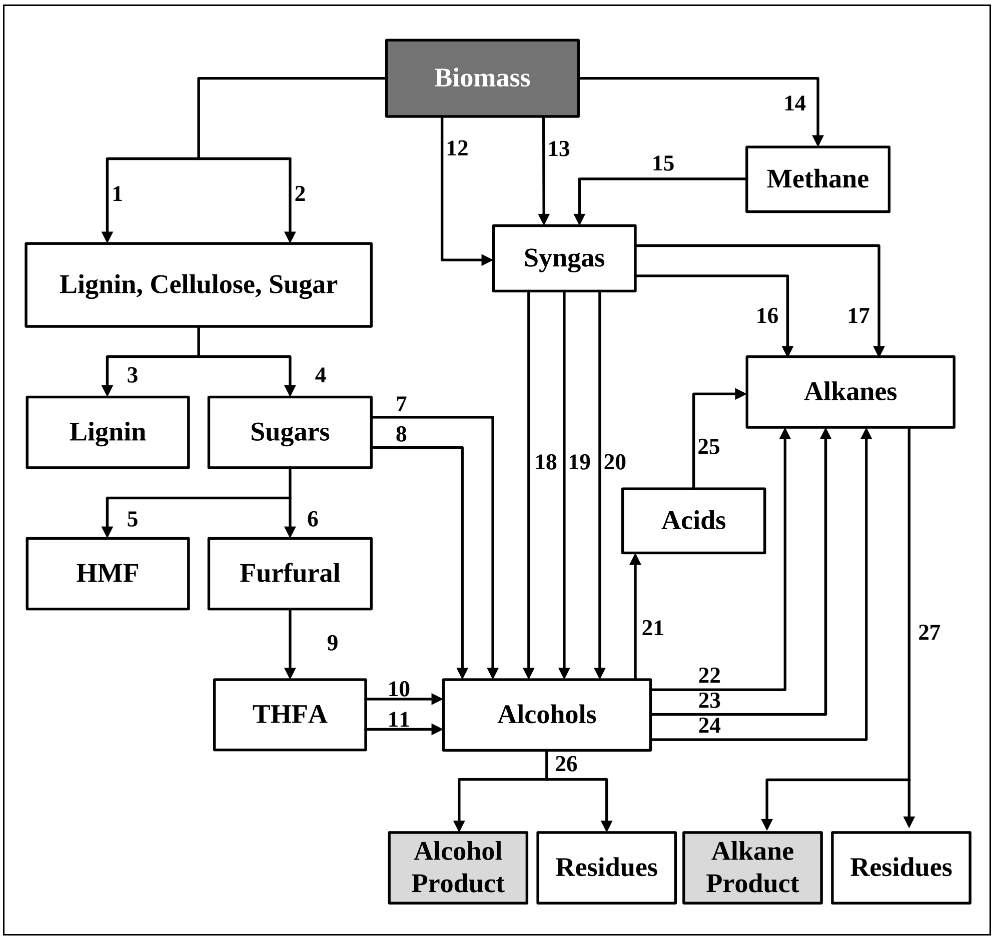


Figure 8.3: Production of additives made from alkane and alcohol from lignocellulosic biomass

In this case study, two scenarios of different production objectives are considered in synthesising the integrated biorefinery:

1. Design for maximum product yield
2. Design for maximum economic potential

Table 8.13 shows the market price of the products and biomass feedstock while the capital and operating costs for each conversion pathway are shown in Table 8.14. Note that the prices of the products, feedstock and conversion pathways can be revised according to the market prices to produce an up-to-date economic analysis.

Table 8.13: List of prices of products and raw material

Final product	**Revenue from final product (U.S.$) per tonne**
Ethane	424
Propane	670
Butane	900
Pentane	1200
Hexane	1600
Heptane	1800
Octane	2000
Nonane	2510
Decane	2750
Methanol	450
Ethanol	770
Propanol	950
Butanol	1120
Pentanol	1770
Pentanediol	3000
Raw material	**Cost of raw material (U.S.$) per tonne**
Biomass (EFB)	170

Table 8.14: List of capital and operating costs for conversion pathways

Pathway	**Process**	**Capital cost (U.S.$)**	**Operating cost (U.S.$) per annual tonne**
1	Ammonia explosion	7.47×10^6	11.30
2	Steam explosion	5.29×10^6	7.97
3	Organosolv separation	1.55×10^7	23.30
4	Organosolv separation	1.55×10^7	23.30
5	Autohydrolysis	2.41×10^7	36.40
6	Dehydration of sugars	1.05×10^7	15.80
7	Yeast fermentation	1.54×10^7	22.00
8	Bacterial fermentation	1.20×10^7	18.00
9	Hydrogenation of furfural	1.15×10^7	17.30
10	Hydrogenation of THFA 1	1.65×10^7	24.90
11	Hydrogenation of THFA 2	1.73×10^7	26.00
12	Pyrolysis	2.39×10^7	36.00
13	Gasification	3.29×10^7	55.00
14	Anaerobic digestion	9.98×10^6	15.00
15	Water gas shift reaction	5.57×10^6	8.66
16	Fischer-Tropsch process 1	7.36×10^7	111.00
17	Fischer-Tropsch process 2	6.92×10^7	104.00
18	Conversion of syngas 1	1.47×10^7	22.10
19	Conversion of syngas 2	1.56×10^7	23.60
20	Hydrogenation of CO	1.53×10^7	23.00
21	Monsanto process	1.55×10^7	23.30
22	Dehydration of alcohols 1	1.54×10^7	23.20
23	Dehydration of alcohols 2	1.43×10^7	21.50
24	Dehydration of alcohols 3	1.31×10^7	19.70
25	Decarboxylation of acids	1.75×10^7	26.30
26	Fractional distillation of alcohols	4.81×10^7	72.50
27	Fractional distillation of alkanes	6.52×10^7	98.20

In this case study, other than the revenue generated by producing the additives, the revenue obtained from the generation of by-products along with the additives is included in the overall economic potential of the integrated biorefinery as well. In addition, please note that the capital costs provided in Table 8.14 are the capital costs for nominal capacity of each conversion technology available in the market. Hence, the solution in terms of flow rate determined by the mathematical model is the operating flow rate into the selected conversion technology with a fixed nominal capacity. The capital cost for each conversion technology can be updated from time to time to provide an up-to-date economic analysis.

From the optimal mixture, Mix. A generated in the first stage of the methodology, it is identified the mixing ratio of additive alkane (Alk. A, 2,2,5,5-tetramethylhexane) and additive alcohol (Alc. C, pentan-1-ol) is 1:1.12. Thus, in order to yield the additives that produce the optimal mixture when mixed with main component, the production ratio of alkane and alcohol in the integrated biorefinery is fixed as 1:1.12. With a feed of 50000 tonnes per year of EFB, a superstructural optimisation model is formulated and solved to identify the optimal conversion pathways in terms of maximum product yield as well as maximum economic potential for the production additives alkane and alcohol.

8.3.2.1.Scenario 1: Design for maximum product yield

In this scenario, an integrated biorefinery is synthesised by solving the optimisation model using the optimisation objective in Equation (8.34) subject to production constraint as shown in Equation (8.35). Note that the optimum additive alkane (Alk. A, 2,2,5,5-tetramethylhexane) is represented as Alkane

C_{10} while the optimum additive alcohol (Alc. C, pentan-1-ol) is represented as alcohol of carbon number 5 (Alcohol C_5) in the case study.

$$\text{Maximise} \quad T^{\text{Prod}}_{\text{AlkaneC}_{10}} \tag{8.34}$$

$$1.12T^{\text{Prod}}_{\text{AlkaneC}_{10}} = T^{\text{Prod}}_{\text{AlcoholC}_{5}} \tag{8.35}$$

Based on the obtained result, the maximum yield for Alkane C_{10} is 952.36 t/y. As the mixing ratio of Alkane C_{10} and Alcohol C_5 is 1:1.12, the yield for the alcohol additive is identified as 1066.64 t/y. The GP^{Total} for the scenario is found to be U.S. $1.75 million (per annum). The conversion pathways selected for the scenario is illustrated in the synthesised integrated biorefinery as shown in Figure 8.4. From Figure 8.4, it can be seen that the additive alcohol is produced from biomass in the conversion pathway sequence of ammonia explosion, Organosolv separation, dehydration of sugars, hydrogenation of furfural, hydrogenation of THFA 2 and fractional of distillation of alcohols. As shown in Figure 8.4, a portion of alcohol is produced from yeast fermentation of sugars as well. Meanwhile, additive alkane is produced from fractional distillation of alkanes, which are produced from pyrolysis of biomass followed by Fischer-Tropsch process 1 together with dehydration of alcohols 1. It is worth pointing out that specific separation processes that suit the identified product can be chosen and included in the integrated biorefinery to refine and separate the final product from by-products. Hence, separation processes for alcohols and alkanes are chosen based on the results of the mixture design identified in stage 1 of the methodology. The performance of the separation processes are then taken into

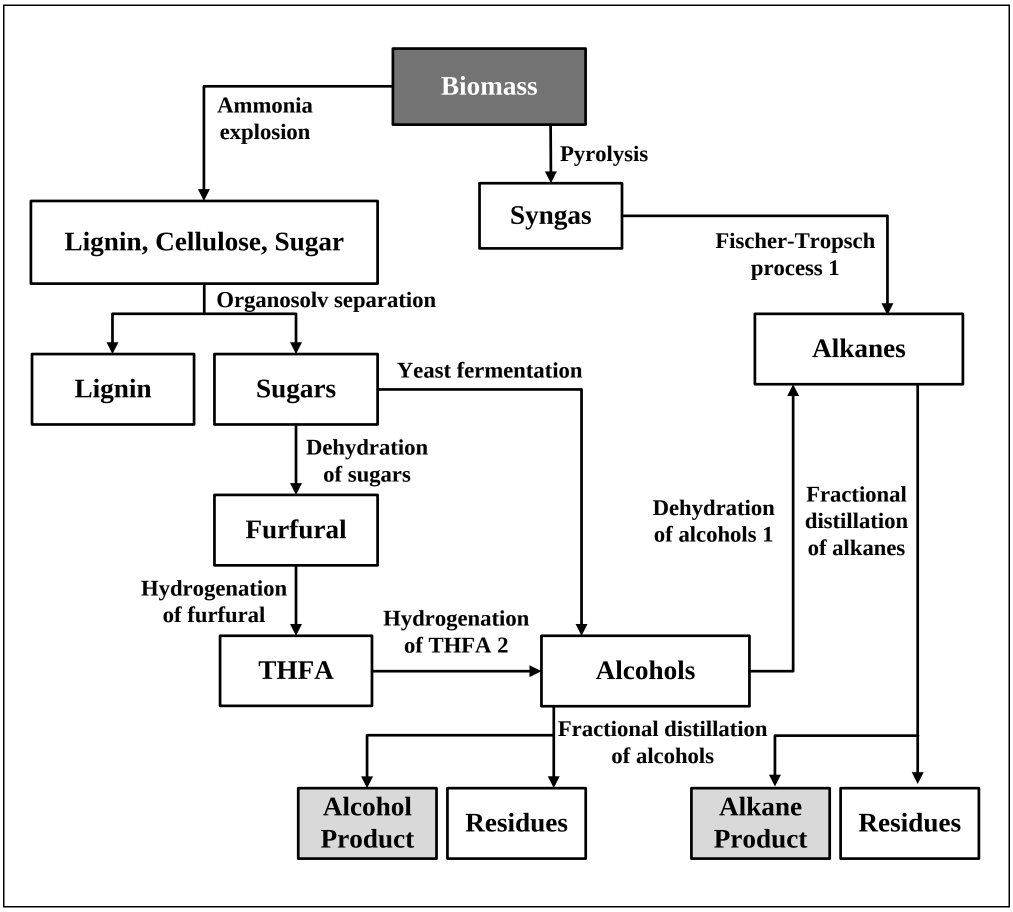


Figure 8.4: Flow diagram of the synthesised integrated biorefinery (maximum product yield)

consideration in identifying the product yield and economic potential of the overall conversion pathway.

8.3.2.2.Scenario 2: Design for maximum economic potential

In this scenario, an integrated biorefinery configuration with maximum economic potential is determined. The optimisation objective for the scenario is shown in Equation (8.36). Similar to scenario 1, production constraint as shown in Equation (8.35) is applied in scenario 2 in solving the optimisation objective to make sure the ratio of Alkane C_{10} and Alcohol C_5 is 1:1.12.

$$\text{Maximise} \quad GP^{\text{Total}} \tag{8.36}$$

Based on the generated optimisation result, the maximum GP^{Total} for the scenario is identified to be U.S. \$19.39 million (per annum). The yield for Alkane C_{10} for this scenario is identified as 357.23 t/y while the annual production of Alcohol C_5 is 400.10 t. The conversion pathways chosen for the scenario is presented in the synthesised integrated biorefinery as shown in Figure 8.5. From Figure 8.5, it can be seen that most of the conversion pathways of scenario 2 is similar to those of scenario 1. However, instead of hydrogenation of THFA 2 that converts THFA to alcohols, hydrogenation of THFA 1 is chosen in this scenario. In addition, yeast fermentation is not selected in this scenario. Meanwhile, in order to produce additive alkane, conversion pathways of pyrolysis, Fischer-Tropsch process 2, dehydration of alcohols 2 and 3 as well as fractional distillation of alkanes are chosen. From Figures 8.4 and 8.5, it is shown that the additive components that produce the optimal mixture when mixed with main component can be produced from biomass via optimal conversion pathways based on different production objectives.

The comparison of the results generated for scenario 1 and 2 are summarised in Table 8.15. It can be seen from Table 8.15 that the production rate for both Alkane C_{10} and Alcohol C_5 are higher for scenario 1 compared

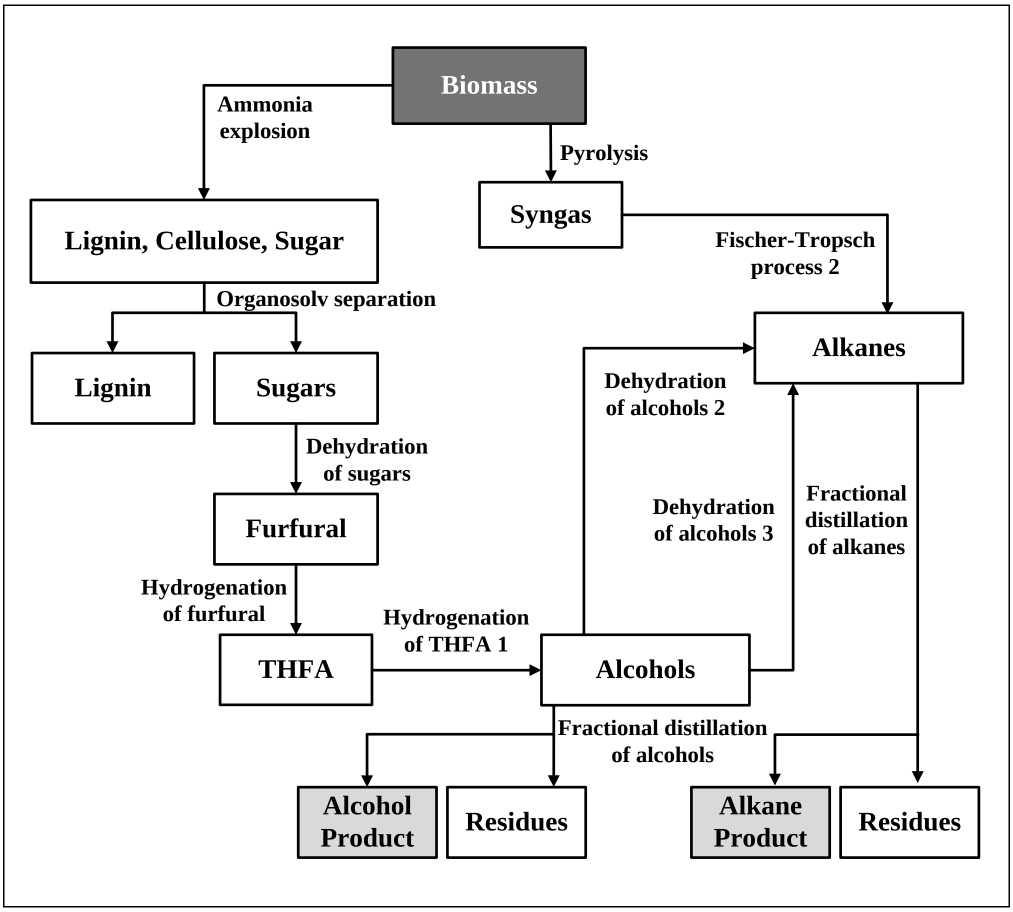


Figure 8.5: Flow diagram of the synthesised integrated biorefinery (maximum economic potential)

Table 8.15: Comparison of results for scenario 1 and 2

Scenario	**1**	**2**
GP^{Total} (U.S \$/y)	1.75×10^6	19.39×10^6
Alkane C_{10} production rate (t/y)	952.36	357.23
Alcohol C_5 production rate (t/y)	1066.64	400.10
Alkane by-product production rate (t/y)	7152.29	9564.93
Alcohol by-product production rate (t/y)	4048.58	9502.29

with scenario 2. However, the GP^{Total} for scenario 2 is better than the GP^{Total} for scenario 1. This is because the revenue obtained from the generation of by-products along with the additives is included in the overall economic potential of the integrated biorefinery. This is clearly shown in Table 8.15 that the production rates of by-products in scenario 2 are greater than the production rate of by-products in scenario 1. Hence, the GP^{Total} identified for scenario 2 is better than the GP^{Total} identified for scenario 1. The mathematical formulations and results generated for this case study can be found in Appendix F of this thesis.

8.4. Conclusion

This chapter introduces a systematic two-stage optimisation approach for the design of optimal mixture from biomass in terms of target product properties by integrating product with process design in an integrated biorefinery. In the first stage, mixture design is done by using signature based molecular design technique. Different classes of property prediction models such as GC models and TIs are adapted in this approach to estimate the molecule structure from a set of target properties. Main component of the mixture is first identified from the target properties. This is followed by the identification of additive components to form the mixture with the main component. Hence, the optimal mixture that possesses optimal product properties can be designed by mixing the identified main component and additive components together. In the second stage, the optimal conversion pathways are determined via superstructural mathematical optimisation approach. Note that the optimum conversion pathways based on different optimisation objective (e.g. highest product yield, highest economic performance, lowest environmental impact etc.) can be determined by utilising the optimisation approach. To illustrate the proposed methodology, a case study on the design of biofuel as a mixture of different molecules from palm-based biomass is presented. By utilising the developed approach, an optimal fuel with optimised multiple target properties is designed as a mixture of molecules which consists of main and additive components. At the same time, the optimal conversion pathways in terms of highest product yield and highest economic performance which convert the palm-based biomass into the optimal fuel mixture are identified.

CHAPTER 9

CONCLUSIONS AND FUTURE WORK

9.1. Conclusions

This thesis offers several significant contributions which aim to aid in designing potential chemical products from biomass as well as synthesising an integrated biorefinery in producing the potential chemical products that meet the product needs. First of all, approaches that address the product design aspects as well as the process synthesis and design aspects in integrated biorefineries have been presented. The product design aspects in integrated biorefineries have been addressed by utilising computer-aided molecular design (CAMD) techniques while the process synthesis aspects in integrated biorefineries have been addressed by using chemical reaction pathway map (CRPM) and superstructural mathematical optimisation approach. These approaches provide systematic and efficient method to convert biomass into chemical products that possess product properties that meet the product needs. As utilisation of biomass is seen as a promising solution for the depletion of fossil fuel reserves and environmental issues caused by the exploitation of fossil fuels, these developed approaches serve as novel tools for industrial applications to convert biomass into a wide spectrum of potential chemical products. Another achievement is the development of mixture design approach in integrated biorefineries. It is aware that in some situations, the desired target product properties cannot be met by a single component chemical product. In such cases, the design of mixture is preferred as mixtures provide a good mix of target properties which are unattainable by single component chemical products. This design consideration is taken into account in this thesis. The mixture design approach is particularly useful for industrial applications to convert biomass into the desired products which exist in the form of mixture.

In addition, a multi-objective optimisation approach has been developed for chemical product design problems where several important product properties are needed to be considered and optimised simultaneously. This multi-objective optimisation approach treats the target product properties with equal importance and designs optimal chemical products in terms of multiple target product properties without the presence of a decision maker. This is important for chemical product design applications to reduce the impact of prejudice from the decision maker(s) while designing chemical products in terms of multiple target product properties. Furthermore, it is realised that the property prediction models are developed with certain accuracy and uncertainty. The accuracy of property prediction models can affect the effectiveness of CAMD techniques in predicting the product properties. Hence, a robust chemical product design approach has been developed for the design of optimal chemical products with consideration of property prediction model accuracy. As this approach takes the optimality of target product property as well as the property prediction model accuracy into consideration, this approach serves as an important chemical product design approach to design chemical product by using the CAMD techniques. As a whole, this thesis presents various novel approaches with the purpose to support the industries in converting biomass into different potential chemical products under different process and product design considerations.

9.2. Future Work

This thesis presents an integration of the synthesis of integrated biorefinery with chemical product design as well as the development of several novel approaches in the area of chemical product design. In order to enhance the developed approaches, there exists several opportunities for these approaches to be extended. The potential future work are summarised in the following subsections.

9.2.1. Enhancement of Process and Product Details in Integrated Biorefineries

The case studies for the production of chemical products from biomass illustrated in this thesis serve as proofs of concept for the approaches presented this research work. In order to enhance the details of the integrated biorefinery represented in the presented approaches, information such as reactants required, side reactions, handling of by-products, handling of products generated from side reactions as well as separation of isomers will be considered and included in the design and synthesis of integrated biorefineries. In addition, in order to improve the applicability of the presented approaches in industrial applications, manufacturability of product and feasibility of conversion processes in integrated biorefineries can be evaluated for the identification of products as well as the conversion pathways that convert biomass into the products. This is possible by investigating the complexity of the product in addition to the difficulties of the conversion processes in order to produce the product in an efficient manner. Additionally, in order to design integrated process-product design frameworks which can perform with stability and consistency under supply and demand uncertainty, sensitivity analysis can be carried out. Sensitivity analysis can be used to analyse the effect of uncertainties on the robustness of the integrated framework. Furthermore, experimental work such as the synthesis of chemical products identified from the presented approaches can be included for the validation and verification of the chemical products.

9.2.2. Consideration of Business Aspects in Integrated Designs

In order to capture the important aspects of the integrated process-product design, information such as cost evaluation of the whole integrated process should be considered in the overall design. Capital cost, process operating cost as well as the product cost should be taken into account simultaneously to determine the optimal process-product combination for the design of chemical product. Garcia and You (2015) developed a multi-objective optimisation approach for the trade-off between scaling capital and operating expenditures for the design of product and process networks. This approach can be utilised to model the relationship between the capital and operating costs of a biorefinery. In addition, a framework linking business decision-making to process-product design which includes the consideration of cost evaluation is proposed by Ng (2004). The proposed framework utilises the concept which involves the consideration of resources, activities, time, information and objectives. This concept is introduced to bring together business personnel, chemists and chemical engineers within a company so that business decisions with consideration of corporate goals, marketing decisions, product design, plant design and development can be made. A similar approach in the integrated process-product design in integrated biorefineries can provide a comprehensive framework for the integrated design. Furthermore, the consideration of red and blue ocean strategies can be applied in designing and producing chemical products. While red ocean strategy emphasises in competing in an existing market space, blue ocean strategy focus in creating an uncontested market space. By evaluating the weaknesses and strengths of a company or industry, different business concepts and strategies can be applied in developing a profitable design of integrated process and product.

9.2.3. Sustainable Design Framework

To synthesise an optimal chemical product, the best product evaluated based on the property and cost of the product is no longer sufficient in today's society. With the current focus towards a greener future, sustainable consumption and production (SCP) is strongly encouraged. Hence, a chemical product should be designed via a comprehensive product design framework which considers the supply chain management, product properties, manufacturing process, environmental issues as well as related social issues. Apart from the performance and economic evaluation, the design of chemical process-product should go towards a sustainable future. These design aspects can be adapted in the overall process-product design in an integrated biorefinery in order to design a sustainable integrated framework. As proposed by Mehrkesh and Karunanithi (2014), environmental impacts can be integrated within a CAMD framework as an index for environmentally friendliness of a chemical substance. In addition, sustainability indicators such as carbon, land, water and nitrogen footprints that are relevant to the biomass-based systems can be included in analysing the life cycle impact of the chemical product design framework. This can be done by using life cycle optimisation in an enterprise scale to include the consideration from different levels in a business in developing a sustainable integrated process-product design framework. Furthermore, decision-making framework for sustainable chemical product design which considers environment-health, safety related and physicochemical properties presented by Heintz et al. (2014) can be adapted into the integrated process-product design in an integrated biorefinery. This framework which involves the corporate decision-making in considering economic, environmental, inherent safety and inherent occupational health performances can be adapted to add to the completeness of the integrated process-product design in an integrated biorefinery.

9.2.4. Mixture Design

Contrary to the property prediction of pure components where usually only the type of chemical components plays the role, property estimation for mixture is usually affected by temperature, pressure, density, activity coefficient and composition of the mixture components. Hence, in order to design a mixture for design problems where operating conditions are important, detailed verification of the mixture properties as well as the stability of the mixture is required. However, property prediction models for the prediction of mixtures are limited at the moment. In order to solve a mixture design problem efficiently by using the CAMD techniques, property estimation methods which can capture the behaviour and interaction of each component are required. In addition, the verification of mixture properties often requires the utilisation of universal quasichemical functional-group activity coefficients (UNIFAC) models. Estimation of property by using UNIFAC models requires the knowledge of the complete molecule. Hence, this makes it very challenging to solve the product design problem inversely by designing the molecule from the desired target properties. These remain as the challenges to be addressed for mixture design problems.

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APPENDIX A: APPLICATION EXAMPLES FOR MOLECULAR SIGNATURE DESCRIPTOR

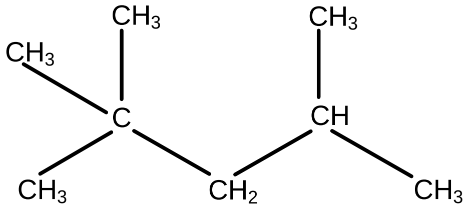
Molecular signature descriptor has been utilised in the research work to represent different structural descriptors on the same platform. Therefore, different classes of property prediction models can be used in a chemical product design problem. This section shows the application of molecular signature descriptor.

Two different property prediction models are utilised to estimate the desired product properties for two different products.

1. 2,2,4-trimethylpentane
    a. Standard enthalpy of vaporisation at 298 K (H_v)
    b. Toxicity (LC_{50})
2. 2-pentanol
    a. Standard enthalpy of vaporisation at 298 K (H_v)
    b. Toxicity (LC_{50})

The example calculations for the estimation of product properties are shown as follows.

Example 1



IUPAC name : 2,2,4-trimethylpentane

CAS registry number : 540-84-1

Molecular formula : C_8H_{18}

Table S1: List of signature and molecular groups for 2,2,4-trimethylpentane

Height 2 signatures	Corresponding 1st order molecular group	Number of occurrence
C1(C4(CCCC))	CH_3	3
C1(C3(CCC))	CH_3	2
C4(C2(CC)C1(C)C1(C)C1(C))	C	1
C2(C4(CCCC)C3(CCC))	CH_2	1
C3(C2(CC)C1(C)C1(C))	CH	1

Target property 1

Standard enthalpy of vaporisation at 298 K (H_v)

Property model

Group contribution method (Marrero and Gani, 2001)

$$H_v = H_{v0} + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k$$

Example calculations

Table S2: Calculation of H_v for 2,2,4-trimethylpentane

1st order molecular group	Number of occurrence	Contribution
CH_3	5	0.217
CH_2	1	4.910
CH	1	7.962
C	1	10.730
$\sum_i N_i C_i$		24.687

H_v = 11.733 kJ/mol + 24.687 kJ/mol

= 36.420 kJ/mol

Target property 2

Toxicity (LC_{50})

Property model

Connectivity index of order two (Koch, 1982)

$$\log LC_{50} = 4.865 - 0.899({}^1\chi^v) \qquad {}^1\chi = \frac{1}{2}\sum_{d=1}^{N} {}^2\alpha_d L_d$$

Example calculations

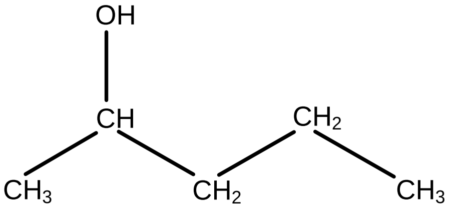
Table S3: Calculation for LC_{50} for 2,2,4-trimethylpentane

Height 2 signatures	Number of occurrence	TI value
C1(C4(CCCC))	3	$(1 \times 4)^{-0.5}$
C1(C3(CCC))	2	$(1 \times 3)^{-0.5}$
C4(C2(CC)C1(C)C1(C)C1(C))	1	$(4 \times 2)^{-0.5} + (4 \times 1)^{-0.5} + (4 \times 1)^{-0.5} + (4 \times 1)^{-0.5}$
C2(C4(CCCC)C3(CCC))	1	$(2 \times 4)^{-0.5} + (2 \times 3)^{-0.5}$
C3(C2(CC)C1(C)C1(C))	1	$(3 \times 2)^{-0.5} + (3 \times 1)^{-0.5} + (3 \times 1)^{-0.5}$
${}^1\chi$		3.417

$$\log LC_{50} = 4.865 - (0.899 \times 3.417)$$

$$= 1.793$$

Example 2



IUPAC name : 2-pentanol

CAS registry number : 6032-29-7

Molecular formula : $C_5H_{12}O$

Table S4: List of signature and molecular groups for 2-pentanol

Height 2 signatures	**Corresponding 1st order molecular group**	**Number of occurrence**
C1(C3(CCO))	CH_3	1
C3(C2(CC)C1(C)O1(C))	CH	1
O1(C3(CCO))	OH	1
C2(C3(CCO)C2(CC))	CH_2	1
C2(C2(CC)C1(C))	CH_2	1
C1(C2(CC))	CH_3	1

Target property 1

Standard enthalpy of vaporisation at 298 K (H_v)

Property model

Group contribution method (Marrero and Gani, 2001)

$$H_v = H_{v0} + \sum_i N_i C_i + z^{\mathrm{I}} \sum_j N_j C_j + z^{\mathrm{II}} \sum_k N_k C_k$$

Example calculations

Table S5: Calculation of H_v for 2-pentanol

1^{st} order molecular group	Number of occurrence	Contribution
CH_3	2	0.217
CH_2	2	4.910
CH	1	7.962
OH	1	24.214
$\sum_i N_i C_i$		42.430

Hv = 11.733 kJ/mol + 42.430 kJ/mol

= 54.163 kJ/mol

Target property 2

Toxicity (LC_{50})

Property prediction model

Connectivity index of order two (Koch, 1982)

$$\log LC_{50} = 4.865 - 0.899({}^{1}\chi^{v}) \qquad {}^{1}\chi = \frac{1}{2}\sum_{d=1}^{N} {}^{2}\alpha_d L_d$$

Example calculations

Table S6: Calculation for LC_{50} for 2-pentanol

Height 2 signatures	Number of occurrence	TI value
C1(C3(CCO))	1	$(1 \times 3)^{-0.5}$
C3(C2(CC)C1(C)O1(C))	1	$(3 \times 2)^{-0.5} + (3 \times 1)^{-0.5} + (3 \times 5)^{-0.5}$
O1(C3(CCO))	1	$(5 \times 3)^{-0.5}$
C2(C3(CCO)C2(CC))	1	$(2 \times 3)^{-0.5} + (2 \times 2)^{-0.5}$
C2(C2(CC)C1(C))	1	$(2 \times 2)^{-0.5} + (2 \times 1)^{-0.5}$
C1(C2(CC))	1	$(1 \times 2)^{-0.5}$
${}^{1}\chi$		2.451

log*LC*₅₀ = 4.865 – (0.899 × 2.451)

= 2.662

APPENDIX B: CASE STUDY IN CHAPTER 4

MATHEMATICAL FORMULATION

```
max=RON;

!RON;
RON=103.6+0.231*((ronc1*(x1))+(ronc2*(x2))+(ronc3*(x3))+(ronc4*
(x4)));
ronc1=-2.315;
ronc2=-8.448;
ronc3=-0.176;
ronc4=11.94;
@free(ronc1);@free(ronc2);@free(ronc3);@free(ronc4);

!Hv;
Hv=11.733+((hvc1*(x1))+(hvc2*(x2))+(hvc3*(x3))+(hvc4*(x4)));
hvc1=0.217;
hvc2=4.91;
hvc3=7.962;
hvc4=10.73;
@free(hvc1);@free(hvc2);@free(hvc3);@free(hvc4);

Lhv=25;
Uhv=55;
Hv>Lhv;
Hv<Uhv;

!Tb;
Tb=164.386+33.638*(tbc1*x1+tbc2*x2+tbc3*x3+tbc4*x4);
tbc1=0.8491;
tbc2=0.7141;
tbc3=0.2925;
tbc4=-0.0671;
@free(tbc1);@free(tbc2);@free(tbc3);@free(tbc4);

Ltb=3.85;
Utb=9.46;
Tf>Ltb;
Tf<Utb;

!Tig;
```

```
Tig=780.42+26.78*((tigc1*(x1))+(tigc2*(x2))+(tigc3*(x3))+(tigc4
*(x4)));
tigc1=-0.8516;
tigc2=-0.4207;
tigc3=0.0249;
tigc4=2.3226;
@free(tigc1);@free(tigc2);@free(tigc3);@free(tigc4);

Ltig=600;
Utig=800;
Tig>Ltig;
Tig<Utig;

!UFL;
UFL=18.14+3.4135*((uflc1*(x1))+(uflc2*(x2))+(uflc3*(x3))+(uflc4
*(x4)));
uflc1=-0.8394;
uflc2=-1.1219;
uflc3=-1.2598;
uflc4=-2.1941;
@free(uflc1);@free(uflc2);@free(uflc3);@free(uflc4);

Lufl=6;
Uufl=20;
UFL>Lufl;
UFL<Uufl;

!LFL;
LFL=18.14+3.4135*((lflc1*(x1))+(lflc2*(x2))+(lflc3*(x3))+(lflc4
*(x4)));
lflc1=-1.4407;
lflc2=-0.8736;
lflc3=-0.2925;
lflc4=0.2747;
@free(lflc1);@free(lflc2);@free(lflc3);@free(lflc4);

Llfl=1;
Ulfl=5;
LFL>Llfl;
LFL<Ulfl;
@free(Llfl);@free(LFL);


!Tf;
Tf=164.386+33.638*(tfc1*x1+tfc2*x2+tfc3*x3+tfc4*x4);
tfc1=0.5;
tfc2=0.35355;
tfc3=0.28868;
tfc4=0.25;
@free(tfc1);@free(tfc2);@free(tfc3);@free(tfc4);

Ltf=230;
Utf=350;
```

```
Tf>Ltf;
Tf<Utf;

!Integers constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);

!Positive constraints;
x1>0;x2>0;x3>0;x4>0;

!handshaking lemma;
(x1)+2*(x2)+3*(x3)+4*(x4)=2*(x1+x2+x3+x4-1);

end
```

RESULTS

```
Global optimal solution found.
Objective value:                              103.6358
Objective bound:                              103.6358
Infeasibilities:                              0.000000
Extended solver steps:                               0
Total solver iterations:                             8

Model Class:                                      MILP

Total variables:                    11
Nonlinear variables:                 0
Integer variables:                   4

Total constraints:                  25
Nonlinear constraints:               0

Total nonzeros:                     55
Nonlinear nonzeros:                  0

Variable      Value               Reduced Cost
RON           103.6358            0.000000
RONC1         -2.315000           0.000000
X1            8.000000            0.1967196
RONC2         -8.448000           0.000000
X2            0.000000            0.3281817
RONC3         -0.1760000          0.000000
X3            0.000000            -0.5751900E-02
RONC4         11.94000            0.000000
X4            3.000000            -0.5365206
HV            45.65900            0.000000
HVC1          0.2170000           0.000000
HVC2          4.910000            0.000000
HVC3          7.962000            0.000000
HVC4          10.73000            0.000000
LHV           25.00000            0.000000
UHV           55.00000            0.000000
TB            6.591500            0.000000
TBC1          0.8491000           0.000000
TBC2          0.7141000           0.000000
TBC3          0.2925000           0.000000
TBC4          -0.6710000E-01      0.000000
LTB           3.850000            0.000000
UTB           9.460000            0.000000
TIG           784.5709            0.000000
TIGC1         -0.8516000          0.000000
```

```
TIGC2        -1.420700           0.000000
TIGC3        0.2490000E-01       0.000000
TIGC4        2.322600            0.000000
LTIG         600.0000            0.000000
UTIG         800.0000            0.000000
UFL          18.66909            0.000000
UFLC1        -0.8394000          0.000000
UFLC2        -1.121900           0.000000
UFLC3        -1.259800           0.000000
UFLC4        -2.194100           0.000000
LUFL         6.000000            0.000000
UUFL         20.00000            0.000000
LFL          4.299442            0.000000
LFLC1        -1.440700           0.000000
LFLC2        -0.8736000          0.000000
LFLC3        -0.2925000          0.000000
LFLC4        0.2747000           0.000000
LLFL         1.000000            0.000000
ULFL         5.000000            0.000000
TF           324.1665            0.000000
TFC1         0.5000000           0.000000
TFC2         0.3535500           0.000000
TFC3         0.2886800           0.000000
TFC4         0.2500000           0.000000
LTF          230.0000            0.000000
UTF          350.0000            0.000000
```

APPENDIX C: CASE STUDY IN CHAPTER 5

MATHEMATICAL FORMULATION

STAGE 1: DESIGN OF OPTIMAL PRODUCT

```
max=RON;

!RON;
RON=103.6+0.231*((ronc1*(x1))+(ronc2*(x2))+(ronc3*(x3))+(ronc4*
(x4)));
ronc1=-2.315;
ronc2=-8.448;
ronc3=-0.176;
ronc4=11.94;
@free(ronc1);@free(ronc2);@free(ronc3);@free(ronc4);


!dynamic viscosity;
DV=((dvc1*(x1))+(dvc2*(x2))+(dvc3*(x3))+(dvc4*(x4)));
dvc1=-1.0278;
dvc2=0.2125;
dvc3=1.318;
dvc4=2.8147;
@free(dvc1);@free(dvc2);@free(dvc3);@free(dvc4);@free(DV);@free
(Ldv);@free(Udv);

Ldv=-2.3026;!ln(0.1);
Udv=1.0986;!ln(3);
DV>Ldv;
DV<Udv;

!Hv;
Hv=11.733+((hc1*(x1))+(hv2*(x2))+(hv3*(x3))+(hv4*(x4)));
hv1=0.217;hv2=4.91;hv3=7.962;hv4=10.73;
@free(hv1);@free(hv2);@free(hv3);@free(hv4);
lhv=25;
uhv=55;
Hv>lhv;
Hv<uhv;

!Tf;
```

```
Tf=164.386+33.638*(tfc1*x1+tfc2*x2+tfc3*x3+tfc4*x4);
tfc1=0.5;
tfc2=0.35355;
tfc3=0.28868;
tfc4=0.25;
@free(tfc1);@free(tfc2);@free(tfc3);@free(tfc4);

Ltf=230;
Utf=350;
Tf>Ltf;
Tf<Utf;

!LC50;
LC=4.115-0.762*(lcc1*x1+lcc2*x2+lcc3*x3+lcc4*x4);
lcc1=0.5;
lcc2=0.35355;
lcc3=0.28868;
lcc4=0.25;
@free(lcc1);@free(lcc2);@free(lcc3);@free(lcc4);@free(LC);@free
(Llc);@free(Ulc);

Llc=1;!log10(10);
Ulc=2;!log10(100);
LC>Llc;
LC<Ulc;

!Integers constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);

!Positive constraints;
x1>0;x2>0;x3>0;x4>0;

!handshaking lemma;
(x1)+2*(x2)+3*(x3)+4*(x4)=2*(x1+x2+x3+x4-1);

end
```

STAGE 2: SELECTION OF OPTIMAL CONVERTION PATHWAYS

```
!(use this for maximum product yield);
Max   =     octane;
!(use this for maximum economic potential);
Max   =     Profit;

!Biomass Feedstock Flowrate Input (tonne/y);
B     =     50000;

! Biomass Composition Input;
XL    =     0.29;
XC    =     0.39;
XHC   =     0.22;

! Conversion (or yield if there is no selectivity in the
process);
R1    =     0.98;
R2    =     0.492;
R3    =     0.79; !Separation efficiency;
R4    =     0.97; !Separation efficiency;
R5    =     0.909;
R6    =     0.409;
R7    =     0.619;
R8    =     0.41;
R9    =     0.982;
R10   =     0.99;
R11   =     0.60;
R12   =     0.94;
R13   =     0.90;
R14   =     0.40;
R15   =     1.00;
R16   =     0.40;
R17   =     0.75;
R18   =     0.251;
R19   =     0.246;
R20   =     0.288;
R21   =     0.99;
R22   =     0.67;
R23   =     0.59;
R24   =     0.64;
R25   =     0.62;
R26   =     0.99;

!Annualised capital cost (per annual tonne);
AGCF1  =    19.64;
AGCF2  =    13.90;
```

```
AGCF3  =    40.68;
AGCF4  =    40.68;
AGCF5  =    63.46;
AGCF6  =    27.62;
AGCF7  =    40.62;
AGCF8  =    31.43;
AGCF9  =    30.22;
AGCF10 =    43.52;
AGCF11 =    45.45;
AGCF12 =    62.86;
AGCF13 =    86.43;
AGCF14 =    26.23;
AGCF15 =    15.11;
AGCF16 =    193.41;
AGCF17 =    181.93;
AGCF18 =    38.56;
AGCF19 =    41.10;
AGCF20 =    40.19;
AGCF21 =    40.68;
AGCF22 =    40.50;
AGCF23 =    37.47;
AGCF24 =    34.45;
AGCF25 =    45.94;
AGCF26 =    169.48;

!Operating cost (per annual tonne);
AGOF1  =    11.30;
AGOF2  =    7.97;
AGOF3  =    23.30;
AGOF4  =    23.30;
AGOF5  =    36.40;
AGOF6  =    15.80;
AGOF7  =    22.00;
AGOF8  =    18.00;
AGOF9  =    17.30;
AGOF10 =    24.90;
AGOF11 =    26.00;
AGOF12 =    36.00;
AGOF13 =    55.00;
AGOF14 =    15.00;
AGOF15 =    8.66;
AGOF16 =    111.00;
AGOF17 =    104.00;
AGOF18 =    22.10;
AGOF19 =    23.60;
AGOF20 =    23.00;
AGOF21 =    23.30;
AGOF22 =    23.20;
AGOF23 =    21.50;
AGOF24 =    19.70;
AGOF25 =    26.30;
AGOF26 =    98.20;
```

```
!Price (USD) of ton of feedstock or Products;
Gbiomass          = 170;
Gethane           = 424;
Gpropane          = 670;
Gbutane           = 900;
Gpentane          = 1200;
Ghexane           = 1600;
Gheptane          = 1800;
Goctane           = 2000;
Gnonane           = 2510;
Gdecane           = 2750;
Gmethanol         = 450;
Gethanol          = 770;
Gpropanol         = 950;
Gbutanol          = 1120;
Gpentanol         = 1770;
Gpentanediol      = 3000;

!Flowrates (Into each layer);
Tlcs1       =     (XC+XHC)*R1*F1+(XC+XHC)*R2*F2;
Tlcs2       =     XL*F1+XL*F2;
Tlcs        =     Tlcs1+Tlcs2;
Tlignin     =     R3*F3;
Tsugar      =     R4*F4;
Thmf        =     R5*F5;
Tf          =     R6*F6;
Tthfa       =     R9*F9;
Ts          =     R12*F12+R13*F13+R15*F15;
Tm          =     R14*F14;

Talc1       =     R7*F7+R8*F8;
Talc2       =     R10*F10+R11*F11;
Talc3       =     R18*F18+R19*F19+R20*F20;
Talc        =     Talc1+Talc2+Talc3;

Talk1       =     R16*F16+R17*F17;
Talk2       =     R22*F22+R23*F23+R24*F24;
Talk3       =     R25*F25;
Talk        =     Talk1+Talk2+Talk3;
Talk        =     F26;

Tac         =     R21*F21;

!Flowrates (Out from each layer);
B           =     F1+F2+F12+F13+F14;
F1          <=    B;
F2          <=    B;
F12   <=    B;
F13   <=    B;
F14         <=    B;
Tlcs2       =     F3;
F3          <=    Tlcs2;
Tlcs1       =     F4;
```

```
F4          <=    Tlcs1;
Tsugar      =     F5+F6+F7+F8;
F5          <=    Tsugar;
F6          <=    Tsugar;
F7          <=    Tsugar;
F8          <=    Tsugar;
Tf          =     F9;
F9          <=    Tf;
Tthfa       =     F10+F11;
F10         <=    Tthfa;
F11         <=    Tthfa;
Tm           =    F15;
F15         <=    Tm;
Ts          =     F16+F17+F18+F19+F20;
F16         <=    Ts;
F17         <=    Ts;
F18         <=    Ts;
F19         <=    Ts;
F20         <=    Ts;
Talc         =    F21+F22+F23+F24;
F21         <=    Talc;
F22         <=    Talc;
F23         <=    Talc;
F24         <=    Talc;
Tac         =      F25;
F25         <=    Tac;

!Production rates of alkanes;
ethane      =
      R26*(R16*F16*0.16+R17*F17*0.23+R22*F22*0.103+R25*F25*0.21
      3);
propane     =    R26*(R16*F16*0.16+R17*F17*0.23+R23*F23*0.288);
butane      =    R26*(R16*F16*0.16+R17*F17*0.23+R23*F23*0.373);
pentane     =    R26*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.152);
hexane      =    R26*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.055);
heptane     =    R26*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.056);
octane      =    R26*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.042);
nonane      =     R26*(R16*F16*0.27+R17*F17*0.19);
decane      =     R26*(R16*F16*0.26+R17*F17*0.097);
Talk        >=    ethane+propane+butane+pentane+hexane+heptane+
      octane+nonane+decane;

!Production rates of alcohols;
methanol          =
      R18*F18*0.026+R19*F19*0.039+R20*F20*0.207;
ethanol           =
      R7*F7+R8*F8+R18*F18*0.614+R19*F19*0.561+R20*F20
      *0.238;
propanol          =     R20*F20*0.141;
butanol           =     R20*F20*0.075;
pentanol          =     R10*F10*0.04+R11*F11*0.22;
pentanediol       =     R10*F10*0.95+R11*F11*0.51;
Talc        >=    methanol+ethanol+propanol+butanol+pentanol+
```

```
      pentanediol;

!Revenue of alkanes;
EPethane    =     Gethane*ethane;
EPpropane =       Gpropane*propane;
EPbutane    =     Gbutane*butane;
EPpentane   =     Gpentane*pentane;
EPhexane    =     Ghexane*hexane;
EPheptane   =     Gheptane*heptane;
EPoctane  =       Goctane*octane;
EPnonane  =       Gnonane*nonane;
EPdecane  =       Gdecane*decane;
EPalk     =
      EPethane+EPpropane+EPbutane+EPpentane+EPhexane+
      EPheptane+EPoctane+EPnonane+EPdecane;

!Revenue of alcohols;
EPmethanol        =     Gmethanol*methanol;
EPethanol         =     Gethanol*ethanol;
EPpropanol        =     Gpropanol*propanol;
EPbutanol         =     Gbutanol*butanol;
EPpentanol        =     Gpentanol*pentanol;
EPpentanediol     =     Gpentanediol*pentanediol;
EPalc             =
      EPmethanol+EPethanol+EPpropanol+EPbutanol+
      EPpentanol+EPpentanediol;

!Total revenue;
Revenue     =     EPalc+EPalk;

!Cost for biomass;
CBiomass    =     B*Gbiomass;

!Total capital cost;
TACC     =   F1*AGCF1+F2*AGCF2+F3*AGCF3+F4*AGCF4+F5*AGCF5+
        F6*AGCF6+F7*AGCF7+F8*AGCF8+F9*AGCF9+
        F10*AGCF10+F11*AGCF11+F12*AGCF12+F13*AGCF13+
        F14*AGCF14+F15*AGCF15+
        F16*AGCF16+F17*AGCF17+F18*AGCF18+F19*AGCF19+
        F20*AGCF20+
        F21*AGCF21+F22*AGCF22+F23*AGCF23+F24*AGCF24+
        F25*AGCF25+F26*AGCF26;


!Total operating cost;
TAOC      =  F1*AGOF1+F2*AGOF2+F3*AGOF3+F4*AGOF4+F5*AGOF5+
        F6*AGOF6+F7*AGOF7+F8*AGOF8+F9*AGOF9+
        F10*AGOF10+F11*AGOF11+F12*AGOF12+F13*AGOF13+
        F14*AGOF14+F15*AGOF15+F16*AGOF16+F17*AGOF17+
        F18*AGOF18+F19*AGOF19+F20*AGOF20+F21*AGOF21+
        F22*AGOF22+F23*AGOF23+F24*AGOF24+F25*AGOF25+
        F26*AGOF26;
```

```
!Profit;
Profit   = Revenue-CBiomass-TACC-TAOC;
@free(profit);

end
```

RESULTS

STAGE 1: DESIGN OF OPTIMAL PRODUCT

```
Global optimal solution found.
Objective value:                                 105.9077
Objective bound:                                 105.9077
Infeasibilities:                                 0.000000
Extended solver steps:                                  0
Total solver iterations:                                4

Model Class:                                         MILP

Total variables:                    10
Nonlinear variables:                 0
Integer variables:                   4

Total constraints:                  21
Nonlinear constraints:               0

Total nonzeros:                     47
Nonlinear nonzeros:                  0

Variable     Value               Reduced Cost
R            105.9077            0.000000
RON1         -2.315000           0.000000
X1           6.000000            0.5347650
RON2         -8.448000           0.000000
X2           0.000000            1.951488
RON3         -0.1760000          0.000000
X3           0.000000            0.4065600E-01
RON4         11.94000            0.000000
X4           2.000000            -2.758140
DV           -0.5374000          0.000000
DVC1         -1.027800           0.000000
DVC2         0.2125000           0.000000
DVC3         1.318000            0.000000
DVC4         2.814700            0.000000
LDV          -2.302600           0.000000
UDV          1.098600            0.000000
HV           34.49500            0.000000
HV1          0.2170000           0.000000
HV2          4.910000            0.000000
HV3          7.962000            0.000000
HV4          10.73000            0.000000
LHV          25.00000            0.000000
```

```
UHV          55.00000           0.000000
TF           282.1190           0.000000
TF1          0.5000000          0.000000
TF2          0.3535500          0.000000
TF3          0.2886800          0.000000
TF4          0.2500000          0.000000
LTF          230.0000           0.000000
UTF          350.0000           0.000000
LC           1.448000           0.000000
LC1          0.5000000          0.000000
LC2          0.3535500          0.000000
LC3          0.2886800          0.000000
LC4          0.2500000          0.000000
LLC          1.000000           0.000000
ULC          2.000000           0.000000
```

STAGE 2 SCENARIO 1: SELECTION OF OPTIMAL CONVERSION PATHWAYS WITH MAXIMUM PRODUCT YIELD

```
Global optimal solution found.
Objective value:                                  1979.752
Infeasibilities:                                  0.000000
Total solver iterations:                                10

Model Class:                                            LP

Total variables:                     81
Nonlinear variables:                  0
Integer variables:                    0

Total constraints:                   94
Nonlinear constraints:                0

Total nonzeros:                     316
Nonlinear nonzeros:                   0

Variable     Value               Reduced Cost
OCTANE       1979.752            0.000000
B            50000.00            0.000000
XL           0.2900000           0.000000
XC           0.3900000           0.000000
XHC          0.2200000           0.000000
R1           0.9800000           0.000000
R2           0.4920000           0.000000
R3           0.7900000           0.000000
R4           0.9700000           0.000000
R5           0.9090000           0.000000
R6           0.4090000           0.000000
R7           0.6190000           0.000000
R8           0.4100000           0.000000
R9           0.9820000           0.000000
R10          0.9900000           0.000000
R11          0.6000000           0.000000
R12          0.9400000           0.000000
R13          0.9000000           0.000000
R14          0.4000000           0.000000
R15          1.000000            0.000000
R16          0.4000000           0.000000
R17          0.7500000           0.000000
R18          0.2510000           0.000000
R19          0.2460000           0.000000
R20          0.2880000           0.000000
```

```
R21          0.9900000            0.000000
R22          0.6700000            0.000000
R23          0.5900000            0.000000
R24          0.6400000            0.000000
R25          0.6200000            0.000000
R26          0.9900000            0.000000
AGCF1        19.64000             0.000000
AGCF2        13.90000             0.000000
AGCF3        40.68000             0.000000
AGCF4        40.68000             0.000000
AGCF5        63.46000             0.000000
AGCF6        27.62000             0.000000
AGCF7        40.62000             0.000000
AGCF8        31.43000             0.000000
AGCF9        30.22000             0.000000
AGCF10       43.52000             0.000000
AGCF11       45.45000             0.000000
AGCF12       62.86000             0.000000
AGCF13       86.43000             0.000000
AGCF14       26.23000             0.000000
AGCF15       15.11000             0.000000
AGCF16       193.4100             0.000000
AGCF17       181.9300             0.000000
AGCF18       38.56000             0.000000
AGCF19       41.10000             0.000000
AGCF20       40.19000             0.000000
AGCF21       40.68000             0.000000
AGCF22       40.50000             0.000000
AGCF23       37.47000             0.000000
AGCF24       34.45000             0.000000
AGCF25       45.94000             0.000000
AGCF26       169.4800             0.000000
AGOF1        11.30000             0.000000
AGOF2        7.970000             0.000000
AGOF3        23.30000             0.000000
AGOF4        23.30000             0.000000
AGOF5        36.40000             0.000000
AGOF6        15.80000             0.000000
AGOF7        22.00000             0.000000
AGOF8        18.00000             0.000000
AGOF9        17.30000             0.000000
AGOF10       24.90000             0.000000
AGOF11       26.00000             0.000000
AGOF12       36.00000             0.000000
AGOF13       55.00000             0.000000
AGOF14       15.00000             0.000000
AGOF15       8.660000             0.000000
AGOF16       111.0000             0.000000
AGOF17       104.0000             0.000000
AGOF18       22.10000             0.000000
AGOF19       23.60000             0.000000
AGOF20       23.00000             0.000000
AGOF21       23.30000             0.000000
```

```
AGOF22       23.20000           0.000000
AGOF23       21.50000           0.000000
AGOF24       19.70000           0.000000
AGOF25       26.30000           0.000000
AGOF26       98.20000           0.000000
GBIOMASS     170.0000           0.000000
GETHANE      424.0000           0.000000
GPROPANE     670.0000           0.000000
GBUTANE      900.0000           0.000000
GPENTANE     1200.000           0.000000
GHEXANE      1600.000           0.000000
GHEPTANE     1800.000           0.000000
GOCTANE      2000.000           0.000000
GNONANE      2510.000           0.000000
GDECANE      2750.000           0.000000
GMETHANOL    450.0000           0.000000
GETHANOL     770.0000           0.000000
GPROPANOL    950.0000           0.000000
GBUTANOL     1120.000           0.000000
GPENTANOL    1770.000           0.000000
GPENTANEDIOL 3000.000           0.000000
TLCS1        20965.40           0.000000
F1           35070.93           0.000000
F2           0.000000           0.1971671E-01
TLCS2        10170.57           0.000000
TLCS         31135.97           0.000000
TLIGNIN      8034.750           0.000000
F3           10170.57           0.000000
TSUGAR       20336.44           0.000000
F4           20965.40           0.000000
THMF         0.000000           0.000000
F5           0.000000           0.4522789E-01
TF           0.000000           0.000000
F6           0.000000           0.000000
TTHFA        0.000000           0.000000
F9           0.000000           0.000000
TS           14033.33           0.000000
F12          14929.07           0.000000
F13          0.000000           0.1684895E-02
F15          0.000000           0.000000
TM           0.000000           0.000000
F14          0.000000           0.2274608E-01
TALC1        12588.26           0.000000
F7           20336.44           0.000000
F8           0.000000           0.000000
TALC2        0.000000           0.000000
F10          0.000000           0.000000
F11          0.000000           0.000000
TALC3        0.000000           0.000000
F18          0.000000           0.1443409E-01
F19          0.000000           0.1498565E-01
F20          0.000000           0.1035255E-01
TALC         12588.26           0.000000
```

```
TALK1        10525.00            0.000000
F16          0.000000            0.1360582E-01
F17          14033.33            0.000000
TALK2        8434.131            0.000000
F22          12588.26            0.000000
F23          0.000000            0.7292711E-01
F24          0.000000            0.1793289E-02
TALK3        0.000000            0.000000
F25          0.000000            0.000000
TALK         18959.13            0.000000
F26          18959.13            0.000000
TAC          0.000000            0.000000
F21          0.000000            0.2150798E-01
ETHANE       3256.570            0.000000
PROPANE      2396.542            0.000000
BUTANE       2396.542            0.000000
PENTANE      1979.752            0.000000
HEXANE       1979.752            0.000000
HEPTANE      1979.752            0.000000
NONANE       1979.752            0.000000
DECANE       1010.715            0.000000
METHANOL     0.000000            0.000000
ETHANOL      12588.26            0.000000
PROPANOL     0.000000            0.000000
BUTANOL      0.000000            0.000000
PENTANOL     0.000000            0.000000
PENTANEDIOL  0.000000            0.000000
EPETHANE     1380786.            0.000000
EPPROPANE    1605683.            0.000000
EPBUTANE     2156887.            0.000000
EPPENTANE    2375702.            0.000000
EPHEXANE     3167603.            0.000000
EPHEPTANE    3563553.            0.000000
EPOCTANE     3959503.            0.000000
EPNONANE     4969177.            0.000000
EPDECANE     2779467.            0.000000
EPALK        0.2595836E+08       0.000000
EPMETHANOL   0.000000            0.000000
EPETHANOL    9692957.            0.000000
EPPROPANOL   0.000000            0.000000
EPBUTANOL    0.000000            0.000000
EPPENTANOL   0.000000            0.000000
EPPENTANEDIOL0.000000            0.000000
EPALC        9692957.            0.000000
REVENUE      0.3565132E+08       0.000000
CBIOMASS     8500000.            0.000000
TACC         9996012.            0.000000
TAOC         5719918.            0.000000
PROFIT       0.1143539E+08       0.000000
```

STAGE 2 SCENARIO 2: SELECTION OF OPTIMAL CONVERSION PATHWAYS WITH MAXIMUM ECONOMIC POTENTIAL

```
Global optimal solution found.
Objective value:                          0.2404042E+08
Infeasibilities:                               0.000000
Total solver iterations:                              7

Model Class:                                         LP

Total variables:                     81
Nonlinear variables:                  0
Integer variables:                    0

Total constraints:                   94
Nonlinear constraints:                0

Total nonzeros:                     316
Nonlinear nonzeros:                   0

Variable     Value              Reduced Cost
PROFIT       0.2404042E+08      0.000000
B            50000.00           0.000000
XL           0.2900000          0.000000
XC           0.3900000          0.000000
XHC          0.2200000          0.000000
R1           0.9800000          0.000000
R2           0.4920000          0.000000
R3           0.7900000          0.000000
R4           0.9700000          0.000000
R5           0.9090000          0.000000
R6           0.4090000          0.000000
R7           0.6190000          0.000000
R8           0.4100000          0.000000
R9           0.9820000          0.000000
R10          0.9900000          0.000000
R11          0.6000000          0.000000
R12          0.9400000          0.000000
R13          0.9000000          0.000000
R14          0.4000000          0.000000
R15          1.000000           0.000000
R16          0.4000000          0.000000
R17          0.7500000          0.000000
R18          0.2510000          0.000000
R19          0.2460000          0.000000
R20          0.2880000          0.000000
```

```
R21           0.9900000          0.000000
R22           0.6700000          0.000000
R23           0.5900000          0.000000
R24           0.6400000          0.000000
R25           0.6200000          0.000000
R26           0.9900000          0.000000
AGCF1         19.64000           0.000000
AGCF2         13.90000           0.000000
AGCF3         40.68000           0.000000
AGCF4         40.68000           0.000000
AGCF5         63.46000           0.000000
AGCF6         27.62000           0.000000
AGCF7         40.62000           0.000000
AGCF8         31.43000           0.000000
AGCF9         30.22000           0.000000
AGCF10        43.52000           0.000000
AGCF11        45.45000           0.000000
AGCF12        62.86000           0.000000
AGCF13        86.43000           0.000000
AGCF14        26.23000           0.000000
AGCF15        15.11000           0.000000
AGCF16        193.4100           0.000000
AGCF17        181.9300           0.000000
AGCF18        38.56000           0.000000
AGCF19        41.10000           0.000000
AGCF20        40.19000           0.000000
AGCF21        40.68000           0.000000
AGCF22        40.50000           0.000000
AGCF23        37.47000           0.000000
AGCF24        34.45000           0.000000
AGCF25        45.94000           0.000000
AGCF26        169.4800           0.000000
AGOF1         11.30000           0.000000
AGOF2         7.970000           0.000000
AGOF3         23.30000           0.000000
AGOF4         23.30000           0.000000
AGOF5         36.40000           0.000000
AGOF6         15.80000           0.000000
AGOF7         22.00000           0.000000
AGOF8         18.00000           0.000000
AGOF9         17.30000           0.000000
AGOF10        24.90000           0.000000
AGOF11        26.00000           0.000000
AGOF12        36.00000           0.000000
AGOF13        55.00000           0.000000
AGOF14        15.00000           0.000000
AGOF15        8.660000           0.000000
AGOF16        111.0000           0.000000
AGOF17        104.0000           0.000000
AGOF18        22.10000           0.000000
AGOF19        23.60000           0.000000
AGOF20        23.00000           0.000000
AGOF21        23.30000           0.000000
```

```
AGOF22        23.20000            0.000000
AGOF23        21.50000            0.000000
AGOF24        19.70000            0.000000
AGOF25        26.30000            0.000000
AGOF26        98.20000            0.000000
GBIOMASS      170.0000            0.000000
GETHANE       424.0000            0.000000
GPROPANE      670.0000            0.000000
GBUTANE       900.0000            0.000000
GPENTANE      1200.000            0.000000
GHEXANE       1600.000            0.000000
GHEPTANE      1800.000            0.000000
GOCTANE       2000.000            0.000000
GNONANE       2510.000            0.000000
GDECANE       2750.000            0.000000
GMETHANOL     450.0000            0.000000
GETHANOL      770.0000            0.000000
GPROPANOL     950.0000            0.000000
GBUTANOL      1120.000            0.000000
GPENTANOL     1770.000            0.000000
GPENTANEDIOL  3000.000            0.000000
TLCS1         24845.54            0.000000
F1            41561.63            0.000000
F2            0.000000            339.6521
TLCS2         12052.87            0.000000
TLCS          36898.42            0.000000
TLIGNIN       9521.770            0.000000
F3            12052.87            0.000000
TSUGAR        24100.18            0.000000
F4            24845.54            0.000000
THMF          0.000000            0.000000
F5            0.000000            1373.516
TF            9856.973            0.000000
F6            24100.18            0.000000
TTHFA         9679.547            0.000000
F9            9856.973            0.000000
TS            7932.064            0.000000
F12           8438.366            0.000000
F13           0.000000            74.47078
F15           0.000000            0.000000
TM            0.000000            0.000000
F14           0.000000            382.5385
TALC1         0.000000            0.000000
F7            0.000000            544.2183
F8            0.000000            798.4597
TALC2         9582.752            0.000000
F10           9679.547            0.000000
F11           0.000000            0.000000
TALC3         0.000000            0.000000
F18           0.000000            608.6714
F19           0.000000            626.2819
F20           0.000000            571.5759
TALC          9582.752            0.000000
```

```
TALK1        5949.048            0.000000
F16          0.000000            253.0004
F17          7932.064            0.000000
TALK2        6132.961            0.000000
F22          0.000000            122.1429
F23          0.000000            213.8343
F24          9582.752            0.000000
TALK3        0.000000            0.000000
F25          0.000000            0.000000
TALK         12082.01            0.000000
F26          12082.01            0.000000
TAC          0.000000            0.000000
F21          0.000000            270.2645
ETHANE       1354.598            0.000000
PROPANE      1354.598            0.000000
BUTANE       1354.598            0.000000
PENTANE      2041.904            0.000000
HEXANE       1452.956            0.000000
HEPTANE      1459.027            0.000000
OCTANE       1374.025            0.000000
NONANE       1119.016            0.000000
DECANE       571.2871            0.000000
METHANOL     0.000000            0.000000
ETHANOL      0.000000            0.000000
PROPANOL     0.000000            0.000000
BUTANOL      0.000000            0.000000
PENTANOL     383.3101            0.000000
PENTANEDIOL  9103.614            0.000000
EPETHANE     574349.7            0.000000
EPPROPANE    907580.9            0.000000
EPBUTANE     1219138.            0.000000
EPPENTANE    2450285.            0.000000
EPHEXANE     2324729.            0.000000
EPHEPTANE    2626249.            0.000000
EPOCTANE     2748049.            0.000000
EPNONANE     2808730.            0.000000
EPDECANE     1571040.            0.000000
EPALK        0.1723015E+08       0.000000
EPMETHANOL   0.000000            0.000000
EPETHANOL    0.000000            0.000000
EPPROPANOL   0.000000            0.000000
EPBUTANOL    0.000000            0.000000
EPPENTANOL   678458.8            0.000000
EPPENTANEDIOL0.2731084E+08       0.000000
EPALC        0.2798930E+08       0.000000
REVENUE      0.4521945E+08       0.000000
CBIOMASS     8500000.            0.000000
TACC         8053378.            0.000000
TAOC         4625658.            0.000000
```

APPENDIX D: CASE STUDY IN CHAPTER 6

MATHEMATICAL FORMULATION

BI-LEVEL OPTIMISATION APPCOACH

```
!use this to obtain maximum value;
max=koc;
!use this to obtain minimum value;
min=koc;

!Vp (annotated as A);
A=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10
+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x1
8+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x
26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*
x34+a35*x35+a36*x36;

a1=0.8491;a2=0.8491;a3=0.7141;a4=0.7141;a5=0.7141;
a6=0.7141;a7=0.7141;a8=0.7141;a9=0.7141;a10=0.7141;
a11=0.7141;a12=0.7141;a13=0.7141;a14=0.7141;
a15=0.7141;a16=0.7141;a17=0.7141;a18=2.7987;a19=0;
a20=0;a21=0;a22=0;a23=0;a24=0;a25=0;a26=1.3368;
a27=2.0509;a28=2.0509;a28=2.0509;a29=2.0509;
a30=2.0509;a31=0;a32=1.5596;a33=1.5596;a34=0.8491;
a35=0;a36=0.8491;

La=4.50;
Ua=12.00;
A>La;
A<Ua;

!Hv (annotated as B);
B=b1*x1+b2*x2+b3*x3+b4*x4+b5*x5+b6*x6+b7*x7+b8*x8+b9*x9+b10*x10
+b11*x11+b12*x12+b13*x13+b14*x14+b15*x15+b16*x16+b17*x17+b18*x1
8+b19*x19+b20*x20+b21*x21+b22*x22+b23*x23+b24*x24+b25*x25+b26*x
26+b27*x27+b28*x28+b29*x29+b30*x30+b31*x31+b32*x32+b33*x33+b34*
x34+b35*x35+b36*x36;

b1=0.217;b2=0.217;b3=4.91;b4=4.91;b5=4.91;b6=4.91;
b7=4.91;b8=4.91;b9=4.91;b10=4.91;b11=4.91;b12=4.91;
b13=4.91;b14=4.91;b15=4.91;b16=4.91;b17=4.91;
```

```
b18=15.432;b19=0;b20=0;b21=0;b22=0;b23=0;b24=0;
b25=0;b26=9.997;b27=14.907;b28=14.907;b29=14.907;
b30=14.907;b31=0;b32=4.031;b33=4.031;b34=0.217;
b35=0;b36=0.217;

Lb=16.81;
Ub=53.46;
B>Lb;
B<Ub;

!Vm (annotated as C);
C=c1*x1+c2*x2+c3*x3+c4*x4+c5*x5+c6*x6+c7*x7+c8*x8+c9*x9+c10*x10
+c11*x11+c12*x12+c13*x13+c14*x14+c15*x15+c16*x16+c17*x17+c18*x1
8+c19*x19+c20*x20+c21*x21+c22*x22+c23*x23+c24*x24+c25*x25+c26*x
26+c27*x27+c28*x28+c29*x29+c30*x30+c31*x31+c32*x32+c33*x33+c34*
x34+c35*x35+c36*x36;

c1=0.354;c2=0.417;c3=0.25;c4=0.264;c5=0.278;
c6=0.604;c7=0.617;c8=0.5;c9=0.514;c10=0.506;
c11=0.454;c12=0.613;c13=0.528;c14=0.631;c15=0.454;
c16=0.558;c17=0.566;c18=0.256;c19=0.278;c20=0.65;
c21=0.482;c22=0.541;c23=0.68;c24=0.577;c25=0.363;
c26=0.278;c27=0.694;c28=0.556;c29=0.5;c30=0.612;
c31=0.204;c32=0.289;c33=0.299;c34=0.417;c35=0.223;
c36=0.373;

Lc=0.89;
Uc=5.50;
C>Lc;
C<Uc;




!TLC (annotated as D);
D=d1*x1+d2*x2+d3*x3+d4*x4+d5*x5+d6*x6+d7*x7+d8*x8+d9*x9+d10*x10
+d11*x11+d12*x12+d13*x13+d14*x14+d15*x15+d16*x16+d17*x17+d18*x1
8+d19*x19+d20*x20+d21*x21+d22*x22+d23*x23+d24*x24+d25*x25-
d26*x26-d27*x27-d28*x28-d29*x29-
d30*x30+d31*x31+d32*x32+d33*x33+d34*x34+d35*x35+d36*x36;

d1=0.25;d2=0.1443;d3=0.1768;d4=0.1768;d5=0.1021;
d6=0.4268;d7=0.4268;d8=0.3536;d9=0.3536;d10=0.3536;
d11=0.3211;d12=0.3211;d13=0.2788;d14=0.3521;d15=0;
d16=0.3211;d17=0.2464;d18=0.1768;d19=0.1021;
d20=0.3521;d21=0.2464;d22=0.2788;d23=0.3211;
d24=0.2464;d25=0.1443;d26=0.1021;d27=0.2464;
d28=0.2041;d29=0.1854;d30=0.1854;d31=0.1443;
d32=0.1443;d33=0.1443;d34=0.1443;d35=0.0833;d36=0.25;


Ud=2.31;
```

```
D<Ud;

!koc;
koc=0.53*(e1*x1+e2*x2+e3*x3+e4*x4+e5*x5+e6*x6+e7*x7+e8*x8+e9*x9
+e10*x10+e11*x11+e12*x12+e13*x13+e14*x14+e15*x15+e16*x16+e17*x1
7+e18*x18+e19*x19+e20*x20+e21*x21+e22*x22+e23*x23+e24*x24+e25*x
25+e26*x26+e27*x27+e28*x28+e29*x29+e30*x30+e31*x31+e32*x32+e33*
x33+e34*x34+e35*x35+e36*x36)-1.25*
(f1*x1+f2*x2+f3*x3+f4*x4+f5*x5+f6*x6+f7*x7+f8*x8+f9*x9+f10*x10+
f11*x11+f12*x12+f13*x13+f14*x14+f15*x15+f16*x16+f17*x17+f18*x18
+f19*x19+f20*x20+f21*x21+f22*x22+f23*x23+f24*x24+f25*x25+f26*x2
6+f27*x27+f28*x28+f29*x29+f30*x30+f31*x31+f32*x32+f33*x33+f34*x
34+f35*x35+f36*x36)-
0.72*(g1*x1+g2*x2+g3*x3+g4*x4+g5*x5+g6*x6+g7*x7+g8*x8+g9*x9+g10
*x10+g11*x11+g12*x12+g13*x13+g14*x14+g15*x15+g16*x16+g17*x17+g1
8*x18+g19*x19+g20*x20+g21*x21+g22*x22+g23*x23+g24*x24+g25*x25+g
26*x26+g27*x27+g28*x28+g29*x29+g30*x30+g31*x31+g32*x32+g33*x33+
g34*x34+g35*x35+g36*x36);



!values height 1 CI simple degree (annotated as e);
e1=0.3536;e2=0.3536;e3=0.6036;e4=0.6036;e5=0.7071;e6=0.5;e7=0.5
;e8=0.5;e9=0.5;e10=0.5;
e11=0.5;e12=0.5;e13=0.5;e14=0.5;e15=0.5;e16=0.5;e17=0.5;e18=0.4
541;e19=0.4979;e20=0.3943;e21=0.3943;e22=0.3943;e23=0.3943;e24=
0.3943;e25=0.2041;e26=0.3485;e27=0.2887;e28=0.2887;e29=0.2887;e
30=0.2887;e31=0.6036;e32=0.3536;e33=0.3536;e34=0.7071;
e35=0.4979;e36=0.3536;

!values height 1 CI delta X (annotated as f);
f1=0;f2=0;f3=0;f4=0;f5=0;f6=0;f7=0;f8=0;f9=0;f10=0;f11=0;f12=0;
f13=0;f14=0;f15=0.0459;f16=0.0459;f17=0.0459;f18=0.1494;f19=0.1
057;f20=0.1057;f21=0.1057;f22=0.1057;f23=0.1057;f24=0.1515;f25=
0.1494;f26=0.2551;f27=0.2113;f28=0.2113;f29=0.2113;f30=0.2378;f
31=0.1953;f32=0.1494;f33=0.1494;f34=0.1494;f35=0.2816;f36=0;

!values height 0 CI delta X (annotated as g);
g1=0;g2=0;g3=0;g4=0;g5=0;g6=0;g7=0;g8=0;g9=0;g10=0;g11=0;g12=0;
g13=0;g14=0;g15=.0;g16=0;g17=0;g18=0;g19=0;g20=0;g21=0;g22=0;g2
3=0;g24=0;g25=0.4227;g26=0.2989;g27=0.2989;g28=0.2989;g29=0.298
9;g30=0.2989;g31=0.1298;g32=0.2929;g33=0.2929;g34=0;g35=0.1298;
g36=0;

!Structural Constraints;
x1=x3+x4;
x2=x19;
x3=x6+x7;
x4=x14;
x5=x36;
x9=x13;
x10=x12;
x11=x16;
```

```
x12=x18;
x13+x14=x22+x23;
x17=x31;
x17=x21;
x26=x34;
x18=x25;
x19=x27;
x23=x26;
x26=x34;
x20=x5;
x30=x35;
x20+x21+x22=x27+2*x28+x29;
x31=x32;
x16=x31;
x15=0;
x24=0;
x29=0;
x33=0;
x35=0;
x6+2*x8+x9+x10+x11=2*h1;
2*x8<x6+x8+x9+x10+x11;
2*x28<x27+x28+x29;

!Handshaking lemma;
(x1+x2+x25+x34+x36)+2*(x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14
+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x26+x27+x28+x29+x30+x3
2+x33)+3*(x31+x35)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+
x14+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29
+x30+x31+x32+x33+x34+x35+x36+0.5*(x31+x32+x33+x35)-1)*2;

!Integer constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x13);@GIN(
x14);@GIN(x15);@GIN(x16);@GIN(x17);@GIN(x18);@GIN(x19);@GIN(x20
);@GIN(x21);@GIN(x22);@GIN(x23);@GIN(x24);@GIN(x25);@GIN(x26);@
GIN(x27);@GIN(x28);@GIN(x29);@GIN(x30);@GIN(x31);@GIN(x32);@GIN
(x33);@GIN(x34); @GIN(x35);@GIN(x36);@GIN(h1);

!Positive value constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;x33>0;
x34>0;x35>0;x36>0;

!Total number of signatures equation;
k=x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x15+x16+x17+x1
8+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x31+x32+x33+x
34+x35+x36;

end
```

MAX-MIN AGGREGATION APPROACH

```
max=lamda;

lamda<=lamda1;
lamda<=lamda2;
lamda<=lamda3;

!Vp (annotated as A);
A=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10
+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x1
8+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x
26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*
x34+a35*x35+a36*x36;

a1=0.8491;a2=0.8491;a3=0.7141;a4=0.7141;a5=0.7141;
a6=0.7141;a7=0.7141;a8=0.7141;a9=0.7141;a10=0.7141;
a11=0.7141;a12=0.7141;a13=0.7141;a14=0.7141;
a15=0.7141;a16=0.7141;a17=0.7141;a18=2.7987;a19=0;
a20=0;a21=0;a22=0;a23=0;a24=0;a25=0;a26=1.3368;
a27=2.0509;a28=2.0509;a28=2.0509;a29=2.0509;
a30=2.0509;a31=0;a32=1.5596;a33=1.5596;a34=0.8491;
a35=0;a36=0.8491;

La=4.50;
Ua=12.00;
A>La;
A<Ua;

lamda1=(A-La)/(Ua-La);

!Hv (annotated as B);
B=b1*x1+b2*x2+b3*x3+b4*x4+b5*x5+b6*x6+b7*x7+b8*x8+b9*x9+b10*x10
+b11*x11+b12*x12+b13*x13+b14*x14+b15*x15+b16*x16+b17*x17+b18*x1
8+b19*x19+b20*x20+b21*x21+b22*x22+b23*x23+b24*x24+b25*x25+b26*x
26+b27*x27+b28*x28+b29*x29+b30*x30+b31*x31+b32*x32+b33*x33+b34*
x34+b35*x35+b36*x36;

b1=0.217;b2=0.217;b3=4.91;b4=4.91;b5=4.91;b6=4.91;
b7=4.91;b8=4.91;b9=4.91;b10=4.91;b11=4.91;b12=4.91;
b13=4.91;b14=4.91;b15=4.91;b16=4.91;b17=4.91;
b18=15.432;b19=0;b20=0;b21=0;b22=0;b23=0;b24=0;
b25=0;b26=9.997;b27=14.907;b28=14.907;b29=14.907;
b30=14.907;b31=0;b32=4.031;b33=4.031;b34=0.217;
b35=0;b36=0.217;

Lb=16.81;
```

```
Ub=53.46;
B>Lb;
B<Ub;

!Vm (annotated as C);
C=c1*x1+c2*x2+c3*x3+c4*x4+c5*x5+c6*x6+c7*x7+c8*x8+c9*x9+c10*x10
+c11*x11+c12*x12+c13*x13+c14*x14+c15*x15+c16*x16+c17*x17+c18*x1
8+c19*x19+c20*x20+c21*x21+c22*x22+c23*x23+c24*x24+c25*x25+c26*x
26+c27*x27+c28*x28+c29*x29+c30*x30+c31*x31+c32*x32+c33*x33+c34*
x34+c35*x35+c36*x36;

c1=0.354;c2=0.417;c3=0.25;c4=0.264;c5=0.278;
c6=0.604;c7=0.617;c8=0.5;c9=0.514;c10=0.506;
c11=0.454;c12=0.613;c13=0.528;c14=0.631;c15=0.454;
c16=0.558;c17=0.566;c18=0.256;c19=0.278;c20=0.65;
c21=0.482;c22=0.541;c23=0.68;c24=0.577;c25=0.363;
c26=0.278;c27=0.694;c28=0.556;c29=0.5;c30=0.612;
c31=0.204;c32=0.289;c33=0.299;c34=0.417;c35=0.223;
c36=0.373;

Lc=0.89;
Uc=5.50;
C>Lc;
C<Uc;

lamda2=(Uc-C)/(Uc-Lc);

!TLC (annotated as D);
D=d1*x1+d2*x2+d3*x3+d4*x4+d5*x5+d6*x6+d7*x7+d8*x8+d9*x9+d10*x10
+d11*x11+d12*x12+d13*x13+d14*x14+d15*x15+d16*x16+d17*x17+d18*x1
8+d19*x19+d20*x20+d21*x21+d22*x22+d23*x23+d24*x24+d25*x25-
d26*x26-d27*x27-d28*x28-d29*x29-
d30*x30+d31*x31+d32*x32+d33*x33+d34*x34+d35*x35+d36*x36;

d1=0.25;d2=0.1443;d3=0.1768;d4=0.1768;d5=0.1021;
d6=0.4268;d7=0.4268;d8=0.3536;d9=0.3536;d10=0.3536;
d11=0.3211;d12=0.3211;d13=0.2788;d14=0.3521;d15=0;
d16=0.3211;d17=0.2464;d18=0.1768;d19=0.1021;
d20=0.3521;d21=0.2464;d22=0.2788;d23=0.3211;
d24=0.2464;d25=0.1443;d26=0.1021;d27=0.2464;
d28=0.2041;d29=0.1854;d30=0.1854;d31=0.1443;
d32=0.1443;d33=0.1443;d34=0.1443;d35=0.0833;d36=0.25;

Ud=2.31;
D<Ud;

!koc;
koc=0.53*(e1*x1+e2*x2+e3*x3+e4*x4+e5*x5+e6*x6+e7*x7+e8*x8+e9*x9
+e10*x10+e11*x11+e12*x12+e13*x13+e14*x14+e15*x15+e16*x16+e17*x1
7+e18*x18+e19*x19+e20*x20+e21*x21+e22*x22+e23*x23+e24*x24+e25*x
25+e26*x26+e27*x27+e28*x28+e29*x29+e30*x30+e31*x31+e32*x32+e33*
x33+e34*x34+e35*x35+e36*x36)-1.25*
```

```
(f1*x1+f2*x2+f3*x3+f4*x4+f5*x5+f6*x6+f7*x7+f8*x8+f9*x9+f10*x10+
f11*x11+f12*x12+f13*x13+f14*x14+f15*x15+f16*x16+f17*x17+f18*x18
+f19*x19+f20*x20+f21*x21+f22*x22+f23*x23+f24*x24+f25*x25+f26*x2
6+f27*x27+f28*x28+f29*x29+f30*x30+f31*x31+f32*x32+f33*x33+f34*x
34+f35*x35+f36*x36)-
0.72*(g1*x1+g2*x2+g3*x3+g4*x4+g5*x5+g6*x6+g7*x7+g8*x8+g9*x9+g10
*x10+g11*x11+g12*x12+g13*x13+g14*x14+g15*x15+g16*x16+g17*x17+g1
8*x18+g19*x19+g20*x20+g21*x21+g22*x22+g23*x23+g24*x24+g25*x25+g
26*x26+g27*x27+g28*x28+g29*x29+g30*x30+g31*x31+g32*x32+g33*x33+
g34*x34+g35*x35+g36*x36);

!values height 1 CI simple degree (annotated as e);
e1=0.3536;e2=0.3536;e3=0.6036;e4=0.6036;e5=0.7071;e6=0.5;e7=0.5
;e8=0.5;e9=0.5;e10=0.5;
e11=0.5;e12=0.5;e13=0.5;e14=0.5;e15=0.5;e16=0.5;e17=0.5;e18=0.4
541;e19=0.4979;e20=0.3943;e21=0.3943;e22=0.3943;e23=0.3943;e24=
0.3943;e25=0.2041;e26=0.3485;e27=0.2887;e28=0.2887;e29=0.2887;e
30=0.2887;e31=0.6036;e32=0.3536;e33=0.3536;e34=0.7071;
e35=0.4979;e36=0.3536;

!values height 1 CI delta X (annotated as f);
f1=0;f2=0;f3=0;f4=0;f5=0;f6=0;f7=0;f8=0;f9=0;f10=0;f11=0;f12=0;
f13=0;f14=0;f15=0.0459;f16=0.0459;f17=0.0459;f18=0.1494;f19=0.1
057;f20=0.1057;f21=0.1057;f22=0.1057;f23=0.1057;f24=0.1515;f25=
0.1494;f26=0.2551;f27=0.2113;f28=0.2113;f29=0.2113;f30=0.2378;f
31=0.1953;f32=0.1494;f33=0.1494;f34=0.1494;f35=0.2816;f36=0;

!values height 0 CI delta X (annotated as g);
g1=0;g2=0;g3=0;g4=0;g5=0;g6=0;g7=0;g8=0;g9=0;g10=0;g11=0;g12=0;
g13=0;g14=0;g15=.0;g16=0;g17=0;g18=0;g19=0;g20=0;g21=0;g22=0;g2
3=0;g24=0;g25=0.4227;g26=0.2989;g27=0.2989;g28=0.2989;g29=0.298
9;g30=0.2989;g31=0.1298;g32=0.2929;g33=0.2929;g34=0;g35=0.1298;
g36=0;

Lkoc=1.34;
Ukoc=2.34;
koc>Lkoc;
koc<Ukoc;

lamda3=(Ukoc-koc)/(Ukoc-Lkoc);

!Structural Constraints;
x1=x3+x4;
x2=x19;
x3=x6+x7;
x4=x14;
x5=x36;
x9=x13;
x10=x12;
x11=x16;
x12=x18;
x13+x14=x22+x23;
x17=x31;
```

```
x17=x21;
x26=x34;
x18=x25;
x19=x27;
x23=x26;
x26=x34;
x20=x5;
x30=x35;
x20+x21+x22=x27+2*x28+x29;
x31=x32;
x16=x31;
x15=0;
x24=0;
x29=0;
x33=0;
x35=0;
x6+2*x8+x9+x10+x11=2*h1;
2*x8<x6+x8+x9+x10+x11;
2*x28<x27+x28+x29;

!Handshaking lemma;
(x1+x2+x25+x34+x36)+2*(x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14
+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x26+x27+x28+x29+x30+x3
2+x33)+3*(x31+x35)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+
x14+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29
+x30+x31+x32+x33+x34+x35+x36+0.5*(x31+x32+x33+x35)-1)*2;

!Integer constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x13);@GIN(
x14);@GIN(x15);@GIN(x16);@GIN(x17);@GIN(x18);@GIN(x19);@GIN(x20
);@GIN(x21);@GIN(x22);@GIN(x23);@GIN(x24);@GIN(x25);@GIN(x26);@
GIN(x27);@GIN(x28);@GIN(x29);@GIN(x30);@GIN(x31);@GIN(x32);@GIN
(x33);@GIN(x34); @GIN(x35);@GIN(x36);@GIN(h1);

!Positive value constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;x33>0;
x34>0;x35>0;x36>0;

!Total number of signatures equation;
k=x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x15+x16+x17+x1
8+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x31+x32+x33+x
34+x35+x36;

end
```

TWO-PHASE APPROACH

```
max=lamda;

lamda=lamda1+lamda2+lamda3;

!Vp (annotated as A);
A=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10
+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x1
8+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x
26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*
x34+a35*x35+a36*x36;

a1=0.8491;a2=0.8491;a3=0.7141;a4=0.7141;a5=0.7141;
a6=0.7141;a7=0.7141;a8=0.7141;a9=0.7141;a10=0.7141;
a11=0.7141;a12=0.7141;a13=0.7141;a14=0.7141;
a15=0.7141;a16=0.7141;a17=0.7141;a18=2.7987;a19=0;
a20=0;a21=0;a22=0;a23=0;a24=0;a25=0;a26=1.3368;
a27=2.0509;a28=2.0509;a28=2.0509;a29=2.0509;
a30=2.0509;a31=0;a32=1.5596;a33=1.5596;a34=0.8491;
a35=0;a36=0.8491;

La=4.50;
Ua=12.00;
A>La;
A<Ua;

lamda1=(A-La)/(Ua-La);

!Hv (annotated as B);
B=b1*x1+b2*x2+b3*x3+b4*x4+b5*x5+b6*x6+b7*x7+b8*x8+b9*x9+b10*x10
+b11*x11+b12*x12+b13*x13+b14*x14+b15*x15+b16*x16+b17*x17+b18*x1
8+b19*x19+b20*x20+b21*x21+b22*x22+b23*x23+b24*x24+b25*x25+b26*x
26+b27*x27+b28*x28+b29*x29+b30*x30+b31*x31+b32*x32+b33*x33+b34*
x34+b35*x35+b36*x36;

b1=0.217;b2=0.217;b3=4.91;b4=4.91;b5=4.91;b6=4.91;
b7=4.91;b8=4.91;b9=4.91;b10=4.91;b11=4.91;b12=4.91;
b13=4.91;b14=4.91;b15=4.91;b16=4.91;b17=4.91;
b18=15.432;b19=0;b20=0;b21=0;b22=0;b23=0;b24=0;
b25=0;b26=9.997;b27=14.907;b28=14.907;b29=14.907;
b30=14.907;b31=0;b32=4.031;b33=4.031;b34=0.217;
b35=0;b36=0.217;

Lb=16.81;
Ub=53.46;
B>Lb;
```

```
B<Ub;

!Vm (annotated as C);
C=c1*x1+c2*x2+c3*x3+c4*x4+c5*x5+c6*x6+c7*x7+c8*x8+c9*x9+c10*x10
+c11*x11+c12*x12+c13*x13+c14*x14+c15*x15+c16*x16+c17*x17+c18*x1
8+c19*x19+c20*x20+c21*x21+c22*x22+c23*x23+c24*x24+c25*x25+c26*x
26+c27*x27+c28*x28+c29*x29+c30*x30+c31*x31+c32*x32+c33*x33+c34*
x34+c35*x35+c36*x36;

c1=0.354;c2=0.417;c3=0.25;c4=0.264;c5=0.278;
c6=0.604;c7=0.617;c8=0.5;c9=0.514;c10=0.506;
c11=0.454;c12=0.613;c13=0.528;c14=0.631;c15=0.454;
c16=0.558;c17=0.566;c18=0.256;c19=0.278;c20=0.65;
c21=0.482;c22=0.541;c23=0.68;c24=0.577;c25=0.363;
c26=0.278;c27=0.694;c28=0.556;c29=0.5;c30=0.612;
c31=0.204;c32=0.289;c33=0.299;c34=0.417;c35=0.223;
c36=0.373;

Lc=0.89;
Uc=5.50;
C>Lc;
C<Uc;

lamda2=(Uc-C)/(Uc-Lc);

!TLC (annotated as D);
D=d1*x1+d2*x2+d3*x3+d4*x4+d5*x5+d6*x6+d7*x7+d8*x8+d9*x9+d10*x10
+d11*x11+d12*x12+d13*x13+d14*x14+d15*x15+d16*x16+d17*x17+d18*x1
8+d19*x19+d20*x20+d21*x21+d22*x22+d23*x23+d24*x24+d25*x25-
d26*x26-d27*x27-d28*x28-d29*x29-
d30*x30+d31*x31+d32*x32+d33*x33+d34*x34+d35*x35+d36*x36;

d1=0.25;d2=0.1443;d3=0.1768;d4=0.1768;d5=0.1021;
d6=0.4268;d7=0.4268;d8=0.3536;d9=0.3536;d10=0.3536;
d11=0.3211;d12=0.3211;d13=0.2788;d14=0.3521;d15=0;
d16=0.3211;d17=0.2464;d18=0.1768;d19=0.1021;
d20=0.3521;d21=0.2464;d22=0.2788;d23=0.3211;
d24=0.2464;d25=0.1443;d26=0.1021;d27=0.2464;
d28=0.2041;d29=0.1854;d30=0.1854;d31=0.1443;
d32=0.1443;d33=0.1443;d34=0.1443;d35=0.0833;d36=0.25;

Ud=2.31;
D<Ud;

!koc;
koc=0.53*(e1*x1+e2*x2+e3*x3+e4*x4+e5*x5+e6*x6+e7*x7+e8*x8+e9*x9
+e10*x10+e11*x11+e12*x12+e13*x13+e14*x14+e15*x15+e16*x16+e17*x1
7+e18*x18+e19*x19+e20*x20+e21*x21+e22*x22+e23*x23+e24*x24+e25*x
25+e26*x26+e27*x27+e28*x28+e29*x29+e30*x30+e31*x31+e32*x32+e33*
x33+e34*x34+e35*x35+e36*x36)-1.25*
(f1*x1+f2*x2+f3*x3+f4*x4+f5*x5+f6*x6+f7*x7+f8*x8+f9*x9+f10*x10+
f11*x11+f12*x12+f13*x13+f14*x14+f15*x15+f16*x16+f17*x17+f18*x18
+f19*x19+f20*x20+f21*x21+f22*x22+f23*x23+f24*x24+f25*x25+f26*x2
```

```
6+f27*x27+f28*x28+f29*x29+f30*x30+f31*x31+f32*x32+f33*x33+f34*x
34+f35*x35+f36*x36)-
0.72*(g1*x1+g2*x2+g3*x3+g4*x4+g5*x5+g6*x6+g7*x7+g8*x8+g9*x9+g10
*x10+g11*x11+g12*x12+g13*x13+g14*x14+g15*x15+g16*x16+g17*x17+g1
8*x18+g19*x19+g20*x20+g21*x21+g22*x22+g23*x23+g24*x24+g25*x25+g
26*x26+g27*x27+g28*x28+g29*x29+g30*x30+g31*x31+g32*x32+g33*x33+
g34*x34+g35*x35+g36*x36);

!values height 1 CI simple degree (annotated as e);
e1=0.3536;e2=0.3536;e3=0.6036;e4=0.6036;e5=0.7071;e6=0.5;e7=0.5
;e8=0.5;e9=0.5;e10=0.5;
e11=0.5;e12=0.5;e13=0.5;e14=0.5;e15=0.5;e16=0.5;e17=0.5;e18=0.4
541;e19=0.4979;e20=0.3943;e21=0.3943;e22=0.3943;e23=0.3943;e24=
0.3943;e25=0.2041;e26=0.3485;e27=0.2887;e28=0.2887;e29=0.2887;e
30=0.2887;e31=0.6036;e32=0.3536;e33=0.3536;e34=0.7071;
e35=0.4979;e36=0.3536;

!values height 1 CI delta X (annotated as f);
f1=0;f2=0;f3=0;f4=0;f5=0;f6=0;f7=0;f8=0;f9=0;f10=0;f11=0;f12=0;
f13=0;f14=0;f15=0.0459;f16=0.0459;f17=0.0459;f18=0.1494;f19=0.1
057;f20=0.1057;f21=0.1057;f22=0.1057;f23=0.1057;f24=0.1515;f25=
0.1494;f26=0.2551;f27=0.2113;f28=0.2113;f29=0.2113;f30=0.2378;f
31=0.1953;f32=0.1494;f33=0.1494;f34=0.1494;f35=0.2816;f36=0;

!values height 0 CI delta X (annotated as g);
g1=0;g2=0;g3=0;g4=0;g5=0;g6=0;g7=0;g8=0;g9=0;g10=0;g11=0;g12=0;
g13=0;g14=0;g15=.0;g16=0;g17=0;g18=0;g19=0;g20=0;g21=0;g22=0;g2
3=0;g24=0;g25=0.4227;g26=0.2989;g27=0.2989;g28=0.2989;g29=0.298
9;g30=0.2989;g31=0.1298;g32=0.2929;g33=0.2929;g34=0;g35=0.1298;
g36=0;

Lkoc=1.34;
Ukoc=2.34;
koc>Lkoc;
koc<Ukoc;

lamda3=(Ukoc-koc)/(Ukoc-Lkoc);

!Structural Constraints;
x1=x3+x4;
x2=x19;
x3=x6+x7;
x4=x14;
x5=x36;
x9=x13;
x10=x12;
x11=x16;
x12=x18;
x13+x14=x22+x23;
x17=x31;
x17=x21;
x26=x34;
x18=x25;
```

```
x19=x27;
x23=x26;
x26=x34;
x20=x5;
x30=x35;
x20+x21+x22=x27+2*x28+x29;
x31=x32;
x16=x31;
x15=0;
x24=0;
x29=0;
x33=0;
x35=0;
x6+2*x8+x9+x10+x11=2*h1;
2*x8<x6+x8+x9+x10+x11;
2*x28<x27+x28+x29;

!Handshaking lemma;
(x1+x2+x25+x34+x36)+2*(x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14
+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x26+x27+x28+x29+x30+x3
2+x33)+3*(x31+x35)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+
x14+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29
+x30+x31+x32+x33+x34+x35+x36+0.5*(x31+x32+x33+x35)-1)*2;

!Integer constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x13);@GIN(
x14);@GIN(x15);@GIN(x16);@GIN(x17);@GIN(x18);@GIN(x19);@GIN(x20
);@GIN(x21);@GIN(x22);@GIN(x23);@GIN(x24);@GIN(x25);@GIN(x26);@
GIN(x27);@GIN(x28);@GIN(x29);@GIN(x30);@GIN(x31);@GIN(x32);@GIN
(x33);@GIN(x34); @GIN(x35);@GIN(x36);@GIN(h1);

!Positive value constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;x33>0;
x34>0;x35>0;x36>0;

!Total number of signatures equation;
k=x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x15+x16+x17+x1
8+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x31+x32+x33+x
34+x35+x36;

end
```

RESULTS

BI-LEVEL OPTIMISATION APPROACH (MAXIMISATION)

```
Global optimal solution found.
Objective value:                              1.809632
Objective bound:                              1.809632
Infeasibilities:                              0.000000
Extended solver steps:                               0
Total solver iterations:                            28

Model Class:                                      MILP

Total variables:                     37
Nonlinear variables:                  0
Integer variables:                   31

Total constraints:                   76
Nonlinear constraints:                0

Total nonzeros:                     278
Nonlinear nonzeros:                   0

Variable     Value              Reduced Cost
KOC          1.809632           0.000000
A            5.268700           0.000000
A1           0.8491000          0.000000
X1           2.000000           -0.1874080
A2           0.8491000          0.000000
X2           0.000000           -0.1874080
A3           0.7141000          0.000000
X3           2.000000           -0.3199080
A4           0.7141000          0.000000
X4           0.000000           -0.3199080
A5           0.7141000          0.000000
X5           0.000000           -0.3747630
A6           0.7141000          0.000000
X6           2.000000           -0.2650000
A7           0.7141000          0.000000
X7           0.000000           -0.2650000
A8           0.7141000          0.000000
X8           1.000000           -0.2650000
A9           0.7141000          0.000000
X9           0.000000           -0.2650000
A10          0.7141000          0.000000
X10          0.000000           -0.2650000
```

```
A11          0.7141000           0.000000
X11          0.000000            -0.2650000
A12          0.7141000           0.000000
X12          0.000000            -0.2650000
A13          0.7141000           0.000000
X13          0.000000            -0.2650000
A14          0.7141000           0.000000
X14          0.000000            -0.2650000
A15          0.7141000           0.000000
X15          0.000000            0.000000
A16          0.7141000           0.000000
X16          0.000000            -0.2076250
A17          0.7141000           0.000000
X17          0.000000            -0.2076250
A18          2.798700            0.000000
X18          0.000000            -0.5392300E-01
A19          0.000000            0.000000
X19          0.000000            -0.1317620
A20          0.000000            0.000000
X20          0.000000            -0.7685400E-01
A21          0.000000            0.000000
X21          0.000000            -0.7685400E-01
A22          0.000000            0.000000
X22          0.000000            -0.7685400E-01
A23          0.000000            0.000000
X23          0.000000            -0.7685400E-01
A24          0.000000            0.000000
X24          0.000000            0.000000
A25          0.000000            0.000000
X25          0.000000            0.3829210
A26          1.336800            0.000000
X26          0.000000            0.3493780
A27          2.050900            0.000000
X27          0.000000            0.3263220
A28          2.050900            0.000000
X28          0.000000            0.3263220
A29          2.050900            0.000000
X29          0.000000            0.000000
A30          2.050900            0.000000
X30          0.000000            0.000000
A31          0.000000            0.000000
X31          0.000000            0.1767300E-01
A32          1.559600            0.000000
X32          0.000000            0.2102300
A33          1.559600            0.000000
X33          0.000000            0.000000
A34          0.8491000           0.000000
X34          0.000000            -0.1880130
A35          0.000000            0.000000
X35          0.000000            0.000000
A36          0.8491000           0.000000
X36          0.000000            -0.1874080
LA           4.500000            0.000000
```

```
UA            12.00000            0.000000
B             24.98400            0.000000
B1            0.2170000           0.000000
B2            0.2170000           0.000000
B3            4.910000            0.000000
B4            4.910000            0.000000
B5            4.910000            0.000000
B6            4.910000            0.000000
B7            4.910000            0.000000
B8            4.910000            0.000000
B9            4.910000            0.000000
B10           4.910000            0.000000
B11           4.910000            0.000000
B12           4.910000            0.000000
B13           4.910000            0.000000
B14           4.910000            0.000000
B15           4.910000            0.000000
B16           4.910000            0.000000
B17           4.910000            0.000000
B18           15.43200            0.000000
B19           0.000000            0.000000
B20           0.000000            0.000000
B21           0.000000            0.000000
B22           0.000000            0.000000
B23           0.000000            0.000000
B24           0.000000            0.000000
B25           0.000000            0.000000
B26           9.997000            0.000000
B27           14.90700            0.000000
B28           14.90700            0.000000
B29           14.90700            0.000000
B30           14.90700            0.000000
B31           0.000000            0.000000
B32           4.031000            0.000000
B33           4.031000            0.000000
B34           0.2170000           0.000000
B35           0.000000            0.000000
B36           0.2170000           0.000000
LB            16.81000            0.000000
UB            53.46000            0.000000
C             2.916000            0.000000
C1            0.3540000           0.000000
C2            0.4170000           0.000000
C3            0.2500000           0.000000
C4            0.2640000           0.000000
C5            0.2780000           0.000000
C6            0.6040000           0.000000
C7            0.6170000           0.000000
C8            0.5000000           0.000000
C9            0.5140000           0.000000
C10           0.5060000           0.000000
C11           0.4540000           0.000000
C12           0.6130000           0.000000
```

```
C13          0.5280000           0.000000
C14          0.6310000           0.000000
C15          0.4540000           0.000000
C16          0.5580000           0.000000
C17          0.5660000           0.000000
C18          0.2560000           0.000000
C19          0.2780000           0.000000
C20          0.6500000           0.000000
C21          0.4820000           0.000000
C22          0.5410000           0.000000
C23          0.6800000           0.000000
C24          0.5770000           0.000000
C25          0.3630000           0.000000
C26          0.2780000           0.000000
C27          0.6940000           0.000000
C28          0.5560000           0.000000
C29          0.5000000           0.000000
C30          0.6120000           0.000000
C31          0.2040000           0.000000
C32          0.2890000           0.000000
C33          0.2990000           0.000000
C34          0.4170000           0.000000
C35          0.2230000           0.000000
C36          0.3730000           0.000000
LC           0.8900000           0.000000
UC           5.500000            0.000000
D            2.060800            0.000000
D1           0.2500000           0.000000
D2           0.1443000           0.000000
D3           0.1768000           0.000000
D4           0.1768000           0.000000
D5           0.1021000           0.000000
D6           0.4268000           0.000000
D7           0.4268000           0.000000
D8           0.3536000           0.000000
D9           0.3536000           0.000000
D10          0.3536000           0.000000
D11          0.3211000           0.000000
D12          0.3211000           0.000000
D13          0.2788000           0.000000
D14          0.3521000           0.000000
D15          0.000000            0.000000
D16          0.3211000           0.000000
D17          0.2464000           0.000000
D18          0.1768000           0.000000
D19          0.1021000           0.000000
D20          0.3521000           0.000000
D21          0.2464000           0.000000
D22          0.2788000           0.000000
D23          0.3211000           0.000000
D24          0.2464000           0.000000
D25          0.1443000           0.000000
D26          0.1021000           0.000000
```

```
D27          0.2464000            0.000000
D28          0.2041000            0.000000
D29          0.1854000            0.000000
D30          0.1854000            0.000000
D31          0.1443000            0.000000
D32          0.1443000            0.000000
D33          0.1443000            0.000000
D34          0.1443000            0.000000
D35          0.8330000E-01        0.000000
D36          0.2500000            0.000000
UD           2.310000             0.000000
E1           0.3536000            0.000000
E2           0.3536000            0.000000
E3           0.6036000            0.000000
E4           0.6036000            0.000000
E5           0.7071000            0.000000
E6           0.5000000            0.000000
E7           0.5000000            0.000000
E8           0.5000000            0.000000
E9           0.5000000            0.000000
E10          0.5000000            0.000000
E11          0.5000000            0.000000
E12          0.5000000            0.000000
E13          0.5000000            0.000000
E14          0.5000000            0.000000
E15          0.5000000            0.000000
E16          0.5000000            0.000000
E17          0.5000000            0.000000
E18          0.4541000            0.000000
E19          0.4979000            0.000000
E20          0.3943000            0.000000
E21          0.3943000            0.000000
E22          0.3943000            0.000000
E23          0.3943000            0.000000
E24          0.3943000            0.000000
E25          0.2041000            0.000000
E26          0.3485000            0.000000
E27          0.2887000            0.000000
E28          0.2887000            0.000000
E29          0.2887000            0.000000
E30          0.2887000            0.000000
E31          0.6036000            0.000000
E32          0.3536000            0.000000
E33          0.3536000            0.000000
E34          0.7071000            0.000000
E35          0.4979000            0.000000
E36          0.3536000            0.000000
F1           0.000000             0.000000
F2           0.000000             0.000000
F3           0.000000             0.000000
F4           0.000000             0.000000
F5           0.000000             0.000000
F6           0.000000             0.000000
```

```
F7           0.000000            0.000000
F8           0.000000            0.000000
F9           0.000000            0.000000
F10          0.000000            0.000000
F11          0.000000            0.000000
F12          0.000000            0.000000
F13          0.000000            0.000000
F14          0.000000            0.000000
F15          0.4590000E-01       0.000000
F16          0.4590000E-01       0.000000
F17          0.4590000E-01       0.000000
F18          0.1494000           0.000000
F19          0.1057000           0.000000
F20          0.1057000           0.000000
F21          0.1057000           0.000000
F22          0.1057000           0.000000
F23          0.1057000           0.000000
F24          0.1515000           0.000000
F25          0.1494000           0.000000
F26          0.2551000           0.000000
F27          0.2113000           0.000000
F28          0.2113000           0.000000
F29          0.2113000           0.000000
F30          0.2378000           0.000000
F31          0.1953000           0.000000
F32          0.1494000           0.000000
F33          0.1494000           0.000000
F34          0.1494000           0.000000
F35          0.2816000           0.000000
F36          0.000000            0.000000
G1           0.000000            0.000000
G2           0.000000            0.000000
G3           0.000000            0.000000
G4           0.000000            0.000000
G5           0.000000            0.000000
G6           0.000000            0.000000
G7           0.000000            0.000000
G8           0.000000            0.000000
G9           0.000000            0.000000
G10          0.000000            0.000000
G11          0.000000            0.000000
G12          0.000000            0.000000
G13          0.000000            0.000000
G14          0.000000            0.000000
G15          0.000000            0.000000
G16          0.000000            0.000000
G17          0.000000            0.000000
G18          0.000000            0.000000
G19          0.000000            0.000000
G20          0.000000            0.000000
G21          0.000000            0.000000
G22          0.000000            0.000000
G23          0.000000            0.000000
```

```
G24          0.000000            0.000000
G25          0.4227000           0.000000
G26          0.2989000           0.000000
G27          0.2989000           0.000000
G28          0.2989000           0.000000
G29          0.2989000           0.000000
G30          0.2989000           0.000000
G31          0.1298000           0.000000
G32          0.2929000           0.000000
G33          0.2929000           0.000000
G34          0.000000            0.000000
G35          0.1298000           0.000000
G36          0.000000            0.000000
H1           2.000000            0.000000
K            7.000000            0.000000
```

BI-LEVEL OPTIMISATION APPROACH (MINIMISATION)

```
Global optimal solution found.
Objective value:                              0.4020040
Objective bound:                              0.4020040
Infeasibilities:                               0.000000
Extended solver steps:                                0
Total solver iterations:                              8

Model Class:                                       MILP

Total variables:                     37
Nonlinear variables:                  0
Integer variables:                   31

Total constraints:                   76
Nonlinear constraints:                0

Total nonzeros:                     278
Nonlinear nonzeros:                   0

Variable     Value              Reduced Cost
KOC          0.4020040          0.000000
A            8.453800           0.000000
A1           0.8491000          0.000000
X1           0.000000           0.1874080
A2           0.8491000          0.000000
X2           0.000000           0.1874080
A3           0.7141000          0.000000
X3           0.000000           0.3199080
A4           0.7141000          0.000000
X4           0.000000           0.3199080
A5           0.7141000          0.000000
X5           0.000000           0.3747630
A6           0.7141000          0.000000
X6           0.000000           0.2650000
A7           0.7141000          0.000000
X7           0.000000           0.2650000
A8           0.7141000          0.000000
X8           0.000000           0.2650000
A9           0.7141000          0.000000
X9           0.000000           0.2650000
A10          0.7141000          0.000000
X10          2.000000           0.2650000
A11          0.7141000          0.000000
X11          0.000000           0.2650000
A12          0.7141000          0.000000
```

```
X12            2.000000            0.2650000
A13            0.7141000           0.000000
X13            0.000000            0.2650000
A14            0.7141000           0.000000
X14            0.000000            0.2650000
A15            0.7141000           0.000000
X15            0.000000            0.000000
A16            0.7141000           0.000000
X16            0.000000            0.2076250
A17            0.7141000           0.000000
X17            0.000000            0.2076250
A18            2.798700            0.000000
X18            2.000000            0.5392300E-01
A19            0.000000            0.000000
X19            0.000000            0.1317620
A20            0.000000            0.000000
X20            0.000000            0.7685400E-01
A21            0.000000            0.000000
X21            0.000000            0.7685400E-01
A22            0.000000            0.000000
X22            0.000000            0.7685400E-01
A23            0.000000            0.000000
X23            0.000000            0.7685400E-01
A24            0.000000            0.000000
X24            0.000000            0.000000
A25            0.000000            0.000000
X25            2.000000            -0.3829210
A26            1.336800            0.000000
X26            0.000000            -0.3493780
A27            2.050900            0.000000
X27            0.000000            -0.3263220
A28            2.050900            0.000000
X28            0.000000            -0.3263220
A29            2.050900            0.000000
X29            0.000000            0.000000
A30            2.050900            0.000000
X30            0.000000            0.000000
A31            0.000000            0.000000
X31            0.000000            -0.1767300E-01
A32            1.559600            0.000000
X32            0.000000            -0.2102300
A33            1.559600            0.000000
X33            0.000000            0.000000
A34            0.8491000           0.000000
X34            0.000000            0.1880130
A35            0.000000            0.000000
X35            0.000000            0.000000
A36            0.8491000           0.000000
X36            0.000000            0.1874080
LA             4.500000            0.000000
UA             12.00000            0.000000
B              50.50400            0.000000
B1             0.2170000           0.000000
```

```
B2           0.2170000           0.000000
B3           4.910000            0.000000
B4           4.910000            0.000000
B5           4.910000            0.000000
B6           4.910000            0.000000
B7           4.910000            0.000000
B8           4.910000            0.000000
B9           4.910000            0.000000
B10          4.910000            0.000000
B11          4.910000            0.000000
B12          4.910000            0.000000
B13          4.910000            0.000000
B14          4.910000            0.000000
B15          4.910000            0.000000
B16          4.910000            0.000000
B17          4.910000            0.000000
B18          15.43200            0.000000
B19          0.000000            0.000000
B20          0.000000            0.000000
B21          0.000000            0.000000
B22          0.000000            0.000000
B23          0.000000            0.000000
B24          0.000000            0.000000
B25          0.000000            0.000000
B26          9.997000            0.000000
B27          14.90700            0.000000
B28          14.90700            0.000000
B29          14.90700            0.000000
B30          14.90700            0.000000
B31          0.000000            0.000000
B32          4.031000            0.000000
B33          4.031000            0.000000
B34          0.2170000           0.000000
B35          0.000000            0.000000
B36          0.2170000           0.000000
LB           16.81000            0.000000
UB           53.46000            0.000000
C            3.476000            0.000000
C1           0.3540000           0.000000
C2           0.4170000           0.000000
C3           0.2500000           0.000000
C4           0.2640000           0.000000
C5           0.2780000           0.000000
C6           0.6040000           0.000000
C7           0.6170000           0.000000
C8           0.5000000           0.000000
C9           0.5140000           0.000000
C10          0.5060000           0.000000
C11          0.4540000           0.000000
C12          0.6130000           0.000000
C13          0.5280000           0.000000
C14          0.6310000           0.000000
C15          0.4540000           0.000000
```

```
C16          0.5580000           0.000000
C17          0.5660000           0.000000
C18          0.2560000           0.000000
C19          0.2780000           0.000000
C20          0.6500000           0.000000
C21          0.4820000           0.000000
C22          0.5410000           0.000000
C23          0.6800000           0.000000
C24          0.5770000           0.000000
C25          0.3630000           0.000000
C26          0.2780000           0.000000
C27          0.6940000           0.000000
C28          0.5560000           0.000000
C29          0.5000000           0.000000
C30          0.6120000           0.000000
C31          0.2040000           0.000000
C32          0.2890000           0.000000
C33          0.2990000           0.000000
C34          0.4170000           0.000000
C35          0.2230000           0.000000
C36          0.3730000           0.000000
LC           0.8900000           0.000000
UC           5.500000            0.000000
D            1.991600            0.000000
D1           0.2500000           0.000000
D2           0.1443000           0.000000
D3           0.1768000           0.000000
D4           0.1768000           0.000000
D5           0.1021000           0.000000
D6           0.4268000           0.000000
D7           0.4268000           0.000000
D8           0.3536000           0.000000
D9           0.3536000           0.000000
D10          0.3536000           0.000000
D11          0.3211000           0.000000
D12          0.3211000           0.000000
D13          0.2788000           0.000000
D14          0.3521000           0.000000
D15          0.000000            0.000000
D16          0.3211000           0.000000
D17          0.2464000           0.000000
D18          0.1768000           0.000000
D19          0.1021000           0.000000
D20          0.3521000           0.000000
D21          0.2464000           0.000000
D22          0.2788000           0.000000
D23          0.3211000           0.000000
D24          0.2464000           0.000000
D25          0.1443000           0.000000
D26          0.1021000           0.000000
D27          0.2464000           0.000000
D28          0.2041000           0.000000
D29          0.1854000           0.000000
```

```
D30          0.1854000           0.000000
D31          0.1443000           0.000000
D32          0.1443000           0.000000
D33          0.1443000           0.000000
D34          0.1443000           0.000000
D35          0.8330000E-01       0.000000
D36          0.2500000           0.000000
UD           2.310000            0.000000
E1           0.3536000           0.000000
E2           0.3536000           0.000000
E3           0.6036000           0.000000
E4           0.6036000           0.000000
E5           0.7071000           0.000000
E6           0.5000000           0.000000
E7           0.5000000           0.000000
E8           0.5000000           0.000000
E9           0.5000000           0.000000
E10          0.5000000           0.000000
E11          0.5000000           0.000000
E12          0.5000000           0.000000
E13          0.5000000           0.000000
E14          0.5000000           0.000000
E15          0.5000000           0.000000
E16          0.5000000           0.000000
E17          0.5000000           0.000000
E18          0.4541000           0.000000
E19          0.4979000           0.000000
E20          0.3943000           0.000000
E21          0.3943000           0.000000
E22          0.3943000           0.000000
E23          0.3943000           0.000000
E24          0.3943000           0.000000
E25          0.2041000           0.000000
E26          0.3485000           0.000000
E27          0.2887000           0.000000
E28          0.2887000           0.000000
E29          0.2887000           0.000000
E30          0.2887000           0.000000
E31          0.6036000           0.000000
E32          0.3536000           0.000000
E33          0.3536000           0.000000
E34          0.7071000           0.000000
E35          0.4979000           0.000000
E36          0.3536000           0.000000
F1           0.000000            0.000000
F2           0.000000            0.000000
F3           0.000000            0.000000
F4           0.000000            0.000000
F5           0.000000            0.000000
F6           0.000000            0.000000
F7           0.000000            0.000000
F8           0.000000            0.000000
F9           0.000000            0.000000
```

```
F10          0.000000            0.000000
F11          0.000000            0.000000
F12          0.000000            0.000000
F13          0.000000            0.000000
F14          0.000000            0.000000
F15          0.4590000E-01       0.000000
F16          0.4590000E-01       0.000000
F17          0.4590000E-01       0.000000
F18          0.1494000           0.000000
F19          0.1057000           0.000000
F20          0.1057000           0.000000
F21          0.1057000           0.000000
F22          0.1057000           0.000000
F23          0.1057000           0.000000
F24          0.1515000           0.000000
F25          0.1494000           0.000000
F26          0.2551000           0.000000
F27          0.2113000           0.000000
F28          0.2113000           0.000000
F29          0.2113000           0.000000
F30          0.2378000           0.000000
F31          0.1953000           0.000000
F32          0.1494000           0.000000
F33          0.1494000           0.000000
F34          0.1494000           0.000000
F35          0.2816000           0.000000
F36          0.000000            0.000000
G1           0.000000            0.000000
G2           0.000000            0.000000
G3           0.000000            0.000000
G4           0.000000            0.000000
G5           0.000000            0.000000
G6           0.000000            0.000000
G7           0.000000            0.000000
G8           0.000000            0.000000
G9           0.000000            0.000000
G10          0.000000            0.000000
G11          0.000000            0.000000
G12          0.000000            0.000000
G13          0.000000            0.000000
G14          0.000000            0.000000
G15          0.000000            0.000000
G16          0.000000            0.000000
G17          0.000000            0.000000
G18          0.000000            0.000000
G19          0.000000            0.000000
G20          0.000000            0.000000
G21          0.000000            0.000000
G22          0.000000            0.000000
G23          0.000000            0.000000
G24          0.000000            0.000000
G25          0.4227000           0.000000
G26          0.2989000           0.000000
```

```
G27          0.2989000          0.000000
G28          0.2989000          0.000000
G29          0.2989000          0.000000
G30          0.2989000          0.000000
G31          0.1298000          0.000000
G32          0.2929000          0.000000
G33          0.2929000          0.000000
G34          0.000000           0.000000
G35          0.1298000          0.000000
G36          0.000000           0.000000
H1           1.000000           0.000000
K            8.000000           0.000000
```

MAX-MIN AGGREGATION APPROACH

```
Global optimal solution found.
Objective value:                              0.2807333
Objective bound:                              0.2807333
Infeasibilities:                               0.000000
Extended solver steps:                                0
Total solver iterations:                             35

Model Class:                                       MILP

Total variables:                    41
Nonlinear variables:                 0
Integer variables:                  31

Total constraints:                  84
Nonlinear constraints:               0

Total nonzeros:                    292
Nonlinear nonzeros:                  0


Variable     Value               Reduced Cost
LAMDA        0.2807333           0.000000
LAMDA1       0.2807333           0.000000
LAMDA2       0.2982646           0.000000
LAMDA3       0.8571950           0.000000
A            6.605500            0.000000
A1           0.8491000           0.000000
X1           1.000000            -0.1132133
A2           0.8491000           0.000000
X2           0.000000            -0.1132133
A3           0.7141000           0.000000
X3           1.000000            -0.9521333E-01
A4           0.7141000           0.000000
X4           0.000000            -0.9521333E-01
A5           0.7141000           0.000000
X5           0.000000            -0.9521333E-01
A6           0.7141000           0.000000
X6           1.000000            -0.9521333E-01
A7           0.7141000           0.000000
X7           0.000000            -0.9521333E-01
A8           0.7141000           0.000000
X8           1.000000            -0.9521333E-01
A9           0.7141000           0.000000
X9           1.000000            -0.9521333E-01
A10          0.7141000           0.000000
X10          0.000000            -0.9521333E-01
A11          0.7141000           0.000000
```

```
X11          0.000000            -0.9521333E-01
A12          0.7141000           0.000000
X12          0.000000            -0.9521333E-01
A13          0.7141000           0.000000
X13          1.000000            -0.9521333E-01
A14          0.7141000           0.000000
X14          0.000000            -0.9521333E-01
A15          0.7141000           0.000000
X15          0.000000            0.000000
A16          0.7141000           0.000000
X16          0.000000            -0.9521333E-01
A17          0.7141000           0.000000
X17          0.000000            -0.9521333E-01
A18          2.798700            0.000000
X18          0.000000            -0.3731600
A19          0.000000            0.000000
X19          0.000000            0.000000
A20          0.000000            0.000000
X20          0.000000            0.000000
A21          0.000000            0.000000
X21          0.000000            0.000000
A22          0.000000            0.000000
X22          0.000000            0.000000
A23          0.000000            0.000000
X23          1.000000            0.000000
A24          0.000000            0.000000
X24          0.000000            0.000000
A25          0.000000            0.000000
X25          0.000000            0.000000
A26          1.336800            0.000000
X26          1.000000            -0.1782400
A27          2.050900            0.000000
X27          0.000000            -0.2734533
A28          2.050900            0.000000
X28          0.000000            -0.2734533
A29          2.050900            0.000000
X29          0.000000            0.000000
A30          2.050900            0.000000
X30          0.000000            0.000000
A31          0.000000            0.000000
X31          0.000000            0.000000
A32          1.559600            0.000000
X32          0.000000            -0.2079467
A33          1.559600            0.000000
X33          0.000000            0.000000
A34          0.8491000           0.000000
X34          1.000000            -0.1132133
A35          0.000000            0.000000
X35          0.000000            0.000000
A36          0.8491000           0.000000
X36          0.000000            -0.1132133
LA           4.500000            0.000000
UA           12.00000            0.000000
```

```
B            34.98100            0.000000
B1           0.2170000           0.000000
B2           0.2170000           0.000000
B3           4.910000            0.000000
B4           4.910000            0.000000
B5           4.910000            0.000000
B6           4.910000            0.000000
B7           4.910000            0.000000
B8           4.910000            0.000000
B9           4.910000            0.000000
B10          4.910000            0.000000
B11          4.910000            0.000000
B12          4.910000            0.000000
B13          4.910000            0.000000
B14          4.910000            0.000000
B15          4.910000            0.000000
B16          4.910000            0.000000
B17          4.910000            0.000000
B18          15.43200            0.000000
B19          0.000000            0.000000
B20          0.000000            0.000000
B21          0.000000            0.000000
B22          0.000000            0.000000
B23          0.000000            0.000000
B24          0.000000            0.000000
B25          0.000000            0.000000
B26          9.997000            0.000000
B27          14.90700            0.000000
B28          14.90700            0.000000
B29          14.90700            0.000000
B30          14.90700            0.000000
B31          0.000000            0.000000
B32          4.031000            0.000000
B33          4.031000            0.000000
B34          0.2170000           0.000000
B35          0.000000            0.000000
B36          0.2170000           0.000000
LB           16.81000            0.000000
UB           53.46000            0.000000
C            4.125000            0.000000
C1           0.3540000           0.000000
C2           0.4170000           0.000000
C3           0.2500000           0.000000
C4           0.2640000           0.000000
C5           0.2780000           0.000000
C6           0.6040000           0.000000
C7           0.6170000           0.000000
C8           0.5000000           0.000000
C9           0.5140000           0.000000
C10          0.5060000           0.000000
C11          0.4540000           0.000000
C12          0.6130000           0.000000
C13          0.5280000           0.000000
```

```
C14          0.6310000          0.000000
C15          0.4540000          0.000000
C16          0.5580000          0.000000
C17          0.5660000          0.000000
C18          0.2560000          0.000000
C19          0.2780000          0.000000
C20          0.6500000          0.000000
C21          0.4820000          0.000000
C22          0.5410000          0.000000
C23          0.6800000          0.000000
C24          0.5770000          0.000000
C25          0.3630000          0.000000
C26          0.2780000          0.000000
C27          0.6940000          0.000000
C28          0.5560000          0.000000
C29          0.5000000          0.000000
C30          0.6120000          0.000000
C31          0.2040000          0.000000
C32          0.2890000          0.000000
C33          0.2990000          0.000000
C34          0.4170000          0.000000
C35          0.2230000          0.000000
C36          0.3730000          0.000000
LC           0.8900000          0.000000
UC           5.500000           0.000000
D            2.202900           0.000000
D1           0.2500000          0.000000
D2           0.1443000          0.000000
D3           0.1768000          0.000000
D4           0.1768000          0.000000
D5           0.1021000          0.000000
D6           0.4268000          0.000000
D7           0.4268000          0.000000
D8           0.3536000          0.000000
D9           0.3536000          0.000000
D10          0.3536000          0.000000
D11          0.3211000          0.000000
D12          0.3211000          0.000000
D13          0.2788000          0.000000
D14          0.3521000          0.000000
D15          0.000000           0.000000
D16          0.3211000          0.000000
D17          0.2464000          0.000000
D18          0.1768000          0.000000
D19          0.1021000          0.000000
D20          0.3521000          0.000000
D21          0.2464000          0.000000
D22          0.2788000          0.000000
D23          0.3211000          0.000000
D24          0.2464000          0.000000
D25          0.1443000          0.000000
D26          0.1021000          0.000000
D27          0.2464000          0.000000
```

```
D28          0.2041000           0.000000
D29          0.1854000           0.000000
D30          0.1854000           0.000000
D31          0.1443000           0.000000
D32          0.1443000           0.000000
D33          0.1443000           0.000000
D34          0.1443000           0.000000
D35          0.8330000E-01       0.000000
D36          0.2500000           0.000000
UD           2.310000            0.000000
KOC          1.482805            0.000000
E1           0.3536000           0.000000
E2           0.3536000           0.000000
E3           0.6036000           0.000000
E4           0.6036000           0.000000
E5           0.7071000           0.000000
E6           0.5000000           0.000000
E7           0.5000000           0.000000
E8           0.5000000           0.000000
E9           0.5000000           0.000000
E10          0.5000000           0.000000
E11          0.5000000           0.000000
E12          0.5000000           0.000000
E13          0.5000000           0.000000
E14          0.5000000           0.000000
E15          0.5000000           0.000000
E16          0.5000000           0.000000
E17          0.5000000           0.000000
E18          0.4541000           0.000000
E19          0.4979000           0.000000
E20          0.3943000           0.000000
E21          0.3943000           0.000000
E22          0.3943000           0.000000
E23          0.3943000           0.000000
E24          0.3943000           0.000000
E25          0.2041000           0.000000
E26          0.3485000           0.000000
E27          0.2887000           0.000000
E28          0.2887000           0.000000
E29          0.2887000           0.000000
E30          0.2887000           0.000000
E31          0.6036000           0.000000
E32          0.3536000           0.000000
E33          0.3536000           0.000000
E34          0.7071000           0.000000
E35          0.4979000           0.000000
E36          0.3536000           0.000000
F1           0.000000            0.000000
F2           0.000000            0.000000
F3           0.000000            0.000000
F4           0.000000            0.000000
F5           0.000000            0.000000
F6           0.000000            0.000000
```

```
F7            0.000000           0.000000
F8            0.000000           0.000000
F9            0.000000           0.000000
F10           0.000000           0.000000
F11           0.000000           0.000000
F12           0.000000           0.000000
F13           0.000000           0.000000
F14           0.000000           0.000000
F15           0.4590000E-01      0.000000
F16           0.4590000E-01      0.000000
F17           0.4590000E-01      0.000000
F18           0.1494000          0.000000
F19           0.1057000          0.000000
F20           0.1057000          0.000000
F21           0.1057000          0.000000
F22           0.1057000          0.000000
F23           0.1057000          0.000000
F24           0.1515000          0.000000
F25           0.1494000          0.000000
F26           0.2551000          0.000000
F27           0.2113000          0.000000
F28           0.2113000          0.000000
F29           0.2113000          0.000000
F30           0.2378000          0.000000
F31           0.1953000          0.000000
F32           0.1494000          0.000000
F33           0.1494000          0.000000
F34           0.1494000          0.000000
F35           0.2816000          0.000000
F36           0.000000           0.000000
G1            0.000000           0.000000
G2            0.000000           0.000000
G3            0.000000           0.000000
G4            0.000000           0.000000
G5            0.000000           0.000000
G6            0.000000           0.000000
G7            0.000000           0.000000
G8            0.000000           0.000000
G9            0.000000           0.000000
G10           0.000000           0.000000
G11           0.000000           0.000000
G12           0.000000           0.000000
G13           0.000000           0.000000
G14           0.000000           0.000000
G15           0.000000           0.000000
G16           0.000000           0.000000
G17           0.000000           0.000000
G18           0.000000           0.000000
G19           0.000000           0.000000
G20           0.000000           0.000000
G21           0.000000           0.000000
G22           0.000000           0.000000
G23           0.000000           0.000000
```

```
G24          0.000000             0.000000
G25          0.4227000            0.000000
G26          0.2989000            0.000000
G27          0.2989000            0.000000
G28          0.2989000            0.000000
G29          0.2989000            0.000000
G30          0.2989000            0.000000
G31          0.1298000            0.000000
G32          0.2929000            0.000000
G33          0.2929000            0.000000
G34          0.000000             0.000000
G35          0.1298000            0.000000
G36          0.000000             0.000000
LKOC         1.340000             0.000000
UKOC         2.340000             0.000000
H1           2.000000             0.000000
K            9.000000             0.000000
```

TWO-PHASE APPROACH

```
Global optimal solution found.
Objective value:                              1.535049
Objective bound:                              1.535049
Infeasibilities:                              0.000000
Extended solver steps:                               0
Total solver iterations:                            24

Model Class:                                      MILP

Total variables:                     41
Nonlinear variables:                  0
Integer variables:                   31

Total constraints:                   82
Nonlinear constraints:                0

Total nonzeros:                     290
Nonlinear nonzeros:                   0


Variable      Value              Reduced Cost
LAMDA         1.535049           0.000000
LAMDA1        0.2807333          0.000000
LAMDA2        0.2863341          0.000000
LAMDA3        0.9679820          0.000000
A             6.605500           0.000000
A1            0.8491000          0.000000
X1            1.000000           0.1509843
A2            0.8491000          0.000000
X2            1.000000           0.1646502
A3            0.7141000          0.000000
X3            1.000000           0.2789246
A4            0.7141000          0.000000
X4            0.000000           0.2819615
A5            0.7141000          0.000000
X5            0.000000           0.3398534
A6            0.7141000          0.000000
X6            1.000000           0.3008062
A7            0.7141000          0.000000
X7            0.000000           0.3036261
A8            0.7141000          0.000000
X8            0.000000           0.2782465
A9            0.7141000          0.000000
X9            1.000000           0.2812834
A10           0.7141000          0.000000
X10           0.000000           0.2795481
A11           0.7141000          0.000000
```

```
X11           0.000000             0.2682682
A12           0.7141000            0.000000
X12           0.000000             0.3027585
A13           0.7141000            0.000000
X13           1.000000             0.2843203
A14           0.7141000            0.000000
X14           0.000000             0.3066630
A15           0.7141000            0.000000
X15           0.000000             0.000000
A16           0.7141000            0.000000
X16           0.000000             0.2334529
A17           0.7141000            0.000000
X17           0.000000             0.2351882
A18           2.798700             0.000000
X18           0.000000             -0.2637055
A19           0.000000             0.000000
X19           1.000000             0.1920657
A20           0.000000             0.000000
X20           0.000000             0.2178518
A21           0.000000             0.000000
X21           0.000000             0.1814093
A22           0.000000             0.000000
X22           1.000000             0.1942076
A23           0.000000             0.000000
X23           0.000000             0.2243594
A24           0.000000             0.000000
X24           0.000000             0.000000
A25           0.000000             0.000000
X25           0.000000             -0.3041791
A26           1.336800             0.000000
X26           0.000000             -0.4673143
A27           2.050900             0.000000
X27           1.000000             -0.4492330
A28           2.050900             0.000000
X28           0.000000             -0.4791680
A29           2.050900             0.000000
X29           0.000000             0.000000
A30           2.050900             0.000000
X30           0.000000             0.000000
A31           0.000000             0.000000
X31           0.000000             0.2657863E-01
A32           1.559600             0.000000
X32           0.000000             -0.3554869
A33           1.559600             0.000000
X33           0.000000             0.000000
A34           0.8491000            0.000000
X34           0.000000             0.1652552
A35           0.000000             0.000000
X35           0.000000             0.000000
A36           0.8491000            0.000000
X36           0.000000             0.1551057
LA            4.500000             0.000000
UA            12.00000             0.000000
```

```
B            34.98100            0.000000
B1           0.2170000           0.000000
B2           0.2170000           0.000000
B3           4.910000            0.000000
B4           4.910000            0.000000
B5           4.910000            0.000000
B6           4.910000            0.000000
B7           4.910000            0.000000
B8           4.910000            0.000000
B9           4.910000            0.000000
B10          4.910000            0.000000
B11          4.910000            0.000000
B12          4.910000            0.000000
B13          4.910000            0.000000
B14          4.910000            0.000000
B15          4.910000            0.000000
B16          4.910000            0.000000
B17          4.910000            0.000000
B18          15.43200            0.000000
B19          0.000000            0.000000
B20          0.000000            0.000000
B21          0.000000            0.000000
B22          0.000000            0.000000
B23          0.000000            0.000000
B24          0.000000            0.000000
B25          0.000000            0.000000
B26          9.997000            0.000000
B27          14.90700            0.000000
B28          14.90700            0.000000
B29          14.90700            0.000000
B30          14.90700            0.000000
B31          0.000000            0.000000
B32          4.031000            0.000000
B33          4.031000            0.000000
B34          0.2170000           0.000000
B35          0.000000            0.000000
B36          0.2170000           0.000000
LB           16.81000            0.000000
UB           53.46000            0.000000
C            4.180000            0.000000
C1           0.3540000           0.000000
C2           0.4170000           0.000000
C3           0.2500000           0.000000
C4           0.2640000           0.000000
C5           0.2780000           0.000000
C6           0.6040000           0.000000
C7           0.6170000           0.000000
C8           0.5000000           0.000000
C9           0.5140000           0.000000
C10          0.5060000           0.000000
C11          0.4540000           0.000000
C12          0.6130000           0.000000
C13          0.5280000           0.000000
```

```
C14          0.6310000          0.000000
C15          0.4540000          0.000000
C16          0.5580000          0.000000
C17          0.5660000          0.000000
C18          0.2560000          0.000000
C19          0.2780000          0.000000
C20          0.6500000          0.000000
C21          0.4820000          0.000000
C22          0.5410000          0.000000
C23          0.6800000          0.000000
C24          0.5770000          0.000000
C25          0.3630000          0.000000
C26          0.2780000          0.000000
C27          0.6940000          0.000000
C28          0.5560000          0.000000
C29          0.5000000          0.000000
C30          0.6120000          0.000000
C31          0.2040000          0.000000
C32          0.2890000          0.000000
C33          0.2990000          0.000000
C34          0.4170000          0.000000
C35          0.2230000          0.000000
C36          0.3730000          0.000000
LC           0.8900000          0.000000
UC           5.500000           0.000000
D            1.764800           0.000000
D1           0.2500000          0.000000
D2           0.1443000          0.000000
D3           0.1768000          0.000000
D4           0.1768000          0.000000
D5           0.1021000          0.000000
D6           0.4268000          0.000000
D7           0.4268000          0.000000
D8           0.3536000          0.000000
D9           0.3536000          0.000000
D10          0.3536000          0.000000
D11          0.3211000          0.000000
D12          0.3211000          0.000000
D13          0.2788000          0.000000
D14          0.3521000          0.000000
D15          0.000000           0.000000
D16          0.3211000          0.000000
D17          0.2464000          0.000000
D18          0.1768000          0.000000
D19          0.1021000          0.000000
D20          0.3521000          0.000000
D21          0.2464000          0.000000
D22          0.2788000          0.000000
D23          0.3211000          0.000000
D24          0.2464000          0.000000
D25          0.1443000          0.000000
D26          0.1021000          0.000000
D27          0.2464000          0.000000
```

```
D28          0.2041000           0.000000
D29          0.1854000           0.000000
D30          0.1854000           0.000000
D31          0.1443000           0.000000
D32          0.1443000           0.000000
D33          0.1443000           0.000000
D34          0.1443000           0.000000
D35          0.8330000E-01       0.000000
D36          0.2500000           0.000000
UD           2.310000            0.000000
KOC          1.372018           0.000000
E1           0.3536000           0.000000
E2           0.3536000           0.000000
E3           0.6036000           0.000000
E4           0.6036000           0.000000
E5           0.7071000           0.000000
E6           0.5000000           0.000000
E7           0.5000000           0.000000
E8           0.5000000           0.000000
E9           0.5000000           0.000000
E10          0.5000000           0.000000
E11          0.5000000           0.000000
E12          0.5000000           0.000000
E13          0.5000000           0.000000
E14          0.5000000           0.000000
E15          0.5000000           0.000000
E16          0.5000000           0.000000
E17          0.5000000           0.000000
E18          0.4541000           0.000000
E19          0.4979000           0.000000
E20          0.3943000           0.000000
E21          0.3943000           0.000000
E22          0.3943000           0.000000
E23          0.3943000           0.000000
E24          0.3943000           0.000000
E25          0.2041000           0.000000
E26          0.3485000           0.000000
E27          0.2887000           0.000000
E28          0.2887000           0.000000
E29          0.2887000           0.000000
E30          0.2887000           0.000000
E31          0.6036000           0.000000
E32          0.3536000           0.000000
E33          0.3536000           0.000000
E34          0.7071000           0.000000
E35          0.4979000           0.000000
E36          0.3536000           0.000000
F1           0.000000            0.000000
F2           0.000000            0.000000
F3           0.000000            0.000000
F4           0.000000            0.000000
F5           0.000000            0.000000
F6           0.000000            0.000000
```

```
F7           0.000000             0.000000
F8           0.000000             0.000000
F9           0.000000             0.000000
F10          0.000000             0.000000
F11          0.000000             0.000000
F12          0.000000             0.000000
F13          0.000000             0.000000
F14          0.000000             0.000000
F15          0.4590000E-01        0.000000
F16          0.4590000E-01        0.000000
F17          0.4590000E-01        0.000000
F18          0.1494000            0.000000
F19          0.1057000            0.000000
F20          0.1057000            0.000000
F21          0.1057000            0.000000
F22          0.1057000            0.000000
F23          0.1057000            0.000000
F24          0.1515000            0.000000
F25          0.1494000            0.000000
F26          0.2551000            0.000000
F27          0.2113000            0.000000
F28          0.2113000            0.000000
F29          0.2113000            0.000000
F30          0.2378000            0.000000
F31          0.1953000            0.000000
F32          0.1494000            0.000000
F33          0.1494000            0.000000
F34          0.1494000            0.000000
F35          0.2816000            0.000000
F36          0.000000             0.000000
G1           0.000000             0.000000
G2           0.000000             0.000000
G3           0.000000             0.000000
G4           0.000000             0.000000
G5           0.000000             0.000000
G6           0.000000             0.000000
G7           0.000000             0.000000
G8           0.000000             0.000000
G9           0.000000             0.000000
G10          0.000000             0.000000
G11          0.000000             0.000000
G12          0.000000             0.000000
G13          0.000000             0.000000
G14          0.000000             0.000000
G15          0.000000             0.000000
G16          0.000000             0.000000
G17          0.000000             0.000000
G18          0.000000             0.000000
G19          0.000000             0.000000
G20          0.000000             0.000000
G21          0.000000             0.000000
G22          0.000000             0.000000
G23          0.000000             0.000000
```

```
G24          0.000000            0.000000
G25          0.4227000           0.000000
G26          0.2989000           0.000000
G27          0.2989000           0.000000
G28          0.2989000           0.000000
G29          0.2989000           0.000000
G30          0.2989000           0.000000
G31          0.1298000           0.000000
G32          0.2929000           0.000000
G33          0.2929000           0.000000
G34          0.000000            0.000000
G35          0.1298000           0.000000
G36          0.000000            0.000000
LKOC         1.340000            0.000000
UKOC         2.340000            0.000000
H1           1.000000            0.000000
K            9.000000            0.000000
```

APPENDIX E: CASE STUDY IN CHAPTER 7

MATHEMATICAL FORMULATION

MAX-MIN AGGREGATION APPROACH

```
max=lamda;
lamda<=dssve;lamda<=dsrve;lamda<=dssmiu;
lamda<=dsrmiu;lamda<=dssr;lamda<=dsrr;

!Affinity of fungicide (annotated as ve);
ve=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x1
0+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x
18+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*
x26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34
*x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a4
2*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a
50*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+
a58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65;
!Upper and lower limits;
uve=1.42;
lve=1.10;
ve>dve;
ve<ave;
!Standard deviation;
sdve=0.1002;
!normalised shifted target property ranges;
!upper upper limit is annotated as a, upper lower limit is
annotated as b, lower upper limit is annotated as c, lower
lower limit is annotated as d;
ave=((uve+sdve)+0.2942)/0.5751;
bve=((uve-sdve)+0.2942)/0.5751;
cve=((lve+sdve)+0.2942)/0.5751;
dve=((lve-sdve)+0.2942)/0.5751;
!Degrees of satisfaction;
!dss stands for degree of satisfaction for property superiority,
dsr stands for degree of satisfaction for property robustness;
dssve=(ve-dve)/(ave-dve);
dsrve-((ave-ve)/(ave-bve))<0;
dsrve-((ve-dve)/(cve-dve))<0;
dsrve>0;
dsrve<1;
```

```
@free(uve);@free(lve);@free(sdve);@free(ave);@free(bve);@free(c
ve);@free(dve);

!Mobility of fungicide(annotated as miu);
miu=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x
10+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*
x18+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26
*x26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a3
4*x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a
42*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+
a50*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57
+a58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x6
5;
!Upper and lower limits;
umiu=0.1;
lmiu=-0.3;
miu>dmiu;
miu<amiu;
!Standard deviation;
sdmiu=0.1376;
!normalised shifted target property ranges;
dmiu=((umiu+sdmiu)-2.0143)/-0.6983;
cmiu=((umiu-sdmiu)-2.0143)/-0.6983;
bmiu=((lmiu+sdmiu)-2.0143)/-0.6983;
amiu=((lmiu-sdmiu)-2.0143)/-0.6983;
!Degrees of satisfaction;
dssmiu=(amiu-miu)/(amiu-dmiu);
dsrmiu-((amiu-miu)/(amiu-bmiu))<0;
dsrmiu-((miu-dmiu)/(cmiu-dmiu))<0;
dsrmiu>0;
dsrmiu<1;
@free(umiu);@free(lmiu);@free(sdmiu);@free(amiu);@free(bmiu);@f
ree(cmiu);@free(dmiu);

!Retention of fungicide(annotated as r);
r=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10
+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x1
8+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x
26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*
x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a42
*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a5
0*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+a
58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65;
!Upper and lower limits;
ur=0.5;
lr=-0.1;
r>dr;
r<ar;
!Standard deviation;
sdr=0.2269;
!normalised shifted target property ranges;
ar=((ur+sdr)+2)/0.787;
br=((ur-sdr)+2)/0.787;
```

```
cr=((lr+sdr)+2)/0.787;
dr=((lr-sdr)+2)/0.787;
!Degrees of satisfaction;
dssr=(r-dr)/(ar-dr);
dsrr-((ar-r)/(ar-br))<0;
dsrr-((r-dr)/(cr-dr))<0;
dsrr>0;
dsrr<1;
@free(ur);@free(lr);@free(sdr);@free(ar);@free(br);@free(cr);@f
ree(dr);

!Toxic limit concentration for fungicide (annotated as lc);
lc=b1*(x1+x2+x3)+b2*(x4+x5+x6+x7+x8+x9+x10+x11+x12)+b3*(x13+x14
+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x3
0+x31)-
b4*(x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46
+x47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x6
2+x63+x64+x65);
!Upper and lower limits;
lc<(-1*@log10(lcl))+sdlc;
lcl=0.001;
!Standard deviation;
sdlc=0.37;

!TI values;
a1=0.35355;a2=0.28868;a3=0.25000;a4=0.60355;a5=0.55768;a6=0.530
33;a7=0.50000;a8=0.45412;a9=0.42678;a10=0.35355;a11=0.40825;a12
=0.38090;a13=0.43301;a14=0.45534;a15=0.49280;a16=0.57735;a17=0.
47767;a18=0.51513;a19=0.59968;a20=0.55259;a21=0.63714;a22=0.721
69;a23=0.50000;a24=0.53746;a25=0.62201;a26=0.57491;a27=0.65947;
a28=0.74402;a29=0.61237;a30=0.69692;a31=0.78147;a32=0.50000;a33
=0.51934;a34=0.55178;a35=0.62500;a36=0.53868;a37=0.57111;a38=0.
64434;a39=0.60355;a40=0.67678;a41=0.75000;a42=0.53868;a43=0.571
11;a44=0.64434;a45=0.62289;a46=0.69611;a47=0.76934;a48=0.65533;
a49=0.72855;a50=0.80178;a51=0.87500;a52=0.57735;a53=0.60979;a54
=0.68301;a55=0.64223;a56=0.71545;a57=0.78868;a58=0.67467;a59=0.
74789;a60=0.82111;a61=0.89434;a62=0.70711;a63=0.78033;a64=0.853
55;a65=0.92678;

!contribution of molecular groups;
b1=0.6172;b2=0.4464;b3=0.1522;b4=0.1861;

!property constraints written as interval arithmetic;
(a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10+
a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x18
+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x2
6+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*x
34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a42*
x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a50
*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+a5
8*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65)>
2.455;
```

```
(a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10+
a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x18
+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x2
6+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*x
34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a42*
x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a50
*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+a5
8*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65)<
3.314;

!Integers constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x16);@GIN(
x17);@GIN(x18);@GIN(x19);@GIN(x20);@GIN(x21);@GIN(x22);@GIN(x23
);@GIN(x24);@GIN(x25);@GIN(x26);@GIN(x27);@GIN(x28);@GIN(x29);@
GIN(x30);@GIN(x31);@GIN(x35);@GIN(x36);@GIN(x37);@GIN(x38);@GIN
(x39);@GIN(x40);@GIN(x41);@GIN(x42);@GIN(x43);@GIN(x44);@GIN(x4
5);@GIN(x46);@GIN(x47);@GIN(x48);@GIN(x49);@GIN(x50);@GIN(x61);
@GIN(x64);@GIN(x65);@GIN(h1);@GIN(h2);@GIN(h3);

!Positive constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;x33>0;
x34>0;x35>0;x36>0;x37>0;x38>0;x39>0;x40>0;x41>0;x42>0;x43>0;x44
>0;x45>0;x46>0;x47>0;x48>0;x49>0;x50>0;x51>0;x52>0;x53>0;x54>0;
x55>0;x56>0;x57>0;x58>0;x59>0;x60>0;x61>0;x62>0;x63>0;x64>0;x65
>0;

!Consistency equations;
x4+2*x7+x8+x9=2*h1;
x14+x18+x19+x26+x27+x28+((2)*(x17+x24+x25))+((3)*(x23))=2*h2;
4*x32+((3)*(x33+x34+x35))+2*(x36+x37+x38+x39+x40+x41)+x42+x43+x
44+x45+x46+x47+x48+x49+x50+x51=2*h3;

x1=x4+x5+x6;
x2=x16+x19+x21+2*x22+x25+x27+2*x28+x30+2*x31;
x3=x35+x38+x40+2*x41+x44+x46+2*x47+x49+2*x50+3*x51+x54+x56+2*x5
7+x59+2*x60+3*x61+x63+2*x64+3*x65;
x5+x8+2*x11+x12=x15+x18+2*x20+x21+x24+2*x26+x27+3*x29+2*x30+x31;
x6+x9+2*x10+x12=x34+x37+2*x39+x40+x43+2*x45+x46+3*x48+2*x49+x50
+x53+2*x55+3*x58+2*x59+x60+4*x62+3*x63+2*x64+x65;
3*x13+2*x14+2*x15+2*x16+x17+x18+x19+x20+x21+x22=x33+2*x36+x37+x
38+3*x42+2*x43+2*x44+x45+x46+x47+4*x52+3*x53+3*x54+2*x55+2*x56+
2*x57+x58+x59+x60+x61;
!handshaking lemma;
(x1+x2+x3)+2*(x4+x5+x6+x7+x8+x9+x10+x11+x12)+3*(x13+x14+x15+x16
+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x31)+4
*(x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x
47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x62+
x63+x64+x65)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x1
5+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x
31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+
```

```
x47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x62
+x63+x64+x65-1)*2;

!handshaking dilemma;
2*x11<(x15+x18+x20+x21+x24+x26+x27+x29+x30+x31);
2*x10<(x34+x37+x39+x40+x43+x45+x46+x48+x49+x50+x53+x55+x56+x58+
x59+x60+x62+x63+x64+x65);
3*x13<x33+x36+x37+x38+x42+x43+x44+x45+x46+x47+x52+x53+x54+x55+x
56+x57+x58+x59+x60+x61;
2*(x14+x15+x16)<x33+x36+x37+x38+x42+x43+x44+x45+x46+x47+x52+x53
+x54+x55+x56+x57+x58+x59+x60+x61;
x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51>4*x32;
x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51> 3*(x33+x34+x35);
x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51>2*(x36+x37+x38+x39+x40+x41);
(x14+x17+x18+x19+x23+x24+x25+x26+x27+x28)>3*x23;
(x14+x17+x18+x19+x23+x24+x25+x26+x27+x28)>2*(x17+x24+x25);
x4+x7+x8+x9>2*x7;

end
```

TWO-PHASE APPROACH

```
max=lamda;
lamda=dssve+dsrve+dssmiu+dsrmiu+dssr+dsrr;

!Affinity of fungicide (annotated as ve);
ve=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x1
0+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x
18+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*
x26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34
*x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a4
2*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a
50*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+
a58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65;
!Upper and lower limits;
uve=1.42;
lve=1.10;
ve>dve;
ve<ave;
!Standard deviation;
sdve=0.1002;
!normalised shifted target property ranges;
!upper upper limit is annotated as a, upper lower limit is
annotated as b, lower upper limit is annotated as c, lower
lower limit is annotated as d;
ave=((uve+sdve)+0.2942)/0.5751;
bve=((uve-sdve)+0.2942)/0.5751;
cve=((lve+sdve)+0.2942)/0.5751;
dve=((lve-sdve)+0.2942)/0.5751;
!Degrees of satisfaction;
!dss stands for degree of satisfaction for property superiority,
dsr stands for degree of satisfaction for property robustness;
dssve=(ve-dve)/(ave-dve);
dsrve-((ave-ve)/(ave-bve))<0;
dsrve-((ve-dve)/(cve-dve))<0;
dsrve>0;
dsrve<1;
@free(uve);@free(lve);@free(sdve);@free(ave);@free(bve);@free(c
ve);@free(dve);

!Mobility of fungicide(annotated as miu);
miu=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x
10+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*
x18+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26
*x26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a3
4*x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a
42*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+
```

```
a50*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57
+a58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x6
5;
!Upper and lower limits;
umiu=0.1;
lmiu=-0.3;
miu>dmiu;
miu<amiu;
!Standard deviation;
sdmiu=0.1376;
!normalised shifted target property ranges;
dmiu=((umiu+sdmiu)-2.0143)/-0.6983;
cmiu=((umiu-sdmiu)-2.0143)/-0.6983;
bmiu=((lmiu+sdmiu)-2.0143)/-0.6983;
amiu=((lmiu-sdmiu)-2.0143)/-0.6983;
!Degrees of satisfaction;
dssmiu=(amiu-miu)/(amiu-dmiu);
dsrmiu-((amiu-miu)/(amiu-bmiu))<0;
dsrmiu-((miu-dmiu)/(cmiu-dmiu))<0;
dsrmiu>0;
dsrmiu<1;
@free(umiu);@free(lmiu);@free(sdmiu);@free(amiu);@free(bmiu);@f
ree(cmiu);@free(dmiu);

!Retention of fungicide(annotated as r);
r=a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10
+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x1
8+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x
26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*
x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a42
*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a5
0*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+a
58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65;
!Upper and lower limits;
ur=0.5;
lr=-0.1;
r>dr;
r<ar;
!Standard deviation;
sdr=0.2269;
!normalised shifted target property ranges;
ar=((ur+sdr)+2)/0.787;
br=((ur-sdr)+2)/0.787;
cr=((lr+sdr)+2)/0.787;
dr=((lr-sdr)+2)/0.787;
!Degrees of satisfaction;
dssr=(r-dr)/(ar-dr);
dsrr-((ar-r)/(ar-br))<0;
dsrr-((r-dr)/(cr-dr))<0;
dsrr>0;
dsrr<1;
@free(ur);@free(lr);@free(sdr);@free(ar);@free(br);@free(cr);@f
ree(dr);
```

```
!Toxic limit concentration for fungicide (annotated as lc);
lc=b1*(x1+x2+x3)+b2*(x4+x5+x6+x7+x8+x9+x10+x11+x12)+b3*(x13+x14
+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x3
0+x31)-
b4*(x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46
+x47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x6
2+x63+x64+x65);
!Upper and lower limits;
lc<(-1*@log10(lcl))+sdlc;
lcl=0.001;
!Standard deviation;
sdlc=0.37;

!TI values;
a1=0.35355;a2=0.28868;a3=0.25000;a4=0.60355;a5=0.55768;a6=0.530
33;a7=0.50000;a8=0.45412;a9=0.42678;a10=0.35355;a11=0.40825;a12
=0.38090;a13=0.43301;a14=0.45534;a15=0.49280;a16=0.57735;a17=0.
47767;a18=0.51513;a19=0.59968;a20=0.55259;a21=0.63714;a22=0.721
69;a23=0.50000;a24=0.53746;a25=0.62201;a26=0.57491;a27=0.65947;
a28=0.74402;a29=0.61237;a30=0.69692;a31=0.78147;a32=0.50000;a33
=0.51934;a34=0.55178;a35=0.62500;a36=0.53868;a37=0.57111;a38=0.
64434;a39=0.60355;a40=0.67678;a41=0.75000;a42=0.53868;a43=0.571
11;a44=0.64434;a45=0.62289;a46=0.69611;a47=0.76934;a48=0.65533;
a49=0.72855;a50=0.80178;a51=0.87500;a52=0.57735;a53=0.60979;a54
=0.68301;a55=0.64223;a56=0.71545;a57=0.78868;a58=0.67467;a59=0.
74789;a60=0.82111;a61=0.89434;a62=0.70711;a63=0.78033;a64=0.853
55;a65=0.92678;

!contribution of molecular groups;
b1=0.6172;b2=0.4464;b3=0.1522;b4=0.1861;
!property constraints written as interval arithmetic;
(a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10+
a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x18
+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x2
6+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*x
34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a42*
x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a50
*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+a5
8*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65)>
2.455;

(a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x10+
a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*x18
+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26*x2
6+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a34*x
34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a42*
x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+a50
*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57+a5
8*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x65)<
3.314;

!Integers constraints;
```

```
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x16);@GIN(
x17);@GIN(x18);@GIN(x19);@GIN(x20);@GIN(x21);@GIN(x22);@GIN(x23
);@GIN(x24);@GIN(x25);@GIN(x26);@GIN(x27);@GIN(x28);@GIN(x29);@
GIN(x30);@GIN(x31);@GIN(x35);@GIN(x36);@GIN(x37);@GIN(x38);@GIN
(x39);@GIN(x40);@GIN(x41);@GIN(x42);@GIN(x43);@GIN(x44);@GIN(x4
5);@GIN(x46);@GIN(x47);@GIN(x48);@GIN(x49);@GIN(x50);
@GIN(x61);@GIN(x64);@GIN(x65);@GIN(h1);@GIN(h2);@GIN(h3);

!Positive constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;x33>0;
x34>0;x35>0;x36>0;x37>0;x38>0;x39>0;x40>0;x41>0;x42>0;x43>0;x44
>0;x45>0;x46>0;x47>0;x48>0;x49>0;x50>0;x51>0;x52>0;x53>0;x54>0;
x55>0;x56>0;x57>0;x58>0;x59>0;x60>0;x61>0;x62>0;x63>0;x64>0;x65
>0;

!Consistency equations;
x4+2*x7+x8+x9=2*h1;
x14+x18+x19+x26+x27+x28+((2)*(x17+x24+x25))+(( 3)*(x23))=2*h2;
4*x32+((3)*(x33+x34+x35))+2*(x36+x37+x38+x39+x40+x41)+x42+x43+x
44+x45+x46+x47+x48+x49+x50+x51=2*h3;

x1=x4+x5+x6;
x2=x16+x19+x21+2*x22+x25+x27+2*x28+x30+2*x31;
x3=x35+x38+x40+2*x41+x44+x46+2*x47+x49+2*x50+3*x51+x54+x56+2*x5
7+x59+2*x60+3*x61+x63+2*x64+3*x65;
x5+x8+2*x11+x12=x15+x18+2*x20+x21+x24+2*x26+x27+3*x29+2*x30+x31;
x6+x9+2*x10+x12=x34+x37+2*x39+x40+x43+2*x45+x46+3*x48+2*x49+x50
+x53+2*x55+3*x58+2*x59+x60+4*x62+3*x63+2*x64+x65;
3*x13+2*x14+2*x15+2*x16+x17+x18+x19+x20+x21+x22=x33+2*x36+x37+x
38+3*x42+2*x43+2*x44+x45+x46+x47+4*x52+3*x53+3*x54+2*x55+2*x56+
2*x57+x58+x59+x60+x61;

!handshaking lemma;
(x1+x2+x3)+2*(x4+x5+x6+x7+x8+x9+x10+x11+x12)+3*(x13+x14+x15+x16
+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x31)+4
*(x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x
47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x62+
x63+x64+x65)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x1
5+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x
31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+
x47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x62
+x63+x64+x65-1)*2;

!handshaking dilemma;
2*x11<(x15+x18+x20+x21+x24+x26+x27+x29+x30+x31);
2*x10<(x34+x37+x39+x40+x43+x45+x46+x48+x49+x50+x53+x55+x56+x58+
x59+x60+x62+x63+x64+x65);
3*x13<x33+x36+x37+x38+x42+x43+x44+x45+x46+x47+x52+x53+x54+x55+x
56+x57+x58+x59+x60+x61;
```

```
2*(x14+x15+x16)<x33+x36+x37+x38+x42+x43+x44+x45+x46+x47+x52+x53
+x54+x55+x56+x57+x58+x59+x60+x61;
x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51>4*x32;
x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51> 3*(x33+x34+x35);
x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51>2*(x36+x37+x38+x39+x40+x41);
(x14+x17+x18+x19+x23+x24+x25+x26+x27+x28)>3*x23;
(x14+x17+x18+x19+x23+x24+x25+x26+x27+x28)>2*(x17+x24+x25);
x4+x7+x8+x9>2*x7;

end
```

RESULTS

MAX-MIN AGGREGATION APPROACH

```
Global optimal solution found.
Objective value:                              0.5887032
Objective bound:                              0.5887032
Infeasibilities:                               0.000000
Extended solver steps:                               38
Total solver iterations:                           1219

Model Class:                                       MILP

Total variables:                    84
Nonlinear variables:                 0
Integer variables:                  50

Total constraints:                 122
Nonlinear constraints:               0

Total nonzeros:                    925
Nonlinear nonzeros:                  0

Variable      Value               Reduced Cost
OF            0.5887032           0.000000
LAMDA         0.5887032           0.000000
DSSVE         0.7339670           0.000000
DSRVE         0.5887032           0.000000
DSSMIU        0.6174676           0.000000
DSRMIU        0.5887032           0.000000
DSSR          0.5887032           0.000000
DSRR          0.5887032           0.000000
VE            2.914200            0.000000
A1            0.3535500           0.000000
X1            2.000000            -0.2640386
A2            0.2886800           0.000000
X2            0.000000            -0.2155923
A3            0.2500000           0.000000
X3            0.000000            -0.6491551
A4            0.6035500           0.000000
X4            2.000000            -0.4507438
A5            0.5576800           0.000000
X5            0.000000            -1.143834
A6            0.5303300           0.000000
X6            0.000000            -0.5999454
A7            0.5000000           0.000000
```

```
X7            2.000000            -0.3734105
A8            0.4541200           0.000000
X8            0.000000            -1.066494
A9            0.4267800           0.000000
X9            0.000000            -0.5226121
A10           0.3535500           0.000000
X10           0.000000            -0.6718062
A11           0.4082500           0.000000
X11           0.000000            -1.759584
A12           0.3809000           0.000000
X12           0.000000            -1.215695
A13           0.4330100           0.000000
X13           0.000000            0.000000
A14           0.4553400           0.000000
X14           0.000000            0.000000
A15           0.4928000           0.000000
X15           0.000000            0.000000
A16           0.5773500           0.000000
X16           0.000000            -0.7904910
A17           0.4776700           0.000000
X17           0.000000            0.8623518
A18           0.5151300           0.000000
X18           0.000000            0.8623518
A19           0.5996800           0.000000
X19           0.000000            0.7186078E-01
A20           0.5525900           0.000000
X20           0.000000            0.8623518
A21           0.6371400           0.000000
X21           0.000000            0.7186078E-01
A22           0.7216900           0.000000
X22           0.000000            -0.7186302
A23           0.5000000           0.000000
X23           0.000000            1.724704
A24           0.5374600           0.000000
X24           0.000000            1.724704
A25           0.6220100           0.000000
X25           0.000000            0.9342125
A26           0.5749100           0.000000
X26           0.000000            1.724711
A27           0.6594700           0.000000
X27           0.000000            0.9342125
A28           0.7440200           0.000000
X28           0.000000            0.1437216
A29           0.6123700           0.000000
X29           0.000000            1.724711
A30           0.6969200           0.000000
X30           0.000000            0.9342200
A31           0.7814700           0.000000
X31           0.000000            0.1437290
A32           0.5000000           0.000000
X32           0.000000            0.000000
A33           0.5193400           0.000000
X33           0.000000            0.000000
```

```
A34          0.5517800           0.000000
X34          0.000000            0.2874506
A35          0.6250000           0.000000
X35          0.000000            0.4913344
A36          0.5386800           0.000000
X36          0.000000            -0.1829272
A37          0.5711100           0.000000
X37          0.000000            -0.1829197
A38          0.6443400           0.000000
X38          0.000000            0.2095663E-01
A39          0.6035500           0.000000
X39          0.000000            0.1045309
A40          0.6767800           0.000000
X40          0.000000            0.3084072
A41          0.7500000           0.000000
X41          0.000000            0.5122910
A42          0.5386800           0.000000
X42          0.000000            -0.1162219
A43          0.5711100           0.000000
X43          0.000000            -0.1162145
A44          0.6443400           0.000000
X44          0.000000            0.8766185E-01
A45          0.6228900           0.000000
X45          0.000000            -0.1306580
A46          0.6961100           0.000000
X46          0.000000            0.7322580E-01
A47          0.7693400           0.000000
X47          0.000000            0.2771021
A48          0.6553300           0.000000
X48          0.000000            0.1567926
A49          0.7285500           0.000000
X49          0.000000            0.3606764
A50          0.8017800           0.000000
X50          0.000000            0.5645527
A51          0.8750000           0.000000
X51          0.000000            0.7684365
A52          0.5773500           0.000000
X52          0.000000            0.000000
A53          0.6097900           0.000000
X53          0.000000            0.000000
A54          0.6830100           0.000000
X54          0.000000            0.2038838
A55          0.6422300           0.000000
X55          0.000000            0.000000
A56          0.7154500           0.000000
X56          0.000000            0.000000
A57          0.7886800           0.000000
X57          0.000000            0.4077601
A58          0.6746700           0.000000
X58          0.000000            0.000000
A59          0.7478900           0.000000
X59          0.000000            0.2038838
A60          0.8211100           0.000000
```

```
X60          0.000000            0.4077676
A61          0.8943400           0.000000
X61          0.000000            0.6116439
A62          0.7071100           0.000000
X62          0.000000            0.2874506
A63          0.7803300           0.000000
X63          0.000000            0.4913344
A64          0.8535500           0.000000
X64          0.000000            0.6952182
A65          0.9267800           0.000000
X65          0.000000            0.8990945
UVE          1.420000            0.000000
LVE          1.100000            0.000000
DVE          2.250043            0.000000
AVE          3.154930            0.000000
SDVE         0.1002000           0.000000
BVE          2.806468            0.000000
CVE          2.598505            0.000000
MIU          2.914200            0.000000
UMIU         0.1000000           0.000000
LMIU         -0.3000000          0.000000
DMIU         2.544322            0.000000
AMIU         3.511242            0.000000
SDMIU        0.1376000           0.000000
CMIU         2.938422            0.000000
BMIU         3.117142            0.000000
R            2.914200            0.000000
UR           0.5000000           0.000000
LR           -0.1000000          0.000000
DR           2.125921            0.000000
AR           3.464930            0.000000
SDR          0.2269000           0.000000
BR           2.888310            0.000000
CR           2.702541            0.000000
LC           3.020000            0.000000
B1           0.6172000           0.000000
B2           0.4464000           0.000000
B3           0.1522000           0.000000
B4           0.1861000           0.000000
LCL          0.1000000E-02       0.000000
SDLC         0.3700000           0.000000
H1           3.000000            0.000000
H2           0.000000            -1.398743
H3           0.000000            -0.2259034
K            6.000000            0.000000
```

TWO-PHASE APPROACH

```
Global optimal solution found.
Objective value:                                  4.524613
Objective bound:                                  4.524613
Infeasibilities:                                  0.000000
Extended solver steps:                                  62
Total solver iterations:                              1639

Model Class:                                          MILP

Total variables:                    83
Nonlinear variables:                 0
Integer variables:                  50

Total constraints:                 116
Nonlinear constraints:               0

Total nonzeros:                    918
Nonlinear nonzeros:                  0

Variable      Value               Reduced Cost
LAMDA         4.524613            0.000000
DSSVE         0.7339670           0.000000
DSRVE         0.6908362           0.000000
DSSMIU        0.6174676           0.000000
DSRMIU        0.9385387           0.000000
DSSR          0.5887032           0.000000
DSRR          0.9551005           0.000000
VE            2.914200            0.000000
A1            0.3535500           0.000000
X1            2.000000            0.4415334
A2            0.2886800           0.000000
X2            0.000000            0.3605200
A3            0.2500000           0.000000
X3            0.000000            0.3122142
A4            0.6035500           0.000000
X4            2.000000            0.7537476
A5            0.5576800           0.000000
X5            0.000000            0.9513875
A6            0.5303300           0.000000
X6            0.000000            0.6623063
A7            0.5000000           0.000000
X7            2.000000            0.6244285
A8            0.4541200           0.000000
X8            0.000000            0.8220559
A9            0.4267800           0.000000
```

```
X9             0.000000            0.5329872
A10            0.3535500           0.000000
X10            0.000000            0.4415334
A11            0.4082500           0.000000
X11            0.000000            1.019696
A12            0.3809000           0.000000
X12            0.000000            0.7306146
A13            0.4330100           0.000000
X13            0.000000            0.000000
A14            0.4553400           0.000000
X14            0.000000            0.000000
A15            0.4928000           0.000000
X15            0.000000            0.000000
A16            0.5773500           0.000000
X16            0.000000            0.3605159
A17            0.4776700           0.000000
X17            0.000000            0.000000
A18            0.5151300           0.000000
X18            0.000000            0.000000
A19            0.5996800           0.000000
X19            0.000000            0.3605159
A20            0.5525900           0.000000
X20            0.000000            0.000000
A21            0.6371400           0.000000
X21            0.000000            0.3605159
A22            0.7216900           0.000000
X22            0.000000            0.7210317
A23            0.5000000           0.000000
X23            0.000000            0.000000
A24            0.5374600           0.000000
X24            0.000000            0.000000
A25            0.6220100           0.000000
X25            0.000000            0.3605159
A26            0.5749100           0.000000
X26            0.000000            -0.1248857E-04
A27            0.6594700           0.000000
X27            0.000000            0.3605159
A28            0.7440200           0.000000
X28            0.000000            0.7210317
A29            0.6123700           0.000000
X29            0.000000            -0.1248857E-04
A30            0.6969200           0.000000
X30            0.000000            0.3605034
A31            0.7814700           0.000000
X31            0.000000            0.7210192
A32            0.5000000           0.000000
X32            0.000000            0.6244285
A33            0.5193400           0.000000
X33            0.000000            0.8288372
A34            0.5517800           0.000000
X34            0.000000            0.6890943
A35            0.6250000           0.000000
X35            0.000000            0.7805356
```

```
A36           0.5386800           0.000000
X36           0.000000            1.033246
A37           0.5711100           0.000000
X37           0.000000            0.8934905
A38           0.6443400           0.000000
X38           0.000000            0.9849443
A39           0.6035500           0.000000
X39           0.000000            0.7537476
A40           0.6767800           0.000000
X40           0.000000            0.8452014
A41           0.7500000           0.000000
X41           0.000000            0.9366427
A42           0.5386800           0.000000
X42           0.000000            1.213502
A43           0.5711100           0.000000
X43           0.000000            1.073746
A44           0.6443400           0.000000
X44           0.000000            1.165200
A45           0.6228900           0.000000
X45           0.000000            0.9581563
A46           0.6961100           0.000000
X46           0.000000            1.049598
A47           0.7693400           0.000000
X47           0.000000            1.141051
A48           0.6553300           0.000000
X48           0.000000            0.8184134
A49           0.7285500           0.000000
X49           0.000000            0.9098547
A50           0.8017800           0.000000
X50           0.000000            1.001308
A51           0.8750000           0.000000
X51           0.000000            1.092750
A52           0.5773500           0.000000
X52           0.000000            1.442051
A53           0.6097900           0.000000
X53           0.000000            1.302308
A54           0.6830100           0.000000
X54           0.000000            1.393749
A55           0.6422300           0.000000
X55           0.000000            1.162565
A56           0.7154500           0.000000
X56           0.000000            1.254006
A57           0.7886800           0.000000
X57           0.000000            1.345460
A58           0.6746700           0.000000
X58           0.000000            1.022822
A59           0.7478900           0.000000
X59           0.000000            1.114263
A60           0.8211100           0.000000
X60           0.000000            1.205705
A61           0.8943400           0.000000
X61           0.000000            1.297159
A62           0.7071100           0.000000
```

```
X62          0.000000            0.8830792
A63          0.7803300           0.000000
X63          0.000000            0.9745205
A64          0.8535500           0.000000
X64          0.000000            1.065962
A65          0.9267800           0.000000
X65          0.000000            1.157416
UVE          1.420000            0.000000
LVE          1.100000            0.000000
DVE          2.250043            0.000000
AVE          3.154930            0.000000
SDVE         0.1002000           0.000000
BVE          2.806468            0.000000
CVE          2.598505            0.000000
MIU          2.914200            0.000000
UMIU         0.1000000           0.000000
LMIU         -0.3000000          0.000000
DMIU         2.544322            0.000000
AMIU         3.511242            0.000000
SDMIU        0.1376000           0.000000
CMIU         2.938422            0.000000
BMIU         3.117142            0.000000
R            2.914200            0.000000
UR           0.5000000           0.000000
LR           -0.1000000          0.000000
DR           2.125921            0.000000
AR           3.464930            0.000000
SDR          0.2269000           0.000000
BR           2.888310            0.000000
CR           2.702541            0.000000
LC           3.020000            0.000000
B1           0.6172000           0.000000
B2           0.4464000           0.000000
B3           0.1522000           0.000000
B4           0.1861000           0.000000
LCL          0.1000000E-02       0.000000
SDLC         0.3700000           0.000000
H1           3.000000            0.000000
H2           0.000000            0.4162856
H3           0.000000            0.000000
K            6.000000            0.000000
```

APPENDIX F: CASE STUDY IN CHAPTER 8

MATHEMATICAL FORMULATION

DESIGN OF ADDICTIVE ALKANE

```
max=HHV;

!Heat of vaporisation (annotated as H);
H=((hvc1*(x1+x2+x3))+(hvc2*(x4+x5+x6+x7+x8+x9+x10+x11+x12))+(hv
c3*(x13+x14+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27
+x28+x29+x30+x31))+(hvc4*(x32+x33+x34+x35+x36+x37+x38+x39+x40+x
41+x42+x43+x44+x45+x46+x47+x48+x49+x50+x51+x52+x53+x54+x55+x56+
x57+x58+x59+x60+x61+x62+x63+x64+x65)));
!Property target range;
LH=28.267;
UH=38.267;
H>LH;
H<UH;
hvc1=0.217;hvc2=4.910;hvc3=7.962;hvc4=10.730;
@free(hvc1);@free(hvc2);@free(hvc3);@free(hvc4);

!Higher heating value (annotated as HHV);
HHV=((hhvc1*(x1+x2+x3))+(hhvc2*(x4+x5+x6+x7+x8+x9+x10+x11+x12))
+(hhvc3*(x13+x14+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x2
6+x27+x28+x29+x30+x31))+(hhvc4*(x32+x33+x34+x35+x36+x37+x38+x39
+x40+x41+x42+x43+x44+x45+x46+x47+x48+x49+x50+x51+x52+x53+x54+x5
5+x56+x57+x58+x59+x60+x61+x62+x63+x64+x65)));
!Property target range;
LHHV=5853.174;
UHHV=6853.174;
HHV>LHHV;
HHV<UHHV;
hhvc1=710.6822;hhvc2=652.8408;hhvc3=580.8447;hhvc4=525.2059;
@free(hhvc1);@free(hhvc2);@free(hhvc3);@free(hhvc4);

!Dynamic viscosity (annotated as DV);
DV=((dvc1*(x1+x2+x3))+(dvc2*(x4+x5+x6+x7+x8+x9+x10+x11+x12))+(d
vc3*(x13+x14+x15+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x2
7+x28+x29+x30+x31))+(dvc4*(x32+x33+x34+x35+x36+x37+x38+x39+x40+
x41+x42+x43+x44+x45+x46+x47+x48+x49+x50+x51+x52+x53+x54+x55+x56
+x57+x58+x59+x60+x61+x62+x63+x64+x65)));
```

```
!Property target range;
LDV=-0.9162;
UDV=0.0953;
DV>LDV;
DV<UDV;
dvc1=-1.0278;dvc2=0.2125;dvc3=1.318;dvc4=2.8147;
@free(dvc1);@free(dvc2);@free(dvc3);@free(dvc4);@free(DV);

!LC50;
LC=(a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x
10+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+a17*x17+a18*
x18+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24+a25*x25+a26
*x26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x32+a33*x33+a3
4*x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40+a41*x41+a
42*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x48+a49*x49+
a50*x50+a51*x51+a52*x52+a53*x53+a54*x54+a55*x55+a56*x56+a57*x57
+a58*x58+a59*x59+a60*x60+a61*x61+a62*x62+a63*x63+a64*x64+a65*x6
5);
!Property target range;
LLC=3.85;
ULC=4.63;
LC>LLC;
LC<ULC;

!Molecular weight (annotated as MW);
MW=mwx1*x1+mwx2*x2+mwx3*x3+mwx4*x4+mwx5*x5+mwx6*x6+mwx7*x7+mwx8
*x8+mwx9*x9+mwx10*x10+mwx11*x11+mwx12*x12+mwx13*x13+mwx14*x14+m
wx15*x15+mwx16*x16+mwx17*x17+mwx18*x18+mwx19*x19+mwx20*x20+mwx2
1*x21+mwx22*x22+mwx23*x23+mwx24*x24+mwx25*x25+mwx26*x26+mwx27*x
27+mwx28*x28+mwx29*x29+mwx30*x30+mwx31*x31+mwx32*x32+mwx33*x33+
mwx34*x34+mwx35*x35+mwx36*x36+mwx37*x37+mwx38*x38+mwx39*x39+mwx
40*x40+mwx41*x41+mwx42*x42+mwx43*x43+mwx44*x44+mwx45*x45+mwx46*
x46+mwx47*x47+mwx48*x48+mwx49*x49+mwx50*x50+mwx51*x51+mwx52*x52
+mwx53*x53+mwx54*x54+mwx55*x55+mwx56*x56+mwx57*x57+mwx58*x58+mw
x59*x59+mwx60*x60+mwx61*x61+mwx62*x62+mwx63*x63+mwx64*x64+mwx65
*x65;

mwx1=15;mwx2=15;mwx3=15;mwx4=14;mwx5=14;mwx6=14;mwx7=14;mwx8=14
;mwx9=14;mwx10=14;mwx11=14;mwx12=14;mwx13=13;mwx14=12;mwx15=12;
mwx16=13;mwx17=13;mwx18=13;mwx19=13;mwx20=13;mwx21=13;mwx22=13;
mwx23=13;mwx24=13;
mwx25=13;mwx26=13;mwx27=13;mwx28=13;mwx29=13;mwx30=13;mwx31=13;
mwx32=12;mwx33=12;mwx34=12;mwx35=12;mwx36=12;mwx37=12;mwx38=12;
mwx39=12;mwx40=12;mwx41=12;mwx42=12;mwx43=12;mwx44=12;mwx45=12;
mwx46=12;mwx47=12;mwx48=12;mwx49=12;mwx50=12;mwx51=12;mwx52=12;
mwx53=12;mwx54=12;mwx55=12;mwx56=12;mwx57=12;mwx58=12;mwx59=12;
mwx60=12;mwx61=12;mwx62=12;mwx63=12;mwx64=12;mwx65=12;


!TI values;
a1=0.35355;a2=0.28868;a3=0.25000;a4=0.60355;a5=0.55768;a6=0.530
33;a7=0.50000;a8=0.45412;a9=0.42678;a10=0.35355;a11=0.40825;a12
=0.38090;a13=0.43301;a14=0.45534;a15=0.49280;a16=0.57735;a17=0.
```

```
47767;a18=0.51513;a19=0.59968;a20=0.55259;a21=0.63714;a22=0.721
69;a23=0.50000;a24=0.53746;a25=0.62201;a26=0.57491;a27=0.65947;
a28=0.74402;a29=0.61237;a30=0.69692;a31=0.78147;a32=0.50000;a33
=0.51934;a34=0.55178;a35=0.62500;a36=0.53868;a37=0.57111;a38=0.
64434;a39=0.60355;a40=0.67678;a41=0.75000;a42=0.53868;a43=0.571
11;a44=0.64434;a45=0.62289;a46=0.69611;a47=0.76934;a48=0.65533;
a49=0.72855;a50=0.80178;a51=0.87500;a52=0.57735;a53=0.60979;a54
=0.68301;a55=0.64223;a56=0.71545;a57=0.78868;a58=0.67467;a59=0.
74789;a60=0.82111;a61=0.89434;a62=0.70711;a63=0.78033;a64=0.853
55;a65=0.92678;

!Integers constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x13);@GIN(
x14);@GIN(x15);@GIN(x16);@GIN(x17);@GIN(x18);@GIN(x19);@GIN(x20
);@GIN(x21);@GIN(x22);@GIN(x23);@GIN(x24);@GIN(x25);@GIN(x26);@
GIN(x27);@GIN(x28);@GIN(x29);@GIN(x30);@GIN(x31);@GIN(x32);@GIN
(x33);@GIN(x34);@GIN(x35);@GIN(x36);@GIN(x37);@GIN(x38);@GIN(x3
9);@GIN(x40);@GIN(x41);@GIN(x42);@GIN(x43);@GIN(x44);@GIN(x45);
@GIN(x46);@GIN(x47);@GIN(x48);@GIN(x49);@GIN(x50);@GIN(x51);@GI
N(x52);@GIN(x53);@GIN(x54);@GIN(x55);@GIN(x56);@GIN(x57);@GIN(x
58);@GIN(x59);@GIN(x60);
@GIN(x61);@GIN(x62);@GIN(x63);@GIN(x64);@GIN(x65);@GIN(loc1);@G
IN(loc2);@GIN(loc3);

!Positive constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;x33>0;
x34>0;x35>0;x36>0;x37>0;x38>0;x39>0;x40>0;x41>0;x42>0;x43>0;x44
>0;x45>0;x46>0;x47>0;x48>0;x49>0;x50>0;x51>0;x52>0;x53>0;x54>0;
x55>0;x56>0;x57>0;x58>0;x59>0;x60>0;x61>0;x62>0;x63>0;x64>0;x65
>0;

!Consistency equations;
x4+2*x7+x8+x9=2*loc1;
x14+x18+x19+x26+x27+x28+((2)*(x17+x24+x25))+(( 3)*(x23))=2*loc2;
4*x32+((3)*(x33+x34+x35))+2*(x36+x37+x38+x39+x40+x41)+x42+x43+x
44+x45+x46+x47+x48+x49+x50+x51=2*loc3;

x1=x4+x5+x6;
x2=x16+x19+x21+2*x22+x25+x27+2*x28+x30+2*x31;
x3=x35+x38+x40+2*x41+x44+x46+2*x47+x49+2*x50+3*x51+x54+x56+2*x5
7+x59+2*x60+3*x61+x63+2*x64+3*x65;
x5+x8+2*x11+x12=x15+x18+2*x20+x21+x24+2*x26+x27+3*x29+2*x30+x31;
x6+x9+2*x10+x12=x34+x37+2*x39+x40+x43+2*x45+x46+3*x48+2*x49+x50
+x53+2*x55+3*x58+2*x59+x60+4*x62+3*x63+2*x64+x65;
3*x13+2*x14+2*x15+2*x16+x17+x18+x19+x20+x21+x22=x33+2*x36+x37+x
38+
3*x42+2*x43+2*x44+x45+x46+x47+4*x52+3*x53+3*x54+2*x55+2*x56+2*x
57+x58+x59+x60+x61;

!handshaking lemma;
```

```
(x1+x2+x3)+2*(x4+x5+x6+x7+x8+x9+x10+x11+x12)+3*(x13+x14+x15+x16
+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x31)+4
*(x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x
47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x62+
x63+x64+x65)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x1
5+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x
31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+
x47+x48+x49+x50+x51+x52+x53+x54+x55+x56+x57+x58+x59+x60+x61+x62
+x63+x64+x65-1)*2;

!handshaking dilemma;
2*x11<(x15+x18+x20+x21+x24+x26+x27+x29+x30+x31);

2*x10<(x34+x37+x39+x40+x43+x45+x46+x48+x49+x50+x53+x55+x56+x58+
x59+x60+x62+x63+x64+x65);

3*x13<x33+x36+x37+x38+x42+x43+x44+x45+x46+x47+x52+x53+x54+x55+x
56+x57+x58+x59+x60+x61;

2*(x14+x15+x16)<x33+x36+x37+x38+x42+x43+x44+x45+x46+x47+x52+x53
+x54+x55+x56+x57+x58+x59+x60+x61;

x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51>4*x32;

x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51> 3*(x33+x34+x35);

x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x47
+x48+x49+x50+x51>2*(x36+x37+x38+x39+x40+x41);

(x14+x17+x18+x19+x23+x24+x25+x26+x27+x28)>3*x23;

(x14+x17+x18+x19+x23+x24+x25+x26+x27+x28)>2*(x17+x24+x25);

x4+x7+x8+x9>2*x7;

end
```

DESIGN OF ADDICTIVE ALCOHOL

```
min=mw;

!Heat of vaporization (annotated as H);
H=((hvc1*(x1+x2+x3+x4+x5+x6))+(hvc2*(x7+x8+x9+x10+x11+x12+x13+x
14+x15+x16+x17+x18+x19+x20+x21))+(hvc3*(x22+x23+x24+x25+x26+x27
+x28+x29+x30+x31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x4
3+x44+x45+x46+x47))+(hvc5*(x48+x49+x50)));
!Target property range;
LH=35.267;
UH=45.267;
H>LH;
H<UHL
hvc1=0.217;hvc2=4.910;hvc3=7.962;hvc5=24.214;
@free(hvc1);@free(hvc2);@free(hvc3);@free(hvc5);

!Higher heating value (annotated as HHV);
HHV=((hhvc1*(x1+x2+x3+x4+x5+x6))+(hhvc2*(x7+x8+x9+x10+x11+x12+x
13+x14+x15+x16+x17+x18+x19+x20+x21))+(hhvc3*(x22+x23+x24+x25+x2
6+x27+x28+x29+x30+x31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x
42+x43+x44+x45+x46+x47))+(hhvc5*(x48+x49+x50)));
!Target property range;
LHHV=1854.174;
UHHV=3853.174;
HHV>LHHV;
HHV<UHHVl
hhvc1=710.6822;hhvc2=652.8408;hhvc3=580.8447;hhvc5=-133.374;
@free(hhvc1);@free(hhvc2);@free(hhvc3);@free(hhvc5);


!dynamic viscosity;
DV=((dvc1*(x1+x2+x3+x4+x5+x6))+(dvc2*(x7+x8+x9+x10+x11+x12+x13+
x14+x15+x16+x17+x18+x19+x20+x21))+(dvc3*(x22+x23+x24+x25+x26+x2
7+x28+x29+x30+x31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x
43+x44+x45+x46+x47))+(dvc5*(x48+x49+x50)));
!Target property range;
LDV=0.69;
UDV=1.16;
DV>LDV;
DV<UDV;
dvc1=-1.0278;dvc2=0.2125;dvc3=1.318;dvc5=1.3057;
@free(dvc1);@free(dvc2);@free(dvc3);@free(dvc5);@free(DV);

!LC50;
LC=(a1*x1+a2*x2+a3*x3+a4*x4+a5*x5+a6*x6+a7*x7+a8*x8+a9*x9+a10*x
10+a11*x11+a12*x12+a13*x13+a14*x14+a15*x15+a16*x16+
```

```
a17*x17+a18*x18+a19*x19+a20*x20+a21*x21+a22*x22+a23*x23+a24*x24
+a25*x25+a26*x26+a27*x27+a28*x28+a29*x29+a30*x30+a31*x31+a32*x3
2+
a33*x33+a34*x34+a35*x35+a36*x36+a37*x37+a38*x38+a39*x39+a40*x40
+a41*x41+a42*x42+a43*x43+a44*x44+a45*x45+a46*x46+a47*x47+a48*x4
8+
a49*x49+a50*x50);
!Target property range;
LLC=1.74;
ULC=2.85;
LC>LLC;
LC<ULC;

!Molecular weight (annotated as MW);
MW=mwx1*x1+mwx2*x2+mwx3*x3+mwx4*x4+mwx5*x5+mwx6*x6+mwx7*x7+mwx8
*x8+mwx9*x9+mwx10*x10+mwx11*x11+mwx12*x12+mwx13*x13+mwx14*x14+m
wx15*x15+mwx16*x16+mwx17*x17+mwx18*x18+mwx19*x19+mwx20*x20+mwx2
1*x21+mwx22*x22+mwx23*x23+mwx24*x24+mwx25*x25+mwx26*x26+mwx27*x
27+mwx28*x28+mwx29*x29+mwx30*x30+mwx31*x31+mwx32*x32+mwx33*x33+
mwx34*x34+mwx35*x35+mwx36*x36+mwx37*x37+mwx38*x38+mwx39*x39+mwx
40*x40+mwx41*x41+mwx42*x42+mwx43*x43+mwx44*x44+mwx45*x45+mwx46*
x46+mwx47*x47+mwx48*x48+mwx49*x49+mwx50*x50;

mwx1=15;mwx2=15;mwx3=15;mwx4=15;mwx5=15;mwx6=15;mwx7=14;mwx8=14
;mwx9=14;mwx10=14;mwx11=14;mwx12=14;mwx13=14;mwx14=14;mwx15=14;
mwx16=14;mwx17=14;mwx18=14;mwx19=14;mwx20=14;mwx21=14;mwx22=13;
mwx23=13;mwx24=13;
mwx25=13;mwx26=13;mwx27=13;mwx28=13;mwx29=13;mwx30=13;mwx31=13;
mwx32=13;mwx33=13;mwx34=13;mwx35=13;mwx36=13;mwx37=13;mwx38=13;
mwx39=13;mwx40=13;mwx41=13;mwx42=13;mwx43=13;mwx44=13;mwx45=13;
mwx46=13;mwx47=13;mwx48=17;mwx49=17;mwx50=17;

!TI values;
a1=0.50000;a2=0.35355;a3=0.35355;a4=0.28868;a5=0.28868;a6=0.223
61;a7=0.70711;a8=0.60355;a9=0.60355;a10=0.55768;a11=0.55768;a12
=0.50000;a13=0.50000;a14=0.45412;a15=0.45412;a16=0.45412;a17=0.
40825;a18=0.40825;a19=0.51167;a20=0.40811;a21=0.36224;a22=0.500
00;a23=0.50000;a24=0.53746;a25=0.53746;a26=0.53746;a27=0.57491;
a28=0.57491;a29=0.57491;a30=0.65947;a31=0.65947;a32=0.65947;a33
=0.74402;a34=0.74402;a35=0.61237;a36=0.61237;a37=0.69692;a38=0.
69692;a39=0.78147;a40=0.78147;a41=0.86603;a42=0.46243;a43=0.499
89;a44=0.58444;a45=0.53735;a46=0.62190;a47=0.70645;a48=0.22361;
a49=0.15811;a50=0.12910;

!Integers constraints;
@GIN(x1);@GIN(x2);@GIN(x3);@GIN(x4);@GIN(x5);@GIN(x6);@GIN(x7);
@GIN(x8);@GIN(x9);@GIN(x10);@GIN(x11);@GIN(x12);@GIN(x13);@GIN(
x14);@GIN(x15);@GIN(x16);
@GIN(x17);@GIN(x18);@GIN(x19);@GIN(x20);@GIN(x21);@GIN(x22);@GI
N(x23);@GIN(x24);@GIN(x25);@GIN(x26);@GIN(x27);@GIN(x28);@GIN(x
29);@GIN(x30);@GIN(x31);@GIN(x32);
```

```
@GIN(x33);@GIN(x34);@GIN(x35);@GIN(x36);@GIN(x37);@GIN(x38);@GI
N(x39);@GIN(x40);@GIN(x41);@GIN(x42);@GIN(x43);@GIN(x44);@GIN(x
45);@GIN(x46);@GIN(x47);@GIN(x48);
@GIN(x49);@GIN(x50);@GIN(loc1);@GIN(loc2);@GIN(loc3);

!Positive constraints;
x1>0;x2>0;x3>0;x4>0;x5>0;x6>0;x7>0;x8>0;x9>0;x10>0;x11>0;x12>0;
x13>0;x14>0;x15>0;x16>0;x17>0;x18>0;x19>0;x20>0;x21>0;x22>0;x23
>0;x24>0;x25>0;x26>0;x27>0;x28>0;x29>0;x30>0;x31>0;x32>0;
x33>0;x34>0;x35>0;x36>0;x37>0;x38>0;x39>0;x40>0;x41>0;x42>0;x43
>0;x44>0;x45>0;x46>0;x47>0;x48>0;x49>0;x50>0;




!handshaking lemma;
(x1+x2+x3+x4+x5+x6+x48+x49+x50)+2*(x7+x8+x9+x10+x11+x12+x13+x14
+x15+x16+x17+x18+x19+x20+x21)+3*(x22+x23+x24+x25+x26+x27+x28+x2
9+x30+x31+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x
45+x46+x47)=(x1+x2+x3+x4+x5+x6+x7+x8+x9+x10+x11+x12+x13+x14+x15
+x16+x17+x18+x19+x20+x21+x22+x23+x24+x25+x26+x27+x28+x29+x30+x3
1+x32+x33+x34+x35+x36+x37+x38+x39+x40+x41+x42+x43+x44+x45+x46+x
47+x48+x49+x50-1)*2;
x1=0;x6=0;x7=0;x19=0;x41=0;x47=0;x48=0;

!Consistency equations and handshaking dilemma;
!C1(C)-C2(CC);
x2=2*x7+x8+x9+x10+x11;
!C1(C)-C2(CO);
x3=x19;
!C1(C)-C3(CCC);
x4=x30+x31+x32+2*x33+2*x34+x37+x38+2*x39+2*x40+3*x41;
!C1(C)-C3(CCO);
x5=x44+x46+2*x47;
!C1(O)-O1(C1);
x6=x48;

!C1(C)-C1(C);
x1=2*loc1;
!C2(CC)-C2(CC);
x8+2*x12+x13+x14+x15=2*loc2;
!C3(CCC)-C3(CCC);
3*x22+2*x23+2*x24+x25+2*x26+x27+x29+x30+x32+x33=2*loc3;

!C2(CC)-C3(CCC);
x10+x14+x16+2*x17+x18=x24+x25+2*x27+2*x28+x29+x30+x31+3*x35+2*x
36+2*x37+x38+x39;
!C2(CC)-C3(CCO);
x11+x15+x18=x43+2*x45+x46;
!C2(CC)-C2(CO);
x9+x13+x16=x20;
!C2(CO)-O1(C2);
x19+x20+x21=x49;
```

```
!C2(CO)-C3(CCC);
x21=x26+x29+x32+x36+x38+x40;
!C3(CCC)-C3(CCO);
x23+x25+x28+x31+x34=2*x42+x43+x44;
!C3(CCO)-O1(C3);
x42+x43+x44+x45+x46+x47=x50;
!OH constraint;
x48+x49+x50=1;

!C2(CC)-C2(CC);
2*x12<x8+x12+x13+x14+x15;
!C2(CC)-C3(CCC);
2*x17<x24+x25+x27+x28+x29+x30+x31+x35+x36+x37+x38+x39;
!C3(CCC)-C3(CCC);
2*x23+2*x24+2*x26<x22+x23+x24+x25+x26+x27+x29+x30+x32+x33;
3*x22<x22+x23+x24+x25+x26+x27+x29+x30+x32+x33;
!C3(CCO)-C3(CCC);
2*x42<x23+x25+x28+x31+x34;

end
```

DESIGN OF OPTIMAL MIXTURE

```
max=lamda;
lamda<=lamda_hhv;
lamda<=lamda_mw;
lamda<=lamda_lc;

!Target properties for main component (annotated as MC);
h_MC=31.07;
hhv_MC=4533.21;
dv_MC=-0.3809;
mw_MC=97.48;
mwom_MC=0;
lc_MC=3.759;

!Target properties for Alkane A;
h_alk1=44.315;
hhv_alk1=6767.013;
dv_alk1=-0.0488;
mw_alk1=142;
mwom_alk1=0;
lc_alk1=1.08;

!Target properties for Alcohol C;
h_alc1=55.804;
hhv_alc1=3335.497;
dv_alc1=0.4898;
mw_alc1=88;
mwom_alc1=16;
lc_alc1=2.5966;

!Mixing constraints;
x_alk<1;
x_alc<1;
x_MC<1;
x_MC>0.55;
x_alk+x_alc+x_MC=1;

!Mixing of heat of vaporisation (annotated as h);
h=h_alk1*x_alk+h_alc1*x_alc+h_MC*x_MC;
!Target property range;
Lh=35;
Uh=45;
h>Lh;
h<Uh;

!Mixing of higher heating value (annotated as HHV);
```

```
hhv=hhv_alk1*x_alk+hhv_alc1*x_alc+hhv_MC*x_MC;
!Target property range;
Lhhv=3500;
Uhhv=5500;
hhv>Lhhv;
hhv<Uhhv;
!Degree of satisfaction (annotated as lamda);
lamda_hhv=(hhv-Lhhv)/(Uhhv-Lhhv);

!Mixing of dynamic viscosity (annotated as DV);
dv=dv_alk1*x_alk+dv_alc1*x_alc+dv_MC*x_MC;
!Target property range;
Ldv=-0.5229;
Udv=-0.0458;
dv>Ldv;
dv<Udv;
@free(Ldv);@free(Udv);@free(dv);@free(dv_MC);@free(dv_alk1);@fr
ee(dv_alc1);

!Mixing of oxygen content (annotated as mwom);
mwom=mwom_alk1*x_alk+mwom_alc1*x_alc+mwom_MC*x_MC;
!Target property range;
Lmwom=2;
Umwom=6.7;
mwom>Lmwom;
mwom<Umwom;
!Degree of satisfaction;
lamda_mw=(mwom-Lmwom)/(Umwom-Lmwom);

!Mixing of molecular weight (annotated as mw);
mw=mw_alk1*x_alk+mw_alc1*x_alc+mw_MC*x_MC;

!Mixing of toxic limit concentration (annotated as LC);
lc=lc_alk1*x_alk+lc_alc1*x_alc+lc_MC*x_MC;
!Target property range;
Llc=2.85;
Ulc=3.15;
lc>Llc;
lc<Ulc;
!Degree of satisfaction;
lamda_lc=(lc-Llc)/(Ulc-Llc);

end
```

SELECTION OF OPTIMAL CONVERTION PATHWAYS

```
!(use this for maximum product yield);
Max   =     decane;
!(use this for maximum economic potential);
Max   =     Profit;

!Production constraint;
1.12*decane =     1*pentanol;

!Biomass Feedstock Flowrate Input (tonne/y);
B     =     50000;

! Biomass Composition Input;
XL    =     0.29;
XC    =     0.39;
XHC   =     0.22;

! Conversion (or yield if there is no selectivity in the
process);
R1    =     0.98;
R2    =     0.492;
R3    =     0.79; !Separation efficiency;
R4    =     0.97; !Separation efficiency;
R5    =     0.909;
R6    =     0.409;
R7    =     0.619;
R8    =     0.41;
R9    =     0.982;
R10   =     0.99;
R11   =     0.60;
R12   =      0.94;
R13   =     0.90;
R14   =     0.40;
R15   =     1.00;
R16   =     0.40;
R17   =     0.75;
R18   =     0.251;
R19   =     0.246;
R20   =     0.288;
R21   =     0.99;
R22   =     0.67;
R23   =     0.59;
R24   =     0.64;
R25   =     0.62;
R26   =     0.97; !Separation efficiency;
R27   =     0.99; !Separation efficiency;
```

```
!Annualised capital cost (per annual tonne);
AGCF1  =    19.64;
AGCF2  =    13.90;
AGCF3  =    40.68;
AGCF4  =    40.68;
AGCF5  =    63.46;
AGCF6  =    27.62;
AGCF7  =    40.62;
AGCF8  =    31.43;
AGCF9  =    30.22;
AGCF10 =    43.52;
AGCF11 =    45.45;
AGCF12 =    62.86;
AGCF13 =    86.43;
AGCF14 =    26.23;
AGCF15 =    15.11;
AGCF16 =    193.41;
AGCF17 =    181.93;
AGCF18 =    38.56;
AGCF19 =    41.10;
AGCF20 =    40.19;
AGCF21 =    40.68;
AGCF22 =    40.50;
AGCF23 =    37.47;
AGCF24 =    34.45;
AGCF25 =    45.94;
AGCF26 =    125.73;
AGCF27 =    169.48;

!Operating cost (per annual tonne);
AGOF1  =    11.30;
AGOF2  =    7.97;
AGOF3  =    23.30;
AGOF4  =    23.30;
AGOF5  =    36.40;
AGOF6  =    15.80;
AGOF7  =    22.00;
AGOF8  =    18.00;
AGOF9  =    17.30;
AGOF10 =    24.90;
AGOF11 =    26.00;
AGOF12 =    36.00;
AGOF13 =    55.00;
AGOF14 =    15.00;
AGOF15 =    8.66;
AGOF16 =    111.00;
AGOF17 =    104.00;
AGOF18 =    22.10;
AGOF19 =    23.60;
AGOF20 =    23.00;
AGOF21 =    23.30;
AGOF22 =    23.20;
```

```
AGOF23 =    21.50;
AGOF24 =    19.70;
AGOF25 =    26.30;
AGOF26 =    72.45;
AGOF27 =    98.20;

!Price (USD) of ton of feedstock or Products;
Gbiomass          = 170;
Gethane           = 424;
Gpropane          = 670;
Gbutane           = 900;
Gpentane          = 1200;
Ghexane           = 1600;
Gheptane          = 1800;
Goctane           = 2000;
Gnonane           = 2510;
Gdecane           = 2750;
Gmethanol         = 450;
Gethanol          = 770;
Gpropanol         = 950;
Gbutanol          = 1120;
Gpentanol         = 1770;
Gpentanediol      = 3000;

!Flowrates (Into each layer);
Tlcs1       =     (XC+XHC)*R1*F1+(XC+XHC)*R2*F2;
Tlcs2       =     XL*F1+XL*F2;
Tlcs        =     Tlcs1+Tlcs2;
Tlignin     =     R3*F3;
Tsugar      =     R4*F4;
Thmf        =     R5*F5;
Tf          =     R6*F6;
Tthfa       =     R9*F9;
Ts          =     R12*F12+R13*F13+R15*F15;
Tm          =     R14*F14;

Talc1       =     R7*F7+R8*F8;
Talc2       =     R10*F10+R11*F11;
Talc3       =     R18*F18+R19*F19+R20*F20;
Talc        =     Talc1+Talc2+Talc3;
Talc        =     F26;

Talk1       =     R16*F16+R17*F17;
Talk2       =     R22*F22+R23*F23+R24*F24;
Talk3       =     R25*F25;
Talk        =     Talk1+Talk2+Talk3;
Talk        =     F27;

Tac         =     R21*F21;

!Flowrates (Out from each layer);
B           =     F1+F2+F12+F13+F14;
F1          <=    B;
```

```
F2          <=    B;
F12         <=    B;
F13         <=    B;
F14         <=    B;
Tlcs2       =     F3;
F3          <=    Tlcs2;
Tlcs1       =     F4;
F4          <=    Tlcs1;
Tsugar      =     F5+F6+F7+F8;
F5          <=    Tsugar;
F6          <=    Tsugar;
F7          <=    Tsugar;
F8          <=    Tsugar;
Tf          =     F9;
F9          <=    Tf;
Tthfa       =     F10+F11;
F10         <=    Tthfa;
F11         <=    Tthfa;
Tm          =     F15;
F15         <=    Tm;
Ts          =     F16+F17+F18+F19+F20;
F16         <=    Ts;
F17         <=    Ts;
F18         <=    Ts;
F19         <=    Ts;
F20         <=    Ts;
Talc        =     F21+F22+F23+F24;
F21         <=    Talc;
F22         <=    Talc;
F23         <=    Talc;
F24         <=    Talc;
Tac         =      F25;
F25         <=    Tac;

!Production rates of alkanes;
ethane      =
R27*(R16*F16*0.16+R17*F17*0.23+R22*F22*0.103+R25*F25*0.213);
propane     =    R27*(R16*F16*0.16+R17*F17*0.23+R23*F23*0.288);
butane      =    R27*(R16*F16*0.16+R17*F17*0.23+R23*F23*0.373);
pentane     =    R27*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.152);
hexane      =    R27*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.055);
heptane     =    R27*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.056);
octane      =    R27*(R16*F16*0.27+R17*F17*0.19+R24*F24*0.042);
nonane      =     R27*(R16*F16*0.27+R17*F17*0.19);
decane      =     R27*(R16*F16*0.26+R17*F17*0.097);
Talk        >=    ethane+propane+butane+pentane+hexane+heptane+
      octane+nonane+decane;

!Production rates of alcohols;
methanol    =     R18*F18*0.026+R19*F19*0.039+R20*F20*0.207;
ethanol     =     R7*F7+R8*F8+R18*F18*0.614+R19*F19*0.561+
      R20*F20*0.238;
propanol          =     R20*F20*0.141;
```

```
butanol           =     R20*F20*0.075;
pentanol          =     R26*(R10*F10*0.04+R11*F11*0.22);
pentanediol       =     R26*(R10*F10*0.95+R11*F11*0.51);
Talc        >=    methanol+ethanol+propanol+butanol+pentanol+
      pentanediol;

!Revenue of alkanes;
EPethane    =     Gethane*ethane;
EPpropane   =     Gpropane*propane;
EPbutane    =     Gbutane*butane;
EPpentane   =     Gpentane*pentane;
EPhexane    =     Ghexane*hexane;
EPheptane   =     Gheptane*heptane;
EPoctane  =       Goctane*octane;
EPnonane  =       Gnonane*nonane;
EPdecane  =       Gdecane*decane;
EPalk     =
      EPethane+EPpropane+EPbutane+EPpentane+EPhexane+
      EPheptane+EPoctane+EPnonane+EPdecane;

!Revenue of alcohols;
EPmethanol        =     Gmethanol*methanol;
EPethanol         =     Gethanol*ethanol;
EPpropanol        =     Gpropanol*propanol;
EPbutanol         =     Gbutanol*butanol;
EPpentanol        =     Gpentanol*pentanol;
EPpentanediol     =     Gpentanediol*pentanediol;
EPalc             =
      EPmethanol+EPethanol+EPpropanol+EPbutanol+
      EPpentanol+EPpentanediol;

!Total revenue;
Revenue     =     EPalc+EPalk;
!Cost for biomass;
CBiomass    =     B*Gbiomass;
!Total capital cost;
TACC     =  F1*AGCF1+F2*AGCF2+F3*AGCF3+F4*AGCF4+F5*AGCF5+
        F6*AGCF6+F7*AGCF7+F8*AGCF8+F9*AGCF9+
        F10*AGCF10+F11*AGCF11+F12*AGCF12+F13*AGCF13+
        F14*AGCF14+F15*AGCF15+F16*AGCF16+F17*AGCF17+F18*AGCF18
        +F19*AGCF19+F20*AGCF20+F21*AGCF21+F22*AGCF22+F23*AGCF2
        3+F24*AGCF24+F25*AGCF25+F26*AGCF26+F27*AGCF27;
!Total operating cost;
TAOC     =  F1*AGOF1+F2*AGOF2+F3*AGOF3+F4*AGOF4+F5*AGOF5+
        F6*AGOF6+F7*AGOF7+F8*AGOF8+F9*AGOF9+F10*
        AGOF10+F11*AGOF11+F12*AGOF12+F13*AGOF13+F14*AGOF14+F15
        *AGOF15+F16*AGOF16+F17*AGOF17+F18*AGOF18+F19*AGOF19+F2
        0*AGOF20+F21*AGOF21+F22*AGOF22+F23*AGOF23+F24*AGOF24+F
        25*AGOF25+F26*AGOF26+F27*AGOF27;
!Profit;
Profit   = Revenue-CBiomass-TACC-TAOC;
@free(profit);
end
```

RESULTS

DESIGN OF ADDICTIVE ALKANE

```
Global optimal solution found.
Objective value:                               6620.187
Objective bound:                               6620.187
Infeasibilities:                               0.000000
Extended solver steps:                                0
Total solver iterations:                             51

Model Class:                                       MILP

Total variables:                    73
Nonlinear variables:                 0
Integer variables:                  67

Total constraints:                 102
Nonlinear constraints:               0

Total nonzeros:                    817
Nonlinear nonzeros:                  0

Variable     Value               Reduced Cost
HHV          6620.187            0.000000
H            32.58200            0.000000
HVC1         0.2170000           0.000000
X1           0.000000            -710.6822
X2           0.000000            -710.6822
X3           6.000000            0.000000
HVC2         4.910000            0.000000
X4           0.000000            -652.8408
X5           0.000000            -652.8408
X6           0.000000            -652.8408
X7           0.000000            -652.8408
X8           0.000000            -652.8408
X9           2.000000            -652.8408
X10          0.000000            -652.8408
X11          0.000000            -652.8408
X12          0.000000            -652.8408
HVC3         7.962000            0.000000
X13          0.000000            -580.8447
X14          0.000000            -580.8447
X15          0.000000            -580.8447
X16          0.000000            -580.8447
X17          0.000000            -580.8447
```

```
X18          0.000000            -580.8447
X19          0.000000            -580.8447
X20          0.000000            -580.8447
X21          0.000000            -580.8447
X22          0.000000            -580.8447
X23          0.000000            -580.8447
X24          0.000000            -580.8447
X25          0.000000            -580.8447
X26          0.000000            -580.8447
X27          0.000000            -580.8447
X28          0.000000            -580.8447
X29          0.000000            -580.8447
X30          0.000000            -580.8447
X31          0.000000            -580.8447
HVC4         10.73000            0.000000
X32          0.000000            -525.2059
X33          0.000000            -525.2059
X34          0.000000            -525.2059
X35          0.000000            -525.2059
X36          0.000000            -525.2059
X37          0.000000            -525.2059
X38          0.000000            -525.2059
X39          0.000000            -525.2059
X40          0.000000            -525.2059
X41          0.000000            -525.2059
X42          0.000000            -525.2059
X43          0.000000            -525.2059
X44          0.000000            -525.2059
X45          0.000000            -525.2059
X46          0.000000            -525.2059
X47          0.000000            -525.2059
X48          0.000000            -525.2059
X49          0.000000            -525.2059
X50          0.000000            -525.2059
X51          0.000000            -525.2059
X52          0.000000            -525.2059
X53          0.000000            -525.2059
X54          0.000000            -525.2059
X55          0.000000            -525.2059
X56          0.000000            -525.2059
X57          0.000000            -525.2059
X58          0.000000            -525.2059
X59          0.000000            -525.2059
X60          0.000000            -525.2059
X61          0.000000            -525.2059
X62          0.000000            -525.2059
X63          0.000000            -525.2059
X64          0.000000            -525.2059
X65          2.000000            -525.2059
LH           28.26700            0.000000
UH           38.26700            0.000000
HHVC1        710.6822            0.000000
HHVC2        652.8408            0.000000
```

```
HHVC3        580.8447            0.000000
HHVC4        525.2059            0.000000
LHHV         5853.174            0.000000
UHHV         6853.174            0.000000
DV           -0.1124000          0.000000
DVC1         -1.027800           0.000000
DVC2         0.2125000           0.000000
DVC3         1.318000            0.000000
DVC4         2.814700            0.000000
LDV          -0.9162000          0.000000
UDV          0.9530000E-01       0.000000
LC           4.207120            0.000000
A1           0.3535500           0.000000
A2           0.2886800           0.000000
A3           0.2500000           0.000000
A4           0.6035500           0.000000
A5           0.5576800           0.000000
A6           0.5303300           0.000000
A7           0.5000000           0.000000
A8           0.4541200           0.000000
A9           0.4267800           0.000000
A10          0.3535500           0.000000
A11          0.4082500           0.000000
A12          0.3809000           0.000000
A13          0.4330100           0.000000
A14          0.4553400           0.000000
A15          0.4928000           0.000000
A16          0.5773500           0.000000
A17          0.4776700           0.000000
A18          0.5151300           0.000000
A19          0.5996800           0.000000
A20          0.5525900           0.000000
A21          0.6371400           0.000000
A22          0.7216900           0.000000
A23          0.5000000           0.000000
A24          0.5374600           0.000000
A25          0.6220100           0.000000
A26          0.5749100           0.000000
A27          0.6594700           0.000000
A28          0.7440200           0.000000
A29          0.6123700           0.000000
A30          0.6969200           0.000000
A31          0.7814700           0.000000
A32          0.5000000           0.000000
A33          0.5193400           0.000000
A34          0.5517800           0.000000
A35          0.6250000           0.000000
A36          0.5386800           0.000000
A37          0.5711100           0.000000
A38          0.6443400           0.000000
A39          0.6035500           0.000000
A40          0.6767800           0.000000
A41          0.7500000           0.000000
```

```
A42            0.5386800            0.000000
A43            0.5711100            0.000000
A44            0.6443400            0.000000
A45            0.6228900            0.000000
A46            0.6961100            0.000000
A47            0.7693400            0.000000
A48            0.6553300            0.000000
A49            0.7285500            0.000000
A50            0.8017800            0.000000
A51            0.8750000            0.000000
A52            0.5773500            0.000000
A53            0.6097900            0.000000
A54            0.6830100            0.000000
A55            0.6422300            0.000000
A56            0.7154500            0.000000
A57            0.7886800            0.000000
A58            0.6746700            0.000000
A59            0.7478900            0.000000
A60            0.8211100            0.000000
A61            0.8943400            0.000000
A62            0.7071100            0.000000
A63            0.7803300            0.000000
A64            0.8535500            0.000000
A65            0.9267800            0.000000
LLC            3.850000             0.000000
ULC            4.630000             0.000000
LOC1           1.000000             0.000000
LOC2           0.000000             0.000000
LOC3           0.000000             0.000000
MW             142.0000             0.000000
MWX1           15.00000             0.000000
MWX2           15.00000             0.000000
MWX3           15.00000             0.000000
MWX4           14.00000             0.000000
MWX5           14.00000             0.000000
MWX6           14.00000             0.000000
MWX7           14.00000             0.000000
MWX8           14.00000             0.000000
MWX9           14.00000             0.000000
MWX10          14.00000             0.000000
MWX11          14.00000             0.000000
MWX12          14.00000             0.000000
MWX13          13.00000             0.000000
MWX14          12.00000             0.000000
MWX15          12.00000             0.000000
MWX16          13.00000             0.000000
MWX17          13.00000             0.000000
MWX18          13.00000             0.000000
MWX19          13.00000             0.000000
MWX20          13.00000             0.000000
MWX21          13.00000             0.000000
MWX22          13.00000             0.000000
MWX23          13.00000             0.000000
```

```
MWX24        13.00000            0.000000
MWX25        13.00000            0.000000
MWX26        13.00000            0.000000
MWX27        13.00000            0.000000
MWX28        13.00000            0.000000
MWX29        13.00000            0.000000
MWX30        13.00000            0.000000
MWX31        13.00000            0.000000
MWX32        12.00000            0.000000
MWX33        12.00000            0.000000
MWX34        12.00000            0.000000
MWX35        12.00000            0.000000
MWX36        12.00000            0.000000
MWX37        12.00000            0.000000
MWX38        12.00000            0.000000
MWX39        12.00000            0.000000
MWX40        12.00000            0.000000
MWX41        12.00000            0.000000
MWX42        12.00000            0.000000
MWX43        12.00000            0.000000
MWX44        12.00000            0.000000
MWX45        12.00000            0.000000
MWX46        12.00000            0.000000
MWX47        12.00000            0.000000
MWX48        12.00000            0.000000
MWX49        12.00000            0.000000
MWX50        12.00000            0.000000
MWX51        12.00000            0.000000
MWX52        12.00000            0.000000
MWX53        12.00000            0.000000
MWX54        12.00000            0.000000
MWX55        12.00000            0.000000
MWX56        12.00000            0.000000
MWX57        12.00000            0.000000
MWX58        12.00000            0.000000
MWX59        12.00000            0.000000
MWX60        12.00000            0.000000
MWX61        12.00000            0.000000
MWX62        12.00000            0.000000
MWX63        12.00000            0.000000
MWX64        12.00000            0.000000
MWX65        12.00000            0.000000
LOC          10.00000            0.000000
```

DESIGN OF ADDICTIVE ALCOHOL

```
Global optimal solution found.
Objective value:                                74.00000
Objective bound:                                74.00000
Infeasibilities:                                0.000000
Extended solver steps:                                 0
Total solver iterations:                             175

Model Class:                                        MILP

Total variables:                       50
Nonlinear variables:                    0
Integer variables:                     44

Total constraints:                     87
Nonlinear constraints:                  0

Total nonzeros:                       472
Nonlinear nonzeros:                     0

Variable      Value               Reduced Cost
MW            74.00000            0.000000
LOC           5.000000            0.000000
H             39.16100            0.000000
HVC1          0.2170000           0.000000
X1            0.000000            0.000000
X2            1.000000            15.00000
X3            0.000000            0.000000
X4            0.000000            15.00000
X5            0.000000            15.00000
X6            0.000000            0.000000
HVC2          4.910000            0.000000
X7            0.000000            0.000000
X8            1.000000            14.00000
X9            0.000000            14.00000
X10           0.000000            14.00000
X11           0.000000            14.00000
X12           0.000000            14.00000
X13           1.000000            14.00000
X14           0.000000            14.00000
X15           0.000000            14.00000
X16           0.000000            14.00000
X17           0.000000            14.00000
X18           0.000000            14.00000
X19           0.000000            0.000000
X20           1.000000            14.00000
```

```
X21          0.000000            14.00000
HVC3         7.962000            0.000000
X22          0.000000            13.00000
X23          0.000000            13.00000
X24          0.000000            13.00000
X25          0.000000            13.00000
X26          0.000000            13.00000
X27          0.000000            13.00000
X28          0.000000            13.00000
X29          0.000000            13.00000
X30          0.000000            13.00000
X31          0.000000            13.00000
X32          0.000000            13.00000
X33          0.000000            13.00000
X34          0.000000            13.00000
X35          0.000000            13.00000
X36          0.000000            13.00000
X37          0.000000            13.00000
X38          0.000000            13.00000
X39          0.000000            13.00000
X40          0.000000            13.00000
X41          0.000000            0.000000
X42          0.000000            13.00000
X43          0.000000            13.00000
X44          0.000000            13.00000
X45          0.000000            13.00000
X46          0.000000            13.00000
X47          0.000000            0.000000
HVC5         24.21400            0.000000
X48          0.000000            0.000000
X49          1.000000            17.00000
X50          0.000000            17.00000
HHV          2535.831            0.000000
HHVC1        710.6822            0.000000
HHVC2        652.8408            0.000000
HHVC3        580.8447            0.000000
HHVC5        -133.3740            0.000000
DV           0.9154000            0.000000
DVC1         -1.027800            0.000000
DVC2         0.2125000            0.000000
DVC3         1.318000             0.000000
DVC5         1.305700             0.000000
LC           2.023320             0.000000
A1           0.5000000            0.000000
A2           0.3535500            0.000000
A3           0.3535500            0.000000
A4           0.2886800            0.000000
A5           0.2886800            0.000000
A6           0.2236100            0.000000
A7           0.7071100            0.000000
A8           0.6035500            0.000000
A9           0.6035500            0.000000
A10          0.5576800            0.000000
```

```
A11          0.5576800             0.000000
A12          0.5000000             0.000000
A13          0.5000000             0.000000
A14          0.4541200             0.000000
A15          0.4541200             0.000000
A16          0.4541200             0.000000
A17          0.4082500             0.000000
A18          0.4082500             0.000000
A19          0.5116700             0.000000
A20          0.4081100             0.000000
A21          0.3622400             0.000000
A22          0.5000000             0.000000
A23          0.5000000             0.000000
A24          0.5374600             0.000000
A25          0.5374600             0.000000
A26          0.5374600             0.000000
A27          0.5749100             0.000000
A28          0.5749100             0.000000
A29          0.5749100             0.000000
A30          0.6594700             0.000000
A31          0.6594700             0.000000
A32          0.6594700             0.000000
A33          0.7440200             0.000000
A34          0.7440200             0.000000
A35          0.6123700             0.000000
A36          0.6123700             0.000000
A37          0.6969200             0.000000
A38          0.6969200             0.000000
A39          0.7814700             0.000000
A40          0.7814700             0.000000
A41          0.8660300             0.000000
A42          0.4624300             0.000000
A43          0.4998900             0.000000
A44          0.5844400             0.000000
A45          0.5373500             0.000000
A46          0.6219000             0.000000
A47          0.7064500             0.000000
A48          0.2236100             0.000000
A49          0.1581100             0.000000
A50          0.1291000             0.000000
MWX1         15.00000              0.000000
MWX2         15.00000              0.000000
MWX3         15.00000              0.000000
MWX4         15.00000              0.000000
MWX5         15.00000              0.000000
MWX6         15.00000              0.000000
MWX7         14.00000              0.000000
MWX8         14.00000              0.000000
MWX9         14.00000              0.000000
MWX10        14.00000              0.000000
MWX11        14.00000              0.000000
MWX12        14.00000              0.000000
MWX13        14.00000              0.000000
```

```
MWX14        14.00000             0.000000
MWX15        14.00000             0.000000
MWX16        14.00000             0.000000
MWX17        14.00000             0.000000
MWX18        14.00000             0.000000
MWX19        14.00000             0.000000
MWX20        14.00000             0.000000
MWX21        14.00000             0.000000
MWX22        13.00000             0.000000
MWX23        13.00000             0.000000
MWX24        13.00000             0.000000
MWX25        13.00000             0.000000
MWX26        13.00000             0.000000
MWX27        13.00000             0.000000
MWX28        13.00000             0.000000
MWX29        13.00000             0.000000
MWX30        13.00000             0.000000
MWX31        13.00000             0.000000
MWX32        13.00000             0.000000
MWX33        13.00000             0.000000
MWX34        13.00000             0.000000
MWX35        13.00000             0.000000
MWX36        13.00000             0.000000
MWX37        13.00000             0.000000
MWX38        13.00000             0.000000
MWX39        13.00000             0.000000
MWX40        13.00000             0.000000
MWX41        13.00000             0.000000
MWX42        13.00000             0.000000
MWX43        13.00000             0.000000
MWX44        13.00000             0.000000
MWX45        13.00000             0.000000
MWX46        13.00000             0.000000
MWX47        13.00000             0.000000
MWX48        17.00000             0.000000
MWX49        17.00000             0.000000
MWX50        17.00000             0.000000
LOC1         0.000000             0.000000
LOC2         1.000000             0.000000
LOC3         0.000000             0.000000
```

DESIGN OF OPTIMAL MIXTURE

```
Global optimal solution found.
Objective value:                              0.5149954
Infeasibilities:                               0.000000
Total solver iterations:                              7

Model Class:                                         LP

Total variables:                     13
Nonlinear variables:                  0
Integer variables:                    0

Total constraints:                   28
Nonlinear constraints:                0

Total nonzeros:                      52
Nonlinear nonzeros:                   0

Variable     Value               Reduced Cost
LAMDA        0.5149954           0.000000
LAMDA_HHV    0.5211545           0.000000
LAMDA_MW     0.5149954           0.000000
LAMDA_LC     0.5846667           0.000000
H_MC         31.07000            0.000000
HHV_MC       4533.210            0.000000
DV_MC        -0.3809000          0.000000
MW_MC        97.48000            0.000000
MWOM_MC      0.000000            0.000000
LC_MC        3.759000            0.000000
H_ALK1       44.31500            0.000000
HHV_ALK1     6767.013            0.000000
DV_ALK1      -0.4880000E-01      0.000000
MW_ALK1      142.0000            0.000000
MWOM_ALK1    0.000000            0.000000
LC_ALK1      1.080000            0.000000
H_ALC1       55.80400            0.000000
HHV_ALC1     3335.497            0.000000
DV_ALC1      0.4898000           0.000000
MW_ALC1      88.00000            0.000000
MWOM_ALC1    16.00000            0.000000
LC_ALC1      2.596600            0.000000
X_ALK        0.1532149           0.000000
X_ALC        0.2781443           0.000000
X_MC         0.5687382           0.000000
H            39.977423           0.000000
LH           35.00000            0.000000
```

```
UH             45.00000               0.000000
HHV            4542.318               0.000000
LHHV           3500.000               0.000000
UHHV           5500.000               0.000000
DV             -0.8843730E-01         0.000000
LDV            -0.5229000             0.000000
UDV            -0.4580000E-01         0.000000
MWOM           4.420483               0.000000
LMWOM          2.000000               0.000000
UMWOM          6.700000               0.000000
MW             101.6534               0.000000
LC             3.025431               0.000000
LLC            2.850000               0.000000
ULC            3.150000               0.000000
```

SELECTION OF OPTIMAL CONVERSION PATHWAYS WITH MAXIMUM PRODUCT YIELD

```
Global optimal solution found.
Objective value:                            952.3589
Infeasibilities:                            0.000000
Total solver iterations:                          10

Model Class:                                      LP

Total variables:                     82
Nonlinear variables:                  0
Integer variables:                    0

Total constraints:                   96
Nonlinear constraints:                0

Total nonzeros:                     322
Nonlinear nonzeros:                   0

Variable     Value               Reduced Cost
DECANE       952.3589            0.000000
PENTANOL     1066.642            0.000000
B            50000.00            0.000000
XL           0.2900000           0.000000
XC           0.3900000           0.000000
XHC          0.2200000           0.000000
R1           0.9800000           0.000000
R2           0.4920000           0.000000
R3           0.7900000           0.000000
R4           0.9700000           0.000000
R5           0.9090000           0.000000
R6           0.4090000           0.000000
R7           0.6190000           0.000000
R8           0.4100000           0.000000
R9           0.9820000           0.000000
R10          0.9900000           0.000000
R11          0.6000000           0.000000
R12          0.9400000           0.000000
R13          0.9000000           0.000000
R14          0.4000000           0.000000
R15          1.000000            0.000000
R16          0.4000000           0.000000
R17          0.7500000           0.000000
R18          0.2510000           0.000000
R19          0.2460000           0.000000
```

```
R20          0.2880000           0.000000
R21          0.9900000           0.000000
R22          0.6700000           0.000000
R23          0.5900000           0.000000
R24          0.6400000           0.000000
R25          0.6200000           0.000000
R26          0.9700000           0.000000
R27          0.9900000           0.000000
AGCF1        19.64000            0.000000
AGCF2        13.90000            0.000000
AGCF3        40.68000            0.000000
AGCF4        40.68000            0.000000
AGCF5        63.46000            0.000000
AGCF6        27.62000            0.000000
AGCF7        40.62000            0.000000
AGCF8        31.43000            0.000000
AGCF9        30.22000            0.000000
AGCF10       43.52000            0.000000
AGCF11       45.45000            0.000000
AGCF12       62.86000            0.000000
AGCF13       86.43000            0.000000
AGCF14       26.23000            0.000000
AGCF15       15.11000            0.000000
AGCF16       193.4100            0.000000
AGCF17       181.9300            0.000000
AGCF18       38.56000            0.000000
AGCF19       41.10000            0.000000
AGCF20       40.19000            0.000000
AGCF21       40.68000            0.000000
AGCF22       40.50000            0.000000
AGCF23       37.47000            0.000000
AGCF24       34.45000            0.000000
AGCF25       45.94000            0.000000
AGCF26       125.7300            0.000000
AGCF27       169.4800            0.000000
AGOF1        11.30000            0.000000
AGOF2        7.970000            0.000000
AGOF3        23.30000            0.000000
AGOF4        23.30000            0.000000
AGOF5        36.40000            0.000000
AGOF6        15.80000            0.000000
AGOF7        22.00000            0.000000
AGOF8        18.00000            0.000000
AGOF9        17.30000            0.000000
AGOF10       24.90000            0.000000
AGOF11       26.00000            0.000000
AGOF12       36.00000            0.000000
AGOF13       55.00000            0.000000
AGOF14       15.00000            0.000000
AGOF15       8.660000            0.000000
AGOF16       111.0000            0.000000
AGOF17       104.0000            0.000000
AGOF18       22.10000            0.000000
```

```
AGOF19       23.60000            0.000000
AGOF20       23.00000            0.000000
AGOF21       23.30000            0.000000
AGOF22       23.20000            0.000000
AGOF23       21.50000            0.000000
AGOF24       19.70000            0.000000
AGOF25       26.30000            0.000000
AGOF26       72.45000            0.000000
AGOF27       98.20000            0.000000
GBIOMASS     170.0000            0.000000
GETHANE      424.0000            0.000000
GPROPANE     670.0000            0.000000
GBUTANE      900.0000            0.000000
GPENTANE     1200.000            0.000000
GHEXANE      1600.000            0.000000
GHEPTANE     1800.000            0.000000
GOCTANE      2000.000            0.000000
GNONANE      2510.000            0.000000
GDECANE      2750.000            0.000000
GMETHANOL    450.0000            0.000000
GETHANOL     770.0000            0.000000
GPROPANOL    950.0000            0.000000
GBUTANOL     1120.000            0.000000
GPENTANOL    1770.000            0.000000
GPENTANEDIOL 3000.000            0.000000
TLCS1        24007.52            0.000000
F1           40159.79            0.000000
F2           0.000000            0.9484718E-02
TLCS2        11646.34            0.000000
TLCS         35653.86            0.000000
TLIGNIN      9200.608            0.000000
F3           11646.34            0.000000
TSUGAR       23287.30            0.000000
F4           24007.52            0.000000
THMF         0.000000            0.000000
F5           0.000000            0.3284755E-01
TF           8483.236            0.000000
F6           20741.41            0.000000
TTHFA        8330.537            0.000000
F9           8483.236            0.000000
TS           9249.795            0.000000
F12          9840.208            0.000000
F13          0.000000            0.8105182E-03
F15          0.000000            0.000000
TM           0.000000            0.000000
F14          0.000000            0.1094200E-01
TALC1        1575.906            0.000000
F7           2545.890            0.000000
F8           0.000000            0.1109069E-01
TALC2        4998.322            0.000000
F10          0.000000            0.000000
F11          8330.537            0.000000
TALC3        0.000000            0.000000
```

```
F18          0.000000            0.6943513E-02
F19          0.000000            0.7208840E-02
F20          0.000000            0.4980089E-02
TALC         6574.229            0.000000
F26          6574.229            0.000000
TALK1        3699.918            0.000000
F16          9249.795            0.000000
F17          0.000000            0.2730672E-01
TALK2        4404.733            0.000000
F22          6574.229            0.000000
F23          0.000000            0.3508157E-01
F24          0.000000            0.1366397E-01
TALK3        0.000000            0.000000
F25          0.000000            0.000000
TALK         8104.651            0.000000
F27          8104.651            0.000000
TAC          0.000000            0.000000
F21          0.000000            0.1034641E-01
ETHANE       1035.218            0.000000
PROPANE      586.0670            0.000000
BUTANE       586.0670            0.000000
PENTANE      988.9881            0.000000
HEXANE       988.9881            0.000000
HEPTANE      988.9881            0.000000
OCTANE       988.9881            0.000000
NONANE       988.9881            0.000000
METHANOL     0.000000            0.000000
ETHANOL      1575.906            0.000000
PROPANOL     0.000000            0.000000
BUTANOL      0.000000            0.000000
PENTANEDIOL  2472.670            0.000000
EPETHANE     438932.3            0.000000
EPPROPANE    392664.9            0.000000
EPBUTANE     527460.3            0.000000
EPPENTANE    1186786.            0.000000
EPHEXANE     1582381.            0.000000
EPHEPTANE    1780179.            0.000000
EPOCTANE     1977976.            0.000000
EPNONANE     2482360.            0.000000
EPDECANE     2618987.            0.000000
EPALK        0.1298773E+08       0.000000
EPMETHANOL   0.000000            0.000000
EPETHANOL    1213448.            0.000000
EPPROPANOL   0.000000            0.000000
EPBUTANOL    0.000000            0.000000
EPPENTANOL   1887956.            0.000000
EPPENTANEDIOL7418010.            0.000000
EPALC        0.1051941E+08       0.000000
REVENUE      0.2350714E+08       0.000000
CBIOMASS     8500000.            0.000000
TACC         8424384.            0.000000
TAOC         4837295.            0.000000
PROFIT       1745462.            0.000000
```

SELECTION OF OPTIMAL CONVERSION PATHWAYS WITH MAXIMUM ECONOMIC POTENTIAL

```
Global optimal solution found.
Objective value:                         0.1939399E+08
Infeasibilities:                              0.000000
Total solver iterations:                             7

Model Class:                                        LP

Total variables:                    82
Nonlinear variables:                 0
Integer variables:                   0

Total constraints:                  96
Nonlinear constraints:               0

Total nonzeros:                    322
Nonlinear nonzeros:                  0

Variable      Value               Reduced Cost
PROFIT        0.1939399E+08       0.000000
DECANE        357.2289            0.000000
PENTANOL      400.0964            0.000000
B             50000.00            0.000000
XL            0.2900000           0.000000
XC            0.3900000           0.000000
XHC           0.2200000           0.000000
R1            0.9800000           0.000000
R2            0.4920000           0.000000
R3            0.7900000           0.000000
R4            0.9700000           0.000000
R5            0.9090000           0.000000
R6            0.4090000           0.000000
R7            0.6190000           0.000000
R8            0.4100000           0.000000
R9            0.9820000           0.000000
R10           0.9900000           0.000000
R11           0.6000000           0.000000
R12           0.9400000           0.000000
R13           0.9000000           0.000000
R14           0.4000000           0.000000
R15           1.000000            0.000000
R16           0.4000000           0.000000
R17           0.7500000           0.000000
R18           0.2510000           0.000000
```

```
R19          0.2460000           0.000000
R20          0.2880000           0.000000
R21          0.9900000           0.000000
R22          0.6700000           0.000000
R23          0.5900000           0.000000
R24          0.6400000           0.000000
R25          0.6200000           0.000000
R26          0.9700000           0.000000
R27          0.9900000           0.000000
AGCF1        19.64000            0.000000
AGCF2        13.90000            0.000000
AGCF3        40.68000            0.000000
AGCF4        40.68000            0.000000
AGCF5        63.46000            0.000000
AGCF6        27.62000            0.000000
AGCF7        40.62000            0.000000
AGCF8        31.43000            0.000000
AGCF9        30.22000            0.000000
AGCF10       43.52000            0.000000
AGCF11       45.45000            0.000000
AGCF12       62.86000            0.000000
AGCF13       86.43000            0.000000
AGCF14       26.23000            0.000000
AGCF15       15.11000            0.000000
AGCF16       193.4100            0.000000
AGCF17       181.9300            0.000000
AGCF18       38.56000            0.000000
AGCF19       41.10000            0.000000
AGCF20       40.19000            0.000000
AGCF21       40.68000            0.000000
AGCF22       40.50000            0.000000
AGCF23       37.47000            0.000000
AGCF24       34.45000            0.000000
AGCF25       45.94000            0.000000
AGCF26       125.7300            0.000000
AGCF27       169.4800            0.000000
AGOF1        11.30000            0.000000
AGOF2        7.970000            0.000000
AGOF3        23.30000            0.000000
AGOF4        23.30000            0.000000
AGOF5        36.40000            0.000000
AGOF6        15.80000            0.000000
AGOF7        22.00000            0.000000
AGOF8        18.00000            0.000000
AGOF9        17.30000            0.000000
AGOF10       24.90000            0.000000
AGOF11       26.00000            0.000000
AGOF12       36.00000            0.000000
AGOF13       55.00000            0.000000
AGOF14       15.00000            0.000000
AGOF15       8.660000            0.000000
AGOF16       111.0000            0.000000
AGOF17       104.0000            0.000000
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AGOF18       22.10000            0.000000
AGOF19       23.60000            0.000000
AGOF20       23.00000            0.000000
AGOF21       23.30000            0.000000
AGOF22       23.20000            0.000000
AGOF23       21.50000            0.000000
AGOF24       19.70000            0.000000
AGOF25       26.30000            0.000000
AGOF26       72.45000            0.000000
AGOF27       98.20000            0.000000
GBIOMASS     170.0000            0.000000
GETHANE      424.0000            0.000000
GPROPANE     670.0000            0.000000
GBUTANE      900.0000            0.000000
GPENTANE     1200.000            0.000000
GHEXANE      1600.000            0.000000
GHEPTANE     1800.000            0.000000
GOCTANE      2000.000            0.000000
GNONANE      2510.000            0.000000
GDECANE      2750.000            0.000000
GMETHANOL    450.0000            0.000000
GETHANOL     770.0000            0.000000
GPROPANOL    950.0000            0.000000
GBUTANOL     1120.000            0.000000
GPENTANOL    1770.000            0.000000
GPENTANEDIOL 3000.000            0.000000
TLCS1        26735.67            0.000000
F1           44723.44            0.000000
F2           0.000000            293.3775
TLCS2        12969.80            0.000000
TLCS         39705.47            0.000000
TLIGNIN      10246.14            0.000000
F3           12969.80            0.000000
TSUGAR       25933.60            0.000000
F4           26735.67            0.000000
THMF         0.000000            0.000000
F5           0.000000            1213.257
TF           10606.84            0.000000
F6           25933.60            0.000000
TTHFA        10415.92            0.000000
F9           10606.84            0.000000
TS           4959.962            0.000000
F12          5276.556            0.000000
F13          0.000000            70.51638
F15          0.000000            0.000000
TM           0.000000            0.000000
F14          0.000000            329.1541
TALC1        0.000000            0.000000
F7           0.000000            750.1398
F8           0.000000            880.7437
TALC2        10311.76            0.000000
F10          10415.92            0.000000
F11          0.000000            0.000000
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TALC3        0.000000            0.000000
F18          0.000000            658.2947
F19          0.000000            672.9473
F20          0.000000            643.0871
TALC         10311.76            0.000000
F26          10311.76            0.000000
TALK1        3719.972            0.000000
F16          0.000000            598.3062
F17          4959.962            0.000000
TALK2        6202.192            0.000000
F22          0.000000            258.5646
F23          7946.715            0.000000
F24          2365.047            0.000000
TALK3        0.000000            0.000000
F25          0.000000            0.000000
TALK         9922.164            0.000000
F27          9922.164            0.000000
TAC          0.000000            0.000000
F21          0.000000            303.3872
ETHANE       847.0376            0.000000
PROPANE      2183.840            0.000000
BUTANE       2578.383            0.000000
PENTANE      927.4978            0.000000
HEXANE       782.1439            0.000000
HEPTANE      783.6424            0.000000
OCTANE       762.6634            0.000000
NONANE       699.7267            0.000000
METHANOL     0.000000            0.000000
ETHANOL      0.000000            0.000000
PROPANOL     0.000000            0.000000
BUTANOL      0.000000            0.000000
PENTANEDIOL  9502.289            0.000000
EPETHANE     359143.9            0.000000
EPPROPANE    1463173.            0.000000
EPBUTANE     2320545.            0.000000
EPPENTANE    1112997.            0.000000
EPHEXANE     1251430.            0.000000
EPHEPTANE    1410556.            0.000000
EPOCTANE     1525327.            0.000000
EPNONANE     1756314.            0.000000
EPDECANE     982379.5            0.000000
EPALK        0.1218187E+08       0.000000
EPMETHANOL   0.000000            0.000000
EPETHANOL    0.000000            0.000000
EPPROPANOL   0.000000            0.000000
EPBUTANOL    0.000000            0.000000
EPPENTANOL   708170.6            0.000000
EPPENTANEDIOL0.2850687E+08       0.000000
EPALC        0.2921504E+08       0.000000
REVENUE      0.4139690E+08       0.000000
CBIOMASS     8500000.            0.000000
TACC         8575109.            0.000000
TAOC         4927800.            0.000000
```