

**The Integration of Environmental Aspects in Computer
Aided Molecular Design Framework**

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ABSTRACT

Chemical product design is the process of identifying optimal products for specific applications based on customer needs. This process is often done by Computer Aided Molecular Design (CAMD) technique, a powerful tool to determine molecular structures that meet targeted properties using property prediction models. Most of the CAMD problems focused on designing molecules with desirable physicochemical properties without considering the environmental aspects of molecules during the decision-making stage. However, chemical products with good functionalities do not imply that they are environmental friendly. Hence, besides physicochemical properties, it was also important to consider environmental properties of molecules as design criteria.

The first focus of this research was to develop a mathematical model to integrate both physical and environmental properties in CAMD framework. The CAMD problem was formulated as a multi objective optimisation problem where targeted physicochemical and environmental properties were to be optimised simultaneously. Nevertheless, a major obstacle faced by multi-objective CAMD problems was the difficulty in assigning weightages to the multiple objectives. To address this issue, Analytic Hierarchy Process (AHP) method was integrated into multi-objective CAMD framework to provide a systematic way in assigning the consistent weightages to multiple objectives involved in CAMD formulation.

The work was further extended to include safety and health aspects as design criteria in CAMD problems. However, there was an increase in complexity and fuzziness of CAMD problem when safety, health and environmental (SHE) aspects

as well as physical properties were all considered as design criteria. This was because information needed for evaluating the relative importance between SHE properties were more uncertain and complex. Fuzzy Analytic Hierarchy Process (FAHP) was embedded into CAMD framework to handle the fuzziness and ambiguity of subjective opinions occurred during the pairwise comparison.

Following that, it was realised that the attributes of a solvent not only affected its functionality but environmental performance of a process. Thus, the next focus of the work was to develop a single stage CAMD framework that can simultaneously identify solvent that meets predefined properties and improves environmental performance of its recovery process. The developed methodology integrated the quantification of environmental impact of solvent recovery process into CAMD framework. IChemE Sustainability Metrics was applied to calculate the total environmental burden of solvent recovery process.

There was also a need to evaluate the effect of various solvent recovery processes on molecular design as each of these separation techniques required different amount of energy for solvent recovery. The total utility cost and energy required for solvent recovery were integrated into CAMD framework. With this approach, the generated solvents can be recovered through a cheaper and cleaner process and gave a better balance of performance for a set of predefined properties. In the last part, the thesis highlighted the potential extension and future works in this area of research work.

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Ooi, J., Ng, D. K. S. and Chemmangattuvalappil, N. G. (2018) ‘Optimal molecular design towards an environmental friendly solvent recovery process’, *Computers & Chemical Engineering*, 117, pp. 391 – 409. Doi: 10.1016/j.compchemeng.2018.06.008

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TABLE OF CONTENTS

TITLE	PAGE
ABSTRACT	i
PUBLICATIONS	iii
ACKNOWLEDGEMENTS	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	xv
LIST OF FIGURES	xxi
LIST OF NOMENCLATURE	xxiii
CHAPTER 1 INTRODUCTION	1
1.1 The Importance of Environmental Aspect in Computer Aided Molecular Design	1
1.2 Background Problems	3
1.3 Outline of the Thesis	7
CHAPTER 2 LITERATURE REVIEW	9
2.1 Introduction	9
2.2 Environmental Indices	10
2.3 Safety Indices	16
2.4 Health Indices	17
2.5 Computer Aided Molecular Design (CAMD)	20
2.5.1 Application of Environmental Properties in CAMD Problems	27
2.5.2 Application of CAMD for Solvent Design in Separation Processes	30
2.6 Group Contribution Method (GCM)	33
2.7 Multi-objective Optimisation	36
2.8 Analytic Hierarchy Process (AHP)	39

2.9	Fuzzy Analytic Hierarchy Process (FAHP)	42
2.10	Summary	43
CHAPTER 3	RESEARCH SCOPES AND METHODOLOGIES	45
3.1	Research Gaps	45
3.2	Scopes of Research	48
3.2.1	Integrate physical property targets and environmental properties into CAMD framework	48
3.2.2	Manage the subjectivity arising from complex and uncertain information needed to incorporate safety, health and environmental (SHE) aspects into CAMD framework	48
3.2.3	Assess the environmental impact of solvent recovery process in which the designed solvent is applied	49
3.2.4	Evaluate the effect of different solvent recovery alternatives on molecular design	50
3.3	Research Objectives	51
3.4	Overall Research Methodology	51
3.4.1	Integrate physical property targets and environmental properties into CAMD framework	52
3.4.2	Manage the highly subjectivity nature arising from complex and uncertain information needed to incorporate safety, health and environmental aspects into CAMD framework	53
3.4.3	Assess the environmental impact of solvent recovery process in which the designed solvent is applied	54
3.4.4	Evaluate the effect of different solvent recovery alternatives on molecular design	55

3.5	Summary	57
CHAPTER 4	A SYSTEMATIC MULTI-OBJECTIVE MOLECULAR DESIGN FRAMEWORK USING ANALYTIC HIERARCHY PROCESS	58
4.1	Introduction	58
4.2	Problem Statement	59
4.3	Methodology	60
4.3.1	Development of decision hierarchy	62
4.3.2	Construction of pairwise comparison matrix	62
4.3.3	Sensitivity analysis	64
4.3.4	Synthesize the pairwise comparison	65
4.3.5	Perform the consistency verification	66
4.3.6	Molecular design stage	67
4.4	Case study	71
4.4.1	Problem Statement	71
4.4.2	Identification of design objective and target properties	72
4.4.3	Determination of property prediction models	73
4.4.4	Development of hierarchical structure	75
4.4.5	Computation of weights from Decision Maker's value judgement	75
4.4.6	Molecular design stage	80
4.4.7	Define objective function and solve the mathematical model	80
4.4.8	Results and discussions	81
4.5	Summary	90

CHAPTER 5	INTEGRATION OF FUZZY ANALYTIC HIERARCHY PROCESS INTO MULTI-OBJECTIVE COMPUTER AIDED MOLECULAR DESIGN	92
5.1	Introduction	92
5.2	Problem statement	93
5.3	Methodology	94
	5.3.1 Identification of design objective	94
	5.3.2 Determination of property prediction model	95
	5.3.3 Identification of safety and health indices	95
	5.3.4 Disjunctive programming on allocation of index score	97
	5.3.5 Development of hierarchical decision structure	99
	5.3.6 Computation of weights from Decision Maker's value judgement	99
	5.3.7 Molecular design stage	102
	5.3.8 Optimisation model	102
5.4	Case study	105
	5.4.1 Problem statement	105
	5.4.2 Determination of design objective	105
	5.4.3 Identification of property prediction models	106
	5.4.4 Disjunctive optimisation	108
	5.4.5 Development of hierarchy model	109
	5.4.6 Computation of weighting factor	110
	5.4.7 Molecular design stage	114
	5.4.8 Optimisation model	114

	5.4.9 Results and discussions	115
	5.5 Summary	126
CHAPTER 6	OPTIMAL MOLECULAR DESIGN TOWARDS AN ENVIRONMENTAL FRIENDLY SOLVENT RECOVERY PROCESS	127
6.1	Introduction	127
6.2	Problem Statement	128
6.3	Methodology	129
	6.3.1 Identification of design objective	129
	6.3.2 Quantification of the environmental performance of a process	130
	6.3.3 Selection of safety and health indices	133
	6.3.4 Identification of property prediction model	135
	6.3.5 Application of disjunctive programming on index scoring	136
	6.3.6 Computation of weighting factor of each objective function	136
	6.3.7 Molecular design stage	136
	6.3.8 Optimisation model	137
6.4	Case study	140
	6.4.1 Problem statement	140
	6.4.2 Determination of design objective	142
	6.4.3 Quantification of the environmental performance of a process	143
	6.4.4 Identification of property prediction model	145
	6.4.5 Application of disjunctive programming on index scoring	146

	6.4.6	Construction of hierarchical decision model	147
	6.4.7	Computation of weighting factor of each objective function	148
	6.4.8	Molecular design stage	150
	6.4.9	Optimisation model	150
	6.4.10	Results and discussions	151
	6.5	Summary	162
CHAPTER 7		A SYSTEMATIC MOLECULAR DESIGN FRAMEWORK WITH THE CONSIDERATION OF COMPETING SOLVENT RECOVERY PROCESSES	163
	7.1	Introduction	163
	7.2	Problem Statement	164
	7.3	Methodology	165
	7.3.1	Identification of design objective	165
	7.3.2	Assessment of separation techniques for solvent recovery	166
	7.3.3	Selection of safety and health indices	169
	7.3.4	Identification of property prediction model	170
	7.3.5	Computation of weighting factor of each objective function	171
	7.3.6	Molecular design phase	171
	7.3.7	Optimisation model	171
	7.4	Case study	174
	7.4.1	Problem statement	174
	7.4.2	Identification of design objective	175

7.4.3	Assessment of separation techniques for solvent recovery	177
7.4.4	Quantification of the yield of extracted carotene	183
7.4.5	Identification of property prediction model	185
7.4.6	Development of hierarchical decision structure	187
7.4.7	Computation of weights for each objective function	187
7.4.8	Molecular design stage	190
7.4.9	Optimisation model	190
7.4.10	Results and discussions	191
7.5	Summary	203
CHAPTER 8	CONCLUSION	204
8.1	Achievements	204
8.1.1	Integration of physical and environmental properties into CAMD framework through AHP	205
8.1.2	Incorporation of SHE aspects into CAMD framework via FAHP	205
8.1.3	Development of a systematic CAMD framework that considers quantitative assessment of environmental impact of solvent recovery process	206
8.1.4	Development of a systematic CAMD framework that considers the effect of various solvent recovery processes on solvent selection	207
8.2	Future Works	207
8.2.1	Develop a systematic CAMD methodology to optimise the minimum deviation from the best	

	profit that leads to huge improvement in SHE aspects	208
8.2.2	Consideration of social aspect in product-process design framework	208
8.2.3	Develop a sustainable integrated product-process framework through Analytic Network Process	209
8.2.4	Validation of CAMD solutions through experimental works	210

REFERENCES 212

APPENDICES 226

	Appendix A: Lingo Coding (Chapter 4)	226
	Appendix B: Lingo Coding (Chapter 5)	232
	Appendix C: Lingo Coding (Chapter 6)	249
	Appendix D: Lingo Coding (Chapter 7)	262

LIST OF TABLES

	Page
Table 2.1: Flammability (I_{FL}) based index (NFPA)	17
Table 2.2: Explosiveness (I_{EX}) based index (modified from ISI)	17
Table 2.3: Viscosity (I_{η}) based index (modified from PRHI)	19
Table 2.4: Material phase (I_{ms}) based index (modified from PRHI)	19
Table 2.5: Exposure limit (I_{EL}) based index (modified from IOHI)	19
Table 2.6: Volatility (I_v) based index	19
Table 2.7: Acute health hazard (I_{AH}) based index (NFPA)	19
Table 4.1: Conventional AHP numerical scale for subjective judgements by Saaty (1980)	64
Table 4.2: Random Index for AHP	67
Table 4.3: GCM equations and empirical correlations for selected properties	74
Table 4.4: Upper and lower bound of properties for solvent design	74
Table 4.5: Pairwise comparison matrix of main properties with respect to goal	76
Table 4.6: Pairwise comparison matrix of sub-physical properties	77
Table 4.7: Pairwise comparison matrix of sub-environmental properties	79
Table 4.8: Final weighting factors of target properties in the overall system	80
Table 4.9: Property and property operator	81
Table 4.10: The generated acyclic solvent with their respective properties	84

Table 4.11: The generated acyclic solvent with their respective properties (continued)	84
Table 4.12: The generated monocyclic solvents with their respective properties	85
Table 4.13: The generated monocyclic solvent with their respective properties (continued)	85
Table 4.14: Properties of hexane	86
Table 4.15: Top ten monocyclic solvent generated for case study 'a'	88
Table 4.16: Top ten monocyclic solvent generated for case study 'a' (continued)	88
Table 4.17: Top ten monocyclic solvent generated for case study 'b'	89
Table 4.18: Top ten monocyclic solvent generated for case study 'b' (continued)	89
Table 5.1: Flammability (I_{FL}) based index (NFPA)	96
Table 5.2: Explosiveness (I_{EX}) based index (modified from ISI)	96
Table 5.3: Exposure limit (I_{EL}) based index (modified from IOHI)	97
Table 5.4: Acute health hazard (IAH) based index (NFPA)	97
Table 5.5: Summary of fuzzy scale (Tan et al., 2016)	100
Table 5.6 The desirable qualitative attributes of designed solvent with their respective translated quantitative properties	105
Table 5.7: Fuzzy pairwise comparison matrix of main criteria for solvent design on oil extraction	111
Table 5.8: Fuzzy pairwise comparison of physical sub properties for solvent design on oil extraction	111
Table 5.9: Fuzzy pairwise comparison of environmental sub properties for solvent design on oil extraction	112
Table 5.10: Fuzzy pairwise comparison of safety sub index for solvent design on oil extraction	112
Table 5.11: Fuzzy pairwise comparison of health sub index for solvent design on oil extraction	113

Table 5.12: Final weighting factors of target properties in the overall system	113
Table 5.13: Property and property operator	115
Table 5.14: The generated acyclic solvents with their respective properties [with FAHP approach]	117
Table 5.15: The generated acyclic solvent with their respective properties [with FAHP approach] (continued)	117
Table 5.16: The generated monocyclic solvent with their respective properties [with FAHP approach]	118
Table 5.17: The generated monocyclic solvent with their respective properties [with FAHP approach] (continued)	118
Table 5.18: The generated acyclic solvents with their sub-index scores [with FAHP approach]	119
Table 5.19: The generated monocyclic solvent with their sub-index scores [with FAHP approach]	119
Table 5.20: Properties of hexane	120
Table 5.21: The generated acyclic solvents with their respective properties [without FAHP approach]	122
Table 5.22: The generated acyclic solvents with their respective properties [without FAHP approach] (continued)	122
Table 5.23: The generated monocyclic solvents with their respective properties [without FAHP approach]	123
Table 5.24: The generated monocyclic solvents with their respective properties [without FAHP approach] (continued)	123
Table 5.25: The generated acyclic solvents with their sub index score [without FAHP approach]	124
Table 5.26: The generated monocyclic solvents with their sub index score [without FAHP approach]	124
Table 6.1: Conversion factors for converting energy consumption into greenhouse gases (GHG) emissions	131
Table 6.2: EB equivalent for various types of pollution (ICChemE, 2002)	132

Table 6.3:	Potency factor of each pollutant (IChemE, 2002)	133
Table 6.4:	Translation of favourable qualitative attributes of designed solvent into their respective measurable properties	142
Table 6.5:	Fuzzy pairwise comparison matrix of main properties for solvent design in residual oil extraction process	149
Table 6.6:	Final weighting factors of target properties in the overall molecular design problem	149
Table 6.7:	Property and property operator	151
Table 6.8:	The generated acyclic solvents with their respective properties	153
Table 6.9:	The generated acyclic solvents with their respective properties (continued)	153
Table 6.10:	The generated monocyclic solvents with their respective properties	154
Table 6.11:	The generated monocyclic solvents with their respective properties (continued)	154
Table 6.12:	The generated acyclic solvents with their safety and health indices scores	155
Table 6.13:	The generated monocyclic solvents with their safety and health indices scores	155
Table 6.14:	Properties of hexane	156
Table 6.15:	The generated acyclic solvents with their respective properties [sensitivity analysis results]	159
Table 6.16:	The generated acyclic solvents with their respective properties [sensitivity analysis results] (continued)	159
Table 6.17:	The generated monocyclic solvents with their respective properties [sensitivity analysis results]	160
Table 6.18:	The generated monocyclic solvents with their respective properties [sensitivity analysis results] (continued)	160
Table 6.19:	The generated acyclic solvents with their safety and health indices scores [sensitivity analysis results]	161

Table 6.20:	The generated monocyclic solvents with their safety and health indices scores [sensitivity analysis results]	161
Table 7.1:	Cost of each utility	169
Table 7.2:	Translation of favourable qualitative attributes of designed solvent into their respective measurable properties	176
Table 7.3:	The relationship between concentration of carotene and temperature	185
Table 7.4:	Upper and lower limit of properties for solvent design	186
Table 7.5:	Fuzzy pairwise comparison matrix of main properties for solvent design in residual oil extraction process	188
Table 7.6:	Fuzzy pairwise comparison matrix of process sub-properties for solvent design in residual oil extraction process	189
Table 7.7:	Final weighting factors of target properties in the overall system	189
Table 7.8:	Properties of Hexane	195
Table 7.9:	The generated acyclic solvents with their respective properties (normal evaporation process)	197
Table 7.10:	The generated acyclic solvents with their respective properties (normal evaporation process) (continued')	197
Table 7.11:	The generated monocyclic solvents with their respective properties (normal evaporation process)	198
Table 7.12:	The generated monocyclic solvents with their respective properties (normal evaporation process) (continued')	198
Table 7.13:	The generated acyclic solvents with their respective properties (vacuum evaporation process)	199
Table 7.14:	The generated acyclic solvents with their respective properties (vacuum evaporation process) (continued')	199
Table 7.15:	The generated monocyclic solvents with their respective properties (vacuum evaporation process)	200
Table 7.16:	The generated monocyclic solvents with their respective properties (vacuum evaporation process) (continued')	200

Table 7.17: The generated acyclic solvents with their respective properties (cooling crystallisation process)	201
Table 7.18: The generated acyclic solvents with their respective properties (cooling crystallisation process) (continued')	201
Table 7.19: The generated monocyclic solvents with their respective properties (cooling crystallisation process)	202
Table 7.20: The generated monocyclic solvents with their respective properties (cooling crystallisation process) (continued')	202

LIST OF FIGURES

	Page
Figure 3.1: Overall methodology developed for this research	56
Figure 4.1: Procedures for research scope 1	70
Figure 4.2: Hierarchy model for this case study	75
Figure 4.3: Molecular structure of the best ten acyclic solvents	82
Figure 4.4: Molecular structures of the best ten monocyclic solvents	82
Figure 5.1: Methodology for research scope 2	104
Figure 5.2: Hierarchical decision structure for this case study	109
Figure 5.3: Molecular structure of the best ten acyclic and monocyclic solvents	116
Figure 6.1: Methodology for research scope 3	139
Figure 6.2: Process flow sheet of residual oil extraction from PPF using solvent extraction method	141
Figure 6.3: Hierarchical decision structure for this case study	148
Figure 6.4: Generated acyclic and monocyclic solvents with their respective molecular structures	152
Figure 6.5: Radar chart representing the target properties of top acyclic, monocyclic solvents and hexane	158
Figure 7.1: Methodology for research scope 4	173
Figure 7.2: Process flow sheet of residual oil extraction from PPF using solvent extraction method	175
Figure 7.3: Process flow diagram of residual oil extraction from PPF using solvent extraction followed by vacuum evaporation process	178
Figure 7.4: Process flow diagram of residual oil extraction from PPF using solvent extraction followed by cooling crystallisation process	178

Figure 7.5: Hierarchical decision model for this case study	187
Figure 7.6: Generated acyclic and monocyclic solvents with their respective molecular structures if solvents were to be recovered through normal evaporation	192
Figure 7.7: Generated acyclic and monocyclic solvents with their respective molecular structures if solvents were to be recovered through vacuum evaporation	192
Figure 7.8: Generated acyclic and monocyclic solvents with their respective molecular structures if solvents were to be recovered through cooling crystallisation	193

LIST OF NOMENCLATURE

Abbreviations

AA	Atmospheric Acidification
AHI	Atmospheric Hazard Index
AHP	Analytic Hierarchy Process (AHP)
CAM ^b D	Computer aided mixture/blend design
CAMD	Computer Aided Molecular Design
CAMPD	Computer Aided Molecular and Process Design
CAOD	Computer aided organic synthesis
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CoMT-CAMD	Continuous-molecular targeting approach for computer aided molecular design
CPO	Crude palm oil
DIPE	Diisopropyl Ether
EACO	Efficient Ant Colony Optimisation
ECI	Environmental Consequence Index
EFRAT	Environmental Fate and Risk Assessment Tool
EHI	Environmental Hazard Index
EIPs	Eco-industrial parks
EPA	Environmental Protection Agency
EPIP	Environmental Performance of Industrial Processes
EU	Eutrophication

FAHP	Fuzzy Analytic Hierarchy Process
FFA	Free fatty acid
FFB	Fresh Fruit Bunches
GCM	Group Contribution Method
GD	Green Degree
GDP	Generalised Disjunctive Programming
GERA	Global Environmental Risk Assessment
GHG	Greenhouse gases
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
GWP	Global warming potential
IChemE	Institution of Chemical Engineers
ICPRI	Inherent Chemical Process Route Index
IETH	Inherent Environmental Toxicity Hazard
IL	Ionic liquid
ILO	International Labour Organisation
IOHI	Inherent Occupational Health Index
IPCCWN	Inter-plant chilled and cooling water network
ISI	Inherent Safety Index
LA	Linoleic acid
LCA	Life Cycle Assessment
MBEI	Material Balance Environmental Indices
MCDM	Multi-criteria Decision Making

MEIM	Environmental Impact Minimisation
MIBK	Methyl Isobutyl Ketone
MIC	Methyl isocyanate
MILP	Mixed-integer linear programming
MINLP	Mixed-integer nonlinear programming
MPK	Methyl Propyl Ketone
N ₂ O	Nitrous Oxide
NFPA	National Fire Protection Association
NLP	Nonlinear Programming
NO _x	Nitrogen oxide
OA	Oleic acid
ODP	Ozone-depletion potential
ORC	Organic Rankine Cycle
PA	Palmitic acid
PCOP	Photochemical ozone formation potential
PCP-SAFT	Perturbed chain polar statistical associating fluid theory
PEI	Potential Environmental Impact
POME	Palm oil mill effluent
PPF	Palm Pressed Fibres
PRHI	Process Route Healthiness Index
QSAR	Qualitative structure activity relationship
SHE	Safety, health and environmental
SO _x	Sulphur oxide

TAGs	Triglycerides
TFNs	Triangular Fuzzy Numbers
THF	Tetrahydrofuran
USDA	United States Department of Agriculture
VOC	Volatile organic compound
WAR	Waste Reduction Algorithm

Sets

U	Set of pollutant $\{u \mid u = 1, 2, \dots, R\}$
B	Set of environmental impact $\{b \mid b = 1, 2, \dots, F\}$
P	Set of target property $\{p \mid p = 1, 2, \dots, E\}$

Parameters

A	Positive reciprocal pairwise comparison matrix
a_{ij}	Relative importance of property i to property j
a_{ij_base}	Intensity of importance given to the base case study
\hat{a}_{ij}	Fuzzy number
A_{LD50}	Universal constant for the GCM of LD_{50}
B_{LD50}	Universal constant for the GCM of LD_{50}
C_0	Initial concentration of carotene
C_i	Contribution of first order group of type- i

CI	Consistency index
C_{poil}	Heat capacity of residual oil
C_{p0i}	Adjustable parameter for GCM of C_p
C_{pli}	Heat capacity contribution of the first order group of type i
CR	Consistency ratio
DAE	Dry air equivalent
D_j	Contribution of second order group of type- j
E_a	Activation energy
E_k	Contribution of third order group of type- k
FM_0	Universal constant for the GCM of LC_{50}
F_{p0}	Universal constant for the GCM of F_p
g	Coefficient to represent the type (acyclic, monocyclic, bicyclic or tricyclic) of compounds
G_T	Total number of groups selected
ΔH_{fus}	Heat of fusion of oil
H_{v0}	Universal constant for the GCM of H_v
I	Binary integer variable
K_{ow0}	Universal constant for the GCM of K_{ow}
\hat{L}_{ij}	Lower bound of triangular fuzzy number
\hat{M}_{ij}	Modal value of triangular fuzzy number
M_{oil}	Mass of residual oil

M_s	Mass of designed solvent fed
$M_{v,s}$	Mass of vaporised solvent
MWc	Molecular weight entrainment ratio of solvent vapour
n	Matrix size
O_k	Frequency of third order group of type- k
P_1	Initial operating pressure of the evaporator
P_2	Designed operating pressure of the evaporator
p_L	Lower bound of feasible p value
P_a	Suction pressure of steam ejector
P_d	Discharge pressure of steam ejector
$PR_{b,u}$	Potency factor of pollutant u for environmental impact b
P_{switch}	Property boundary value
p_U	Upper bound of feasible p value
R	Universal gas constant
R_a	Consumption of motive steam for compressing a unit mass DAE mass of suction gas in a steam ejector
RI	Random index
t	Heating time
T	Operating temperature of separation unit
T_{b0}	Universal constant for the GCM of T_b
T_{b1}	Initial operating temperature of the evaporator

TC_a	Temperature entrainment ratios
T_{crys}	Operating temperature of crystalliser
T_{evp}	Operating temperature of the multistage evaporator
T_{ext}	Operating temperature of the extraction unit
T_{feed}	Temperature of the feed
T_{m0}	Universal constant for the GCM of T_m
T_{mli}	Normal melting point contribution of the first order group of type i
$T_{out,condenser}$	Condenser outlet temperature
$T_{out,heater}$	Heater outlet temperature
T_{sg}	Suction gas temperature
\hat{U}_{ij}	upper bound of triangular fuzzy number
v_A	Molar volume of oil
$V_{gas,std}$	Molar volume of gas or vapour at standard condition
v_i	Valence of group i
V_p	Value of target property p
v_p^L	Lower bound of target property p
v_p^U	Upper bound of target property p
w	Principal eigenvector (optimal priority vector)
w_{AH}	Weighting factor for sub-index I_{AH} .

w_{EL}	Weighting factor for sub-index I_{EL}
w_{EX}	Weighting factor for sub-index I_{EX}
w_{FL}	Weighting factor for sub-index I_{FL}
w_i	Principal eigenvector of property i
w_j	Principal eigenvector of property j
w_i / w_j	Solution ratio
w_m	Weighting factor for each normalised target property operator
y	Binary coefficient for second order molecular group
z	Binary coefficient for third order molecular group

Variables

BCF	Bioconcentration factor
C	Concentration of carotene after time t
C_f	Final concentration of carotene
C_O	Oxygen stoichiometric coefficient
C_p	Specific heat capacity
C_{ps}	Average heat capacity of designed solvent
$Cost_{crys}$	Total utilities cost for cooling crystallisation process
$Cost_{evap,n}$	Total utilities cost for a normal evaporation process
$Cost_{evap,v}$	Total utilities cost for a vacuum evaporation process

D_{AB}	Diffusivity of oil in solvent B
EB	Environmental burden
F_p	Flash point
$F^{weighted\ sum}$	Overall objective function
H_v	Latent heat of vaporisation
$\Delta H^{feed, evap}$	Enthalpy change for feed for the evaporator
$\Delta H^{top, evap}$	Enthalpy change for top product
$\Delta H^{bottom, evap}$	Enthalpy change for bottom product
I_{AH}	Acute health hazard
I_{EL}	Exposure limit based index
I_{EX}	Explosiveness based index
I_{FL}	Flammability based index
I_{ms}	Material phase based index
I_{η}	Viscosity based index
$I_{SHI, w}$	Total weighted penalty score for safety and health aspect of molecules
I_v	Volatility based index
k	Temperature dependent rate constant
LC_{50}	Oral rat acute toxicity
LD_{50}	Fathead minnow toxicity
LEL	Lower explosion limit

LFL	Lower flammability limit
$\log K_{oc}$	Soil sorption coefficient
$\log K_{ow}$	Octanol-water partition coefficient
M_j	Frequency of second order group of type- j
M_{steam}	Mass of steam needed
$M_{steam,motive}$	Total amount of motive steam needed for steam ejector
M_u	Mass of pollutant u emitted
M_w	Molecular weight
N_i	Frequency of first order group of type- i
O_k	Frequency of third order group of type- k
PCO	Photochemical oxidation potential
PEL	Permissible exposure limit (mol/m ³)
PEL'	Permissible exposure limit (ppm)
$q_{c,crys}$	Cooling duty needed for crystallisation
$q_{c,evap}$	Duty of condenser located after evaporator
$q_{H,crys}$	Heating duty needed for heater located after crystalliser
$q_{H,evap}$	Heat transferred from steam to the evaporator
$R_{carotene}$	Difference of Hildebrand solubility parameter between solvent and carotene
S	Explosiveness (UEL – LEL) (vol%)
T_b	Boiling Point

T_{b2}	Estimated boiling point of the solvent at operating pressure, P_2
T_m	Normal melting point
UEL	Upper explosion limit
UFL	Upper flammability limit

Greek Symbols

λ	Consistency index
λ_{\max}	Principal eigenvalue
λ_{pm}	Normalised target property operator
λ_{steam}	Latent heat of steam
Ω_p	Target property operator
$\Omega_{p\min}$	Minimum value of target property operator
$\Omega_{p\max}$	Maximum value of target property operator
φ	Association factor for solvent
δ	Hildebrand solubility parameter
δ_0	Universal constant for the GCM of δ
δ_c	Degree of confidence
μ	Viscosity
σ	Surface tension

CHAPTER 1

INTRODUCTION

1.1 The Importance of Environmental Aspect in Computer Aided Molecular Design

Swift industrialisation, intensive production and resource extraction has been elicited since there is a surge in world population together with their emerging societal demands (Jegasothy, 1999). Unfortunately, rapid development of industrialisation and urbanisation have resulted in negative environmental impacts to the ecosystem. The environmental evaluation on an industrial process can be done by considering two aspects. This includes waste generation and hazardous emissions from the process as well as the product life-cycle from raw material production to use and disposal. There are several systematic methods available for evaluating the environmental impact of process and products. Some of the example of these methods include waste reduction (WAR) algorithm, life cycle assessment (LCA), environmental fate and risk assessment tool (EFRAT) and the methodology for the environmental impact minimization (MEIM).

According to Twelve Principles of Green Chemistry (Jessop et al., 2008), there are twelve basic steps that can be practised to reduce environmental related issues. One of these steps involves the use of safer and less toxic chemical solvents in industries. It means that industries must actively look for solvents that are more favourable in terms of safety, health and environmental (SHE) properties to replace the non-favourable solvents. Traditionally, a substitution solvent is identified through database searches, experiences and experimental studies. However, these conventional methods are very costly, time consuming

and inefficient as they are mainly based on trial and error approaches. Instead, Computer Aided Molecular Design (CAMD) technique can be used to determine the substitution solvent. CAMD technique has been well-known for its effectiveness and ability in designing various types of chemical, biochemical and material products. It is able to determine molecular structures of solvents that match the predefined normal property targets.

To ensure that the generated molecules fulfil environmental regulations, it is necessary to consider physicochemical properties as well as environmental aspects of molecules as design criteria in molecular design problems. The generalized WAR algorithm with a potential environmental impact (PEI) balance can provide a relative indication on the environmental friendliness of a chemical substance. In WAR algorithm, the total PEI of a process is determined based on eight categories of potential impacts which include terrestrial toxicity potential, aquatic toxicity potential, global warming potential, ozone depletion potential, photochemical oxidation potential, acidification potential, human toxicity potential by ingestion and human toxicity potential by exposure to both dermal and inhalation (Hukkerikar et al., 2012a). The eight abovementioned environmental properties of a molecule can be estimated through the property prediction models (Hukkerikar et al., 2012a). Over the years, research on integrating the environmental properties into CAMD problem has attracted considerable interests from researchers worldwide. However, most of the existing works only treated environmental aspects as constraints. The main disadvantage of treating environmental properties as constraints is that molecules that are excellent in physicochemical properties may exert bad environmental index scores. This is not desirable as solvents with bad index

scores may not be able to fulfil the stringent environmental regulations. Additional fines will then be imposed to industry that is not capable in meeting the environmental regulations. Likewise, there will be extra cost needed for treating those chemical solvents to fulfil the requirements. This is because industries must install additional layers of solvent treatment unit in process plant, which will result in higher operating costs. On the other hand, if the solvents were environmental friendly, industries can eliminate the installation of these additional treatment layers in processing. For this reason, it is important to use environmental friendly solvents in a process at the first place. This can be done by considering both target physicochemical and environmental properties as design criteria while designing the molecules.

1.2 Background Problems

Various solution approaches have been proposed for solving CAMD problems. These approaches include stochastic optimisation, enumeration techniques, decomposition-based approach, mathematical programming approaches as well as hybrid approaches (Karunanithi et al., 2006). All solution approaches aimed in generating molecules that meet the customers' requirement. In this research, mathematical programming approach was used to formulate CAMD problem as it can solve problems with large design space more efficiently. In mathematical programming, objective function is represented by the predefined targeted properties whereas property constraints are used as mathematical bounds (Odele and Macchietto, 1993). CAMD problem is either formulated as single or multi-objective optimisation problem based on number of design objectives. Since physical and environmental properties were considered as design criteria, CAMD problem was formulated as a multi-

objective optimisation problem. One of the major challenges in the formulation of multi-objective optimisation problems is the subjectivity involved in identifying the optimal solution from the Pareto set formed. Techniques used to determine the set of optimal solutions can be categorized into the weighting method approaches and the non-weighting approaches (Chen and Shonnard, 2004). Some examples of weighting method approaches include weighted sum, weighted product, Analytic Hierarchy Process (AHP), and median ranking method. On the other hand, ϵ -constraint technique and goal programming are non-weighting method approaches that are more commonly used. Weighting method is more commonly used because for the non-weighting method, generation of all alternatives are required before making any decision (Chen and Shonnard, 2004).

According to weighting method, weighting factor of each objective is specified before solving the multi-objective optimisation. Thus, such method generally inherent subjective in specify the weighting factor. In addition, before fully knowing the trade-offs between different properties, it is rather difficult to evaluate their relative importance. Hence, there will be subjectivity involved during judgement elicitation without having a systematic procedure to evaluate the relative importance between the properties. The assigned relative weights will then provide no insight into the underlying multi-objective molecular design problem. It is particularly important to address this issue as good alternatives may have been eliminated due to the subjective weights assigned to the properties. Moreover, different weighting factors of objectives will generate different optimal molecules. For this reason, a systematic method is needed to assign the weighting factors to the multiple objectives.

In recent years, the enforcement of stricter safety, health and environmental (SHE) protocols have urged most chemical industries to reassess their current processes. It is to be noted that the selection of a suitable solvent will greatly influence the performance of a process in which it is applied (Papadopoulos and Linke, 2009). Organic solvents which are used in large quantities in chemical industry often exert hazardous properties such as being highly volatile or toxic. Various indirect environmental impacts and the use of solvents in an industry have been found to be interrelated (Capello et al., 2007). For example, air emissions usually occur during solvent incineration or solvent recycling process which needs large amount of energy. This is because the characteristics of a solvent can affect both performance and environmental hazard of a chemical process. The physical and thermodynamic properties of a solvent dictate the degree of difficulty of a chemical process especially during solvent recovery. When the solvent recovery process becomes more difficult, more energy consumption is needed to recover the solvent, which will in turn lead to greater negative impact on SHE aspects. Over the past decades, researchers have extensively employed CAMD techniques to design environmental friendly solvents that can reach targeted separation performance. Nevertheless, there is no work reported on an approach that can simultaneously identify solvent that meets predefined properties and improves environmental aspects of the its recovery process. To address this limitation, there is a need to develop a single stage CAMD framework that can simultaneously identify the potential solvent and quantify its corresponding environmental impact of recovery process.

Besides, solvents can be recovered by more than one type of separation process. The separation processes include distillation, crystallisation, filtration, centrifugation etc. Among these existing solvent recovery technologies, more than 95% of the chemical industries select distillation to recover solvent (Luis et al., 2014). Solvent recovery through distillation process usually consumes excessive energy to recover solvent from a mixture, which will have a significant effect on the environmental impact. In conventional practice, the choice between solvent recovery alternatives is made based on the basis of economic analysis. However, environmental hazard of a solvent recovery process should also be taken into consideration when choosing solvent recovery alternatives. Thus far, waste-solvent treatment options were optimised based on environmental point of view. For example, Seyler et al., (2006) assessed the environmental impacts of solvent recycling using distillation, solvent incineration and solvent disposal for Swiss chemical industry. From their work, two case studies were assessed to illustrate the integration of environmental friendly waste-solvent treatment into the planning of a chemical production. Recently, in order to develop a more environmentally friendly solvent recovery processes. Luis et al., (2014) designed a hybrid process that comprised pervaporation and distillation to separate methanol from tetrahydrofuran (THF). Beside energy requirement, they carried out life cycle assessment (LCA) to compare the environmental impact of the hybrid process and pressure swing distillation to that of incineration. The results from this work showed that hybrid process exerted lowest impact on environment. Besides waste-solvent treatment options, it should also be noted that various solvent recovery technologies will lead to different levels of environmental impact. Yet, no work has been done on comparing the effect of

solvent recovery technology on different solvents. Energy consumption during solvent recovery process will vary according to the solvent properties. To bridge the gap, it is of vital importance to develop a CAMD framework that consider the effect of various solvent recovery techniques to minimise pollution together with improvement in economic performance.

1.3 Outline of the Thesis

The thesis had been distributed in 8 chapters. Chapter 2 showed the literature review on environmental indices, safety and health indices, chemical product design, CAMD, Group contribution method (GCM), application of environmental properties in CAMD, multi-objective optimisation approach, disjunctive programming, AHP and FAHP. This led to detailed discussion of research gaps, research scopes as well as research methodologies in chapter 3. Following these, research scopes were then illustrated in chapters 4 to 7. Chapter 4 presented the first research scope, which was to develop a mathematical model to integrate physical property targets and environmental properties in molecular design. The second research scope was depicted in chapter 5, which presented the integration of FAHP into CAMD framework. This framework helped to manage the fuzziness and ambiguity of subjective opinions occurred when performing pairwise comparison for SHE properties. This was because the data required for the evaluation of relative importance between safety, health and environmental properties were more uncertain and complex than comparing physical and environmental properties. Chapter 6 demonstrated the third research scope, which was to develop a single stage CAMD methodology that integrates the quantification of environmental impact of solvent recovery process into CAMD framework. Via this approach, solvent can simultaneously

meet the targeted properties and enhance the environmental performance of its recovery process. Chapter 7 presented an extension of the methodology in chapter 6, by considering the effect of existing solvent recovery alternatives on molecular design. The energy requirement and total utilities cost needed to recover the solvent are integrated into CAMD framework. Chapter 8 depicted the summary of the achievements and contributions of this research work. Besides, the potential future works that can be done in this area of research work are highlighted.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This research work aimed to integrate environmental aspects into CAMD framework for the design of molecules such as solvents or process fluids that satisfy multiple properties. Green engineering and sustainability concept have increasingly become a concern for all chemical industries. Federal agencies such as United States Environmental Protection Agency (EPA) promotes public awareness on environmental and health issues by recognising and rewarding industries that meet safety, health and environmental (SHE) standards. Thus, before applying a solvent in a process, industries should examine a few factors, including performance and SHE aspects. It is of vital importance to ensure that the designed solvents exhibit favourable SHE characteristics to reduce their adverse impacts on people and environment. Hence existing SHE indices, especially environmental indices, were reviewed thoroughly to determine their suitability to be incorporated into CAMD framework. Besides, the current state of art of CAMD was also reviewed to identify the research gaps. Since CAMD must be formulated as multi-objective optimisation problem when different properties are chosen as design criteria, review on multi-objective optimisation techniques had to be carried out thoroughly. Moreover, there also exists a need to review Analytic Hierarchy Process (AHP) and Fuzzy Analytic Hierarchy Process (FAHP) to determine their suitability in treating CAMD as multi-criteria decision-making problem.

2.2 Environmental Indices

An environmental hazard can be defined as a material, a state or an event that has potential to adversely affect the surrounding environment or human's health (Melnick and Everitt, 2008). Some examples from the key consequences of environmental hazards are acidification, global warming, resource depletion, air pollution, land pollution, water pollution, greenhouse effect and human health effects. The increase in awareness has brought global concern for the environmental consequences of industrial releases and development of methods to assess chemical toxicity and environmental impacts of the processes.

Various methods had been developed to assess and quantify the environmental impacts of chemical processes and substances. In an early paper by Cave and Edwards (1997), Environmental Hazard Index (EHI) had been proposed to rank the chemical process routes. The ranking of chemical process routes was based on the estimation of environmental impact of a total release of chemical inventory to aquatic and terrestrial ecosystem. EHI of a chemical process can be determined by assessing the exposure and effects of each chemical in the process. EHI was developed based on two assumptions such that the damage to the environment is directly proportional to the quantity released and the damage due to the discharge of a mixture of chemicals is additive. However, EHI only focused on estimating the environmental impact on aquatic and terrestrial ecosystem without the consideration of its impact on atmosphere. Atmospheric Hazard Index (AHI) was then developed to evaluate the potential effect of airborne releases from a chemical plant (Gunasekera and Edwards, 2003). The atmospheric impact classifications that were considered in AHI included photochemical smog, global warming, toxicity, acid deposition and

stratospheric ozone depletion. The main assumption in developing AHI was that the catastrophic release of chemical inventories was assumed to be at steady state equilibrium distribution. This assumption was oversimplified because the distribution of chemicals in the environment is usually in unsteady state when there is a catastrophic release of chemicals. For this reason, AHI was further extended by Gunasekera and Edwards (2006a) by proposing a method that utilised the dispersion characteristics of the chemical in the atmosphere to determine the volumes of model environment. This newly developed AHI can then be used for the unsteady state impact analysis. In reference to a combination of the work of Cave and Edwards (1997) and Gunasekera and Edwards (2003), a new index called Inherent Environmental Toxicity Hazard (IETH) was derived to estimate the effects on the aquatic, terrestrial and atmospheric environment when catastrophic failure of the chemical plant occurred (Gunasekera and Edwards, 2006b).

Waste Reduction (WAR) algorithm was another methodology developed based on the concept of pollution balance to reduce waste production in chemical processes (Hilaly and Sikdar, 1994). Process simulation software such as CHEMCAD II was applied together with WAR algorithm for calculating mass balance of chemicals in process. This methodology can be easily used for quantifying the waste produced in a process and comparing process alternatives for a product. The main limitation of this developed methodology was that it was strictly mass based. To improve this original WAR algorithm, a generalised WAR algorithm had been developed by Cabezas et al. (1999) to describe the flow and generation of potential environmental impact (PEI) through a chemical process. With this generalised WAR algorithm, the environmental impact of a

process can be calculated by using composition and mass flow rate of streams as well as chemical impact scores. The chemical impact scores were determined from nine impact categories which were further subdivided into two eco-toxicity effects, three human toxicity effects and four environmental physical potential effects. WAR algorithm was then further extended to include the PEI of the energy consumed in a chemical process (Young and Cabezas, 1999). Besides manufacturing processes, the energy generation facility such as power plant, was also considered in the system boundary to incorporate energy consumption into environmental assessment. Apart from designing an environmental friendly chemical process, it is also important to ensure that the chemical process is economically beneficial. Thus, a methodology that combined the detailed engineering economic evaluation together with WAR algorithm was applied for allyl chloride production process (Young et al., 2000).

In another work, IChemE Sustainability Metrics were developed to measure the sustainability within process industries (IChemE, 2002). Environmental, economic and social indicators were the three main indicators defined in IChemE Sustainability Metrics to provide a best-balanced measure of sustainability performance. Environmental burden (EB) for various environmental impacts such as global warming, acidification potential, photochemical smog potential, eutrophication potential and etc were calculated to assess the total environmental performance of a process. IChemE Sustainability Metrics were successfully integrated into multi-objective optimisation models for the design of sustainable systems. For example, using this metrics, the total environmental performance of utility system can be evaluated based on the calculated environmental burden (Papandreou and Shang,

2008). Global Environmental Risk Assessment (GERA) index was another environmental index that can provide effective way for evaluating the environmental risk of a given chemical process (Achour et al., 2005). One of the significant contribution from GERA index was that it can adequately compare the environmental risks faced by competing industrial processes. GERA index of a process can be calculated based on the individual risk indices of the unit operation constituting the given process and an overall component environmental risk balance.

Life Cycle Assessment (LCA) is another important category of methods that can be used for assessing environmental impact of processes. The idea of comprehensive LCA had its first application in both Europe and the USA in the late 1960s and early 1970s (Hunt et al., 1996). LCA is a well-known tool that can be used for analysing the environmental impacts of a product or process from ‘cradle to grave’. With the use of LCA, it can quantify the energy and material used, wastes discharged to the environment as well as perform evaluation on environmental impacts of those inputs and outputs (Miettinen and Hämäläinen, 1997). Khan et al. (2001) proposed GreenPro, a systematic methodology that integrated LCA principles into process design and optimisation framework to evaluate and minimise environmental impacts of a process. A fuzzy linear programming LCA model had been proposed by Tan et al. (2008) to design an optimal system with multiple objectives for different environmental impact categories. This model was suitable for system design and optimisation problems which involved various technological options that strive to provide comparable products or services within the life cycle system. Zhang et al. (2008) introduced a new methodology called Green Degree (GD) method to quantify the

environmental impact of a chemical process as well as energy generation system with the aid of process simulation technology. LCA approach was adapted in this method for evaluating GD of a process which was based on nine environmental impact categories. Environmental Consequence Index (ECI) was introduced to include environmental consequence factors such as dispersion factors, material hazard factors, environmental effects and their uncertainties which were normally not considered in the existing environmental indices (Arunraj and Maiti, 2009). Fuzzy composite programming had been used to derive ECI to account for the uncertainty involved in decision making. Another evaluation tool for assessing the environmental impact of chemical processes was developed by Torres et al. (2011). Referring to this tool, environmental evaluation process was done through three types of indicators such as material balance environmental indices (MBEI), twelve environmental indices which were developed by Eco-Indicator 99 and total index which was computed based on geometric mean. Recently, a new framework called Roadmap for Environmental Impact Retrofit, proposed by Mimoso et al. (2015) was suitable for decision making in chemical process as it offered a shortcut method to choose and assess the retrofit design options based on environmental issues. Life cycle impact assessment method had been integrated into this framework to evaluate different retrofit design alternatives and to figure out the aspect that can be further enhanced to have a more environmental friendly design. Moreover, an integrative index had been developed to merge environmental sustainability indicators reported by oil and gas companies (Frank et al., 2016). By utilizing this index, the environmental performance of oil and gas industries can be analysed and compared. This index was developed by using S-curve scale

transformation and multi-attribute utility theory for standardizing and combining the indicators. Another integrated index called Inherent Chemical Process Route Index (ICPRI) was proposed to choose process alternatives at early design stages based on inherent safety, health and environmental impacts imposed by daily plant operational activities (Warnasooriya and Gunasekera, 2017). When the ICPRI value was small, it indicated that the process route was inherently safer, environmentally friendly and occupationally healthy. A new tool named Environmental Performance of Industrial Processes (EPIP) was developed to serve as a decision-making support tool to assess the environmental performance in industrial processes (Maceno et al., 2018). EPIP was developed based on LCA and IMPACT 2002+ methods. Besides, EPIP combined both economic and environmental analysis, which aided in collecting information on energy, environmental impact, materials and cost to provide a single index results. This newly defined EPIP tool can certainly promote industrial processes towards environmental sustainability.

In conclusion, numerous environmental indices had been developed to aid process designer to evaluate and compare environmental impact of process pathway during early design stage. Nonetheless, those developed environmental indices are only suitable for cases where the process flowsheets and/or commercialised chemical substances are available. For the case where molecular design is yet to be performed to identify suitable solvents for substitution, a systematic framework has to be developed to evaluate the environmental performance of solvents in a process. Since it will be time consuming and costly to improve the current process, early planning and design stage is the most optimum time to reduce environmental impacts of a chemical production process.

Thus, there exists a research gap where methodologies must be developed to integrate environmental aspects into molecular design.

2.3 Safety Indices

The main contribution of this thesis is to develop methodologies for integrating environmental aspect into molecular design. But, owing to the arising sustainability concept, this work also considers safety and health aspect during molecular design. The detailed work on integrating safety and health aspects into molecular design had been performed by Ten et al., (2016b). Hence, this work adapts the methodology developed by Ten et al., (2016b) in integrating safety and health aspects into molecular design framework. The section below provides a brief discussion on the importance of considering safety aspect in molecular design.

There is an increased emphasis on process safety in chemical industries owing to the growing number of industrial accidents in the recent years. For instance, the Bhopal disaster, which was known as the worst chemical disasters in history, has resulted in a death toll of at least 3,800 people immediately after the incident. This industrial catastrophe was caused by the leakage of more than 40 tons of methyl isocyanate (MIC) gas, which is extremely toxic to human, from the pesticide plant. Inherent safety is a type of safety concept that was introduced by Trevor Kletz in 1970s. Inherent safety aims in eliminating or minimizing the hazard presents in the plant through the introduction of inherent safety principles into process design. The main principles consist of avoiding the use of hazardous materials, reducing the inventories of hazardous material and striving for simpler processes with milder process conditions (Kletz and

Amyotte, 2010). Since the objective of inherent safety design is to minimise the use of hazardous substance in process, it is best to apply this principle during early design phase. CAMD techniques are adequate tools to focus on one aspects of inherent safety design, which is to generate less hazardous solvent for a process. The safety impact of a chemical product can be assessed by safety indices namely explosiveness based index (I_{EX}) and flammability based index (I_{FL}) (Ten et al., 2016b). The index score for I_{EX} were obtained from ISI (Heikkilä, 1999) whereas the scores for I_{FL} were taken from NFPA flammability rating (National Fire Protection Association, 2007). Both I_{FL} and I_{EX} index scores were presented in Table 2.1 and Table 2.2.

Table 2.1: Flammability (I_{FL}) based index (NFPA)

Flammability, I_{FL}	Penalty scores
Non-flammable	0
Flash point ≥ 93.4 °C	1
Flash point < 93.4 °C	2
Flash point < 37.8 °C	3
Flash point < 22.8 °C & boiling point < 37.8 °C	4

Table 2.2: Explosiveness (I_{EX}) based index (modified from ISI)

Explosiveness, I_{EX}	Penalty scores
Non-explosive	0
$0 \leq S \text{ (vol\%)} \leq 20$	1
$20 \leq S \text{ (vol\%)} \leq 45$	2
$45 \leq S \text{ (vol\%)} \leq 70$	3
$70 \leq S \text{ (vol\%)} \leq 100$	4
where S = Upper explosion limit (UEL) – lower explosion limit (LEL)	

2.4 Health Indices

As mentioned in Section 2.3, it is also important to consider health aspect as decision making components in process plant development and design. This

is because health hazards often resulted in chronic diseases after a prolonged exposure. According to the International Labour Organisation (ILO), an estimation of over two million people worldwide died from work-related diseases yearly whereas over three hundred thousand people died annually owing to fatal occupational accidents. For this reason, inherent occupational health had been established by Hassim and Edwards (2006), aiming to minimize the inherent occupational health hazards caused by chemical processes to the workers. Inherent occupational health is a new health assessment concept originated from the concept of inherent safety. It strives in eliminating or reducing the usage of hazardous substances and process operating conditions that may give rise to occupational hazards to the workers (Hassim and Hurme, 2010). For this reason, it is important to include health assessment during molecular design stage to ensure that the generated molecules will pose low occupational health hazards. There were two indices available for inherent occupational health assessment, namely Process Route Healthiness Index (PRHI) and Inherent Occupational Health Index (IOHI). PRHI was introduced by Hassim and Edwards (2006) to quantify the potential occupational health hazards resulted from chemical processes during early process stage. On the other hand, Hassim and Hurme (2010) established IOHI for the assessment of possible health hazards of alternative process routes during the research and development stage. Some parameters can be chosen from these health indices to assess the health hazards of molecule, such as viscosity from PRHI as well as material phase, volatility and exposure limit from IOHI (Ten et al., 2016a). In addition, another parameter called acute health hazard can be used to evaluate the health hazards of a molecule. The index score for acute health hazard was

based on National Fire Protection Association (NFPA) health hazard rating (National Fire Protection Association, 2007). The index scores for all the mentioned parameters were listed in the tables below:

Table 2.3: Viscosity (I_{η}) based index (modified from PRHI)

Viscosity, I_{η}	Penalty scores
$0.1 \text{ cp} \leq \eta < 1 \text{ cp}$	1
$1 \text{ cp} \leq \eta < 10 \text{ cp}$	2
$10 \text{ cp} \leq \eta < 100 \text{ cp}$	3

Table 2.4: Material phase (I_{ms}) based index (modified from PRHI)

Material phase, I_{ms}	Penalty scores
Gas	1
Liquid	2

Table 2.5: Exposure limit (I_{EL}) based index (modified from IOHI)

Exposure limit, I_{EL}	Penalty scores
PEL > 1000 ppm	0
PEL \leq 1000 ppm	1
PEL \leq 100 ppm	2
PEL \leq 10 ppm	3
PEL \leq 1 ppm	4

Table 2.6: Volatility (I_v) based index

Volatility, I_v	Penalty scores
Boiling point > 150 °C	0
$150 \text{ °C} \geq \text{boiling point} > 50 \text{ °C}$	1
$50 \text{ °C} \geq \text{boiling point} > 0 \text{ °C}$	2
Boiling point $\leq 0 \text{ °C}$	3

Table 2.7: Acute health hazard (I_{AH}) based index (NFPA)

Acute health hazard, I_{AH}	Penalty scores
$LD_{50} \text{ (mg/kg)} > 2000$	0
$500 < LD_{50} \text{ (mg/kg)} \leq 2000$	1
$50 < LD_{50} \text{ (mg/kg)} \leq 500$	2
$5 < LD_{50} \text{ (mg/kg)} \leq 50$	3
$LD_{50} \text{ (mg/kg)} \leq 5$	4

2.5 Computer Aided Molecular Design (CAMD)

Chemical product design is a procedure by which customer needs are identified and translated into commercial products. A chemical product is described as a system formed by various chemical substances that is designed and manufactured for one or more purposes (Cisternas and Gálvez, 2006). Bottom up approach is the conventional technique used in determining new chemical products, which is normally based on design heuristics, experimental studies and expert judgements (Odele and Macchietto, 1993). These traditional methods are very costly, time consuming and inefficient since they are primarily based on trial and error approaches (Venkatasubramanian et al., 1994). On the other hand, top down approaches start with identifying the needs to fulfil, followed by finding the molecules that exhibits properties that can meet the needs. This is also known as reverse engineering approaches, which can be done by various CAMD techniques. CAMD techniques are important tools for chemical product design as they are able to predict, estimate and design molecules with a set of predefined target properties.

CAMD techniques have emerged as powerful tools in the field of chemical product design as they are able to predict, estimate and design molecules with a set of predefined target properties. CAMD is described as reverse property prediction, which aims at designing molecules with certain chemical structures based on a given set of target properties and molecular building blocks (Gani, 2004). In order to validate whether a molecule satisfies the specification of target property, property prediction models such as group contribution method (GCM) can be applied to compute the physicochemical properties. Numerous CAMD techniques had been developed to provide reliable

and accurate solutions based on the given properties. Over the recent decades, CAMD techniques had been applied to design different chemical products such as polymers, solvents, catalysts and refrigerants.

The design of solvents for liquid extraction and gas absorption process through CAMD techniques had been demonstrated (Odele and Macchietto, 1993). As presented in their work, molecular design problems were formulated as mixed-integer nonlinear programming (MINLP) problem and are solved by using augmented-penalty/outer approximation algorithm. Churi and Achenie (1996) applied a mathematical programming model for designing compounds that had predefined target properties in a refrigerant design problem. Their work also involved the development of a hybrid property estimation technique that capable in approximating properties with high accuracy. Venkatasubramanian et al. (1994) proposed a CAMD approach by using genetic algorithm to design polymer molecules. Unlike the conventional techniques, genetic algorithm implemented a guided stochastic search to obtain improved solutions by sampling areas of the parameter space that have a greater probability for better solutions. Besides, polymer design problem being formulated as mixed-integer nonlinear programming (MINLP) problem and solved by using global optimisation technique was presented by Vaidyanathan and El-Halwagi (1996). Moreover, polymer design problem can also be solved by formulating the problem as mixed-integer linear programming (MILP) problem (Maranas, 1996). This can be done by transforming a class of optimal molecular design problems with non-linear structure-property functionalities into MILP problems using the proposed framework (Maranas, 1996). Through this framework, the convergence to suboptimal molecular designs can be eliminated and thus led to

the generation of novel and superior solutions. A CAMD framework which used topological indices as descriptors in structure-property correlation in estimating the target properties of polymer repeat unit had also been developed (Camarda and Maranas, 1999). A new set of correlations for properties such as refractive index, cohesive energy, heat capacity etc were successfully developed and integrated into their optimisation model. Hostrup et al. (1999) proposed a hybrid methodology that integrated CAMD approach with molecular modelling techniques to design extractive agent for distillation process and solvent for wastewater treatment.

In addition to the design of solvents, polymers and refrigerant, CAMD techniques were also applied to design pharmaceutical compounds. In the work presented in Siddhaye et al. (2000), connectivity indices was used to relate molecular structure to physical properties of pharmaceutical compounds while looking for the optimal molecule from the formulated MINLP model. Chavali et al. (2003) applied CAMD techniques to design transition metal catalysts by formulating the design problem as MINLP problem where the optimisation model was then solved by using stochastic and outer approximation methods respectively. Other than the abovementioned works, an integrated methodology which combined targeted bench scale experiments, CAMD approach and database search approach was also developed to design solvents for crystallization of carboxylic acids (Karunanithi et al., 2009). By using this integrated methodology, the effect of solvent on the crystal morphology of aliphatic dicarboxylic acid can be examined in a more systematic and comprehensive way. Moreover, a continuous-molecular targeting approach for computer-aided molecular design (CoMT-CAMD) was presented by Bardow et

al. (2010) to solve an integrated solvent and process design problem. The proposed approach was demonstrated through the design of solvent and process for carbon dioxide capture where perturbed chain polar statistical associating fluid theory (PCP-SAFT) equation of state was used as a thermodynamic model. Hechinger et al. (2010) explored the design of biofuels through the integration of product and process design. As presented in his work, CAMD techniques was applied to design the molecular structures of biofuels while reaction network flux analysis was used to look for the alternative biofuel production pathways. Quantum mechanical computations of the reaction rate constant of solvents were integrated into CAMD framework to identify high performance solvents with improved reaction rate constants (Struebing et al., 2013). The approach was illustrated through a case study called Menshutkin reaction and the results obtained were validated by the kinetic experiments. Instead of maximising reaction rate constant, the methodology was extended to design solvents that can maximise the reaction rate (Struebing et al., 2017). In addition, solvent density and solubility of solid reactant were also considered in this methodology. Hence, this developed framework was able to identify the trade-offs between various physicochemical properties that leads to the determination of optimal solvents that can improve the reaction rates. The key performance of the reaction can then be measured by its respective reaction rate. Polymer molecules that were likely to be effective carriers in drug delivery can be generated using CAMD approach proposed by Pavurala and Achenie (2014). The designed polymer molecules were ranked based on desirability curves, which were developed using water absorption and glass transition temperature properties. A framework that can be applied for the synthesis, design and analysis of chemical and biochemical

processes was described by Tula et al., (2014) through the HAD process case study. Through this framework, flowsheet property was predicted and alternatives can be ranked without the need of rigorous simulation work. Recently, the application of CAMD techniques in the design of ionic liquids had also been reported. Karunanithi and Mehrkesh (2013) developed a computer aided ionic liquid design (CAILD) approach to generate ionic liquids through genetic algorithm and decomposition-based solution approach. By incorporating proper structural constraints, CAMD approach was extended to design optimal ionic liquids for CO₂ capture (Chong et al., 2015). The mixed integer non-linear programming (MINLP) model formulated in their work was able to identify optimal ionic liquid with the highest CO₂ solubility. In addition to the generation of ionic liquid solvent for CO₂ separation from bioenergy system, a systematic methodology that identified the optimal operating conditions of carbon capture process was developed (Chong et al., 2017). Besides, CoMT-CAMD approach was also applied to design working fluid for organic Rankine cycle (ORC) (Lampe et al., 2014). In this work, a framework that allowed for the optimisation of the process and working fluid based on process performance had been developed for the design of ORCs. Lately, 1-stage CoMT-CAMD approach was successfully developed for the integrated design of ORC process and working fluid (Schilling et al., 2017). Through their proposed framework, molecular design optimisation was directly combined with process model. Thus, optimal working fluid and corresponding process parameters can be determined simultaneously in a single optimisation problem. In another contribution, the molecular based, group contribution SAFT- γ Mie equation of state was integrated into CAMD framework for the optimisation of ORC power systems

(White et al., 2017). Their proposed framework has been demonstrated through three industrial waste-heat recovery applications. Their results showed that simple compounds, such as propane and propene, were the optimal ORC working fluid for low-grade heat source whereas compounds with higher complexity were preferred at higher temperatures. Meanwhile, a systematic framework for the development of pure, mixed and blended chemical based products using CAMD technique had been developed (Cignitti et al., 2015). Ten et al. (2016) proposed a novel methodology by integrating both safety and healthy aspects into CAMD framework to ensure that the generated molecules are safe and does not bring health-related risks to the consumers. In this work, the measurement of safety and health indicators were based on the molecular properties that had effect on both of these aspects. Besides, generalized disjunctive programming was incorporated into the computer-aided mixture/blend design (CAM^bD) to design an optimal solvent mixture that maximizes the solubility of ibuprofen (Jonuzaj et al., 2016). In another contribution, a systematic two stage procedure was developed by Papadopoulos et al., (2016) to identify and choose a set of promising solvents for chemical absorption of carbon dioxide. As shown in Papadopoulos et al. (2016), reactivity, thermodynamic behaviour and sustainability criteria were chosen as performance criteria in the solvent design. Another genetic algorithm based CAMD framework was proposed to generate optimal solvents for heterogenous liquid phase reaction (Zhou et al., 2016). A biphasic esterification reaction was applied to illustrate the proposed framework. The combined chemical and phase equilibria can be calculated for complex liquid system using their newly proposed rate-based dynamic method. A COSMO-CAMD framework for the

generation of novel solvents based on property prediction with COSMO-RS was developed (Scheffczyk et al., 2017). The framework combined a computationally efficient Design Phase using medium accuracy quantum mechanics methods with most accurate property prediction for promising molecules in a Refinement Phase. This presented framework was illustrated through two case studies for solvent design in liquid-liquid extraction. Furthermore, CAMD technique was recently adapted to design sustainable solvents to extract residual oil from palm pressed fibres (PPF) (Khor et al., 2017). In order to design solvents which are safe for food industry, safety and health properties were optimised simultaneously together with physical properties. CAMD technique was also applied along with process simulation to determine suitable ionic liquids (IL) for extractive distillation of n-hexane-methylcyclopentane (Chao et al., 2018). In their work, UNIFAC-IL model which was used to predict the thermodynamic properties of the system, was further validated by experimental activity coefficient and vapor-liquid equilibrium (VLE) data.

From the abovementioned works, it showed that there were various solution approaches applied to solve the CAMD problems. These approaches can be grouped into few categories such as stochastic approaches, decomposition-based approaches, mathematical programming approaches, hybrid approaches and enumeration and knowledge based approaches (Karunanithi et al. 2006). The similarity of most of these approaches was that the CAMD problem was formulated as MINLP model; the difference was the solution strategies used to solve the model that made the difference among them. Ng et al. (2015) highlighted the key development, existing challenges and

prospects in the chemical product design area using CAMD techniques. As discussed by Ng et al. (2015), there is a need to explore and develop property models and sustainable chemical product design framework which takes environment, health and safety performance into consideration. Once SHE aspects are integrated into CAMD framework, CAMD techniques are capable in managing part of the SHE issues as solvents with favourable SHE attributes can be generated. The designed solvents with good SHE characteristics can then be applied in a process. The following section presents the review on existing CAMD problems that involved the application of environmental properties.

2.5.1 Application of Environmental Properties in CAMD Problems

The main goal of a conventional CAMD problem was to design a set of molecules which attained targeted physicochemical properties. Over the years, environmental aspects were taken into consideration in molecular design problems. With the aid of mathematical programming, environmental aspects were considered when designing refrigerants (Duvedi and Achenie, 1996). Ozone-depletion potential (ODP) was the environmental constraint introduced in the model where it can be estimated through the correlation which was related to the number of halogenated groups present in the molecules. Besides, an iterative step-wise procedure was developed for the design of environmentally benign solvents (Pistikopoulos and Stefanis, 1998). In this work, methodology for environmental impact minimisation (MEIM) had been integrated into CAMD framework to generate molecules with desired physicochemical and environmental properties. Environmental properties that were considered in this work included lethal concentration, LC_{50} and ODP. A framework that simultaneously considered process constraints, property requirements and

environmental restrictions had been applied to design cleaning solvent blends that satisfied target physicochemical property as well as environmental regulations (Sinha et al., 2003). Chavali et al. (2003) introduced environmental aspects into CAMD methodology for the design of environmentally benign transition metal catalyst. The environmental impact was measured by the LC_{50} of the component to represent its toxicity to the environment. A mathematical programming framework that successfully designed blanket wash solvents with reduced environmental impact was developed (Achenie and Sinha, 2004). A few environmental properties were set as property constraints in the design problem such as LC_{50} , $\log K_{oc}$, bioconcentration factor (BCF) and octanol-water partition coefficient ($\log K_{ow}$). Papadopoulos and Linke (2006) developed a novel CAMD methodology to design solvents based on a number of performance and environmental indices for the application in liquid-liquid extraction and gas absorption process. The environmental constraint used in this work was $\log LC_{50}$ toxicity which can be estimated using group contribution techniques. Both safety and environmental aspects were integrated into a CAMD framework as property constraints for the design of crystallization solvents (Karunanithi et al., 2006). The safety and environmental aspects of the designed solvents were characterised by the flash point and $\log LC_{50}$ toxicity respectively. Furthermore, a new algorithm that used the concept of molecular signature descriptors for solving molecular design problems of reactive system on a property-based platform was introduced (Chemangattuvalappil and Eden, 2013). To ensure that the designed molecules met the environmental regulations, toxic limit concentration and soil sorption coefficient ($\log K_{oc}$) had been served as the environment constraints. Both toxic limit concentration and $\log K_{oc}$ can be

estimated through qualitative structure activity relationship (QSAR) models. The methodology of Heintz et al., (2014), which involved all stakeholders within the chemical enterprise, had been extended to identify commodity chemicals by a combined CAMD and computer-aided organic synthesis (CAOD) techniques (Gerbaud et al., 2017). Property constraints such as BCF, log K_{ow} , LC_{50} and flash point (F_p) were introduced in their work to design new products which fulfil the strict safety, health and environmental regulations.

All the above-mentioned works depicted that environmental properties were considered in molecular design problems. However, environmental properties were only being treated as constraints rather than design criteria. It is important to consider environmental properties as design objectives due to the reason that having them as constraints may screen out the solvents that are excel in terms of physical properties but do not meet the environmental constraints. Moreover, there is no work reported on a methodology that can estimate the environmental impact caused by a designed solvent to a process. There is a need to devise a methodology to quantify the environmental impact of a process in which the designed solvent is applied. The actual environmental performance between various designed solvents can only be effectively compared through the quantification of environmental impact.

Green Chemistry stated that the replacement of hazardous solvent with a new substitute solvent that is more efficient and meets SHE regulations can improve the overall performance of a process. CAMD has always been one of the most reliable techniques for solvent design and selection. Through CAMD approach, solvents that achieve expected functionalities and SHE characteristics can be designed and applied to replace those non-favourable solvents. Separation

process plays a major role in processing industries as it usually dictates the core energy requirement of the whole process. Hence, to minimise energy consumptions, solvents with good functionalities shall be applied in separation process for improving the overall efficiency. Next section reports on application of CAMD techniques for solvent design in separation processes.

2.5.2 Application of CAMD for Solvent Design in Separation Processes

Over the years, researchers had extensively applied CAMD techniques to design solvents that can be used as extracting agents and as process liquids in various process industries (Gebreslassie and Diwekar, 2015). In order to design environmentally friendly solvents that can achieve separation performance targets at the lowest cost, Pistikopoulos and Stefanis (1998) developed an iterative step-wise procedure. Their framework included a methodology for environmental impact minimisation (MEIM) that considered environmental properties and economics during early design stage for the design of promising mass separating agents. A systematic CAMD framework for crystallisation solvent design, specifically tailored for the pharmaceutical industry had been proposed (Karunanithi et al., 2006). Besides solubility, safety and toxicity properties were treated as constraints in their crystallization solvent design problem, which was then solved using decomposition approach. Later, a systematic methodology which combined targeted bench-scale experiments, database search approach and CAMD technique for the crystallisation solvent design of carboxylic acid was developed (Karunanithi et al., 2009). Moreover, a novel CAMD framework which incorporated both stochastic optimization method and group contribution method was established to design environmental

benign solvents for liquid-liquid extraction and extractive distillation application (Song and Song, 2008).

In the recent years, fuzzy and bilevel optimisation were integrated into CAMD techniques for the design of amine-based solvents with desirable performance and environmental characteristics (Ng et al., 2014). A novel CAMD methodology has been proposed to design optimal solvents for extracting acetic acid from process waste streams based on an efficient ant colony optimisation (EACO) algorithm (Gebreslassie and Diwekar, 2015). Their work successfully identified new solvents with better thermodynamic properties for the acetic acid extraction. In another contribution, a set of potential solvents were identified and selected for chemical absorption of carbon dioxide using systematic two stage approach proposed by Papadopoulos et al., (2016). As reported in their work, the solvent design was carried out by choosing reactivity, thermodynamic behaviour and sustainability as performance criteria. The sustainability performance of designed solvents was assessed and compared by two categories of indices such as LCA and a SHE assessment. LCA allowed the calculation of cumulative environmental impacts during the solvent production process chain whereas the SHE assessment estimated the potential hazards in CO₂ capture plant. CAMD techniques were also applied for the development of novel chelating resin polymers in removing metal ions from water (Mukherjee et al., 2017). The results indicated that the designed resin polymers with enhanced adsorption capacity were effective in removing copper ions from drinking water. Besides, Scheffczyk et al., (2017) presented a novel COSMO-CAMD optimisation based framework for the design of novel solvents based on property prediction with COSMO-RS. Their results reported that novel

promising solvents had been successfully designed for extracting phenol and hydroxymethylfurfural from water. Outer-approximation algorithm has been recently modified to solve Computer Aided Molecular and Process Design (CAMPD) problems for separation system such as separation of CO₂ and methane at high pressure (Gopinath et al., 2016). This proposed methodology allowed the simultaneous optimisation of solvent and process variables. Moreover, this approach can address the numerical challenges that usually encounter owing to the highly non-linear interactions between process and solvent. Another systematic approach employing the use of Generalized Disjunctive Programming (GDP) had been proposed by Jonuzaj et al., (2018) to design solvent and solvent mixtures for separation processes. By using their proposed approach, promising solvents and solvents mixture were found for both crystallisation and liquid-liquid extraction process. A method of structural characteristic integrated CAMD had been developed to select solvents for extracting dihydric phenols from coal gasification wastewater (Guo et al., 2018). The extraction efficiencies of selected solvents were further verified by experiment. Based on the experimental results, percentage removal of phenols using methyl propyl ketone (MPK) was higher than that of using diisopropyl ether (DIPE) or methyl isobutyl ketone (MIBK). Besides, the cost estimation on wastewater treatment process showed that phenols recovery process using MPK solvent exerted good economic feasibility.

The aforementioned works showed that numerous CAMD techniques had developed to design solvents for various separation processes. . However, there is no work reported on a method that quantifies the environmental impact of solvent recovery process when a solvent is designed for a certain separation

process. In addition, no work has been found on considering the entire cycle of solvent from its application to its recovery process. It should be noted that physicochemical properties of a solvent not only affect its performance on an application but also its recovery process. Therefore, there is a need to develop multi-objective CAMD methodologies that can simultaneously identify the potential solvent and improve its corresponding environmental aspects of the recovery process. Various multi-objective optimisation tools that can be used to solve multi-objective CAMD problem will be discussed in Section 2.7. CAMD techniques often use property prediction models to estimate the properties of the chemical products. Property prediction models are computational tools used to estimate the physical properties from molecular structures, which are quantified in terms of structural descriptors such as molecular geometry and chemical bonds. Property prediction models such as topological indices and group contribution methods are generally used to validate whether the designed molecules exhibit the predefined target properties. The following section provides a brief overview and development of group contribution methods over the years.

2.6 Group Contribution Method (GCM)

Group Contribution Method (GCM), a powerful predictive thermodynamic model, is one of the most commonly used property prediction models. GCM is suitable for preliminary screening as it can provide fast and satisfactorily accurate property predictions. The property can be determined by adding up the frequency of each group appearing in the molecule multiplied by its contribution. UNIFAC model which was developed based on the concept of GCM, is widely used for predicting non-ideal liquid-phase activity coefficients

of mixtures. With reference to UNIFAC model, group interactions parameters are used to represent the interactions of each functional group present in the molecules. GCMs had been extensively utilised in estimating thermodynamic properties of organic compounds. For examples, GCMs in predicting critical temperature, critical pressure as well as critical volume are presented by Ambrose (1978). Joback and Reid (1987) developed GCM in estimating heat capacity, liquid viscosity as well as other thermodynamic properties. Besides, prediction of thermodynamic properties such as normal boiling and melting points, standard enthalpy of vaporisation, standard enthalpy of formation and critical properties using GCM were also developed by Constantinou and Gani (1994). Marrero and Gani (2001) then further extended the GCM by incorporating third order molecular groups into the property prediction model, which was expressed by:

$$f(p) = \sum_i N_i C_i + y \sum_j M_j D_j + z \sum_k O_k E_k \quad (2.1)$$

where C_i represents the contribution of the first-order group of type- i that occurs N_i times, D_j the contribution of the second-order group of type- j that occurs M_j times and E_k the contribution of the third-order group of type- k that has O_k occurrences in a compound. The left-hand side of Equation (2.1) is the simple function $f(p)$ of the target property p . The first-order groups consisted of a large set of simple and basic molecular groups that cover a wide range of organic compounds. Some of the examples were CH₃, CH₂, CH, OH, CHO, etc. In the meantime, the second and third order groups were used for more detailed structural information about the molecular blocks whose description was insufficient through the first-order groups. By incorporating second order

molecular groups, isomers and compounds with functional groups can be distinguished as different types of interactions and the effect of interactions among the first order molecular groups were captured. Third order molecular groups allowed the detailed descriptions of poly-functional and structural groups such as fused ring compounds, multi-ring compounds and compounds with different functional groups. The constant y and z will be assigned zero values during the first level of estimation as only first-order groups are involved. During the second level of estimation, y and z were assigned unity and zero values. Both constants were set to unity values for third-level of estimation.

Over the years, GCMs were applied to develop property prediction models for properties such as acute toxicity (Martin and Young, 2001), viscosity and surface tension (Conte et al., 2008), heat capacity of organic liquids as a function of temperature (Kolská et al., 2008) standard Gibbs free energy of formation and reaction (Jankowski et al., 2008), more than 20 environmental-related properties of organic chemicals (Hukkerikar et al., 2012a), standard enthalpy of formation in the solid state (Argoub et al., 2014), flash point temperature (Albahri, 2014), normal boiling point (Ghasemitabar and Movagharnejad, 2016) and acid dissociation constants of organic compounds (Zhou et al., 2018). Apart from pure compounds, GCM can also be used for predicting properties of ionic liquid. The properties of ionic liquid that can be estimated using GCM include glass-transition temperature and fragility (Gaciño et al., 2011), thermal stability, viscosity and density (Adamová et al., 2011), heat capacity (Gardas and Coutinho, 2008) etc. Moreover, GCM for estimating thermochemical properties such as heat capacity and heat of formation were also developed for polysaccharides (Lobanova et al., 2011).

It can be seen that GCMs had been developed for estimating various physical and thermodynamic properties. Besides, some efforts have been found on developing GCMs for predicting environmental related properties. GCM models are not limited to only organic compounds but for predicting properties of ionic liquids and even polysaccharides. The benefit of employing GCM is that the properties can be estimated based on merely the knowledge of molecular structures. Due to its simplicity and reliability, GCMs can be applied for the prediction of properties of organic solvents.

2.7 Multi-objective Optimisation

Optimisation problems can be classified into two categories such as single objective or multi objectives, depending on the number of objective functions. Multi-objective optimisation problem occurs when the problems need simultaneous optimisation of more than one objective function. For examples, CAMD is formulated as multi-objective optimisation problem when physical properties as well as safety, health and environmental criteria are chosen as objective functions. There is no single optimal solution in a multi-objective optimisation with conflicting objectives, but rather is a nondominated set, which also known as Pareto set. Pareto set is a collection of alternatives that represent potential compromise solutions among the objectives (Diwekar, 2003).

Preference-based methods and generating methods are the two commonly used categories in solving multi-objective optimisation problem (Diwekar, 2003). Goal programming method is the most common preference-based method, whereas the ϵ -constraint method and weighting methods are the two common generating methods. In goal programming method, decision maker

needs to decide a goal for each objective and utilise optimisation technique to minimise the total deviations from goals. The ϵ -constraint method generates a set of Pareto optimal solutions whereas weighting method can identify a unique optimal solution for actual implementation (Diwekar, 2003). Weighted sum method is one of the most commonly used classical approaches in solving multi-objective optimisation problems (Fishburn, 1967). This method allows a set of objectives to be converted into an aggregated scalar objective function by assigning a weighting factor to each of the individual objective. By adding up all the contributions of each individual objective, an optimised overall objective function can be determined. Weighted sum method has been widely applied in different applications. In the early years, Koski and Silvennoinen (1987) had utilized weighted sum method to generate Pareto optimal solutions with a systematic change in the weighting factor, while minimizing the nodal displacement and volume of a four-bar space truss. This method was also used by Kassaimah et al. (1995) for the simultaneous optimisation of two objectives function where critical buckling shear stress of laminated plates is maximized and its deflection is minimized. A graphical explanation of the weighted sum method for two objective functions problem was also presented to discuss some of its limitations (Das and Dennis, 1997).

The main issue with weighted sum method is that suitable weighting factor must be allocated to each objective. This method is considered subjective as the weighting factors given to the objectives are based on personal judgement. Some of the general approaches for selecting proper weighting factors include rating methods, ranking methods, categorization methods and pairwise comparison methods. By using rating methods, decision makers allocate the

independent values of relative importance to each objective function. On the other hand, ranking method, which is a subset of rating methods, their objective functions are arranged by the order of importance. With categorization methods, different objectives are classified into categories such as moderately important and highly important. Pairwise comparison methods are also commonly used for selecting the weighting factor for each objective by comparing two objectives at the same time. Besides, a method which utilized fuzzy set theory for identifying the weighting factors was also reported by Rao and Roy (1989).

Fuzzy optimisation algorithm is another alternative that can be utilised to solve multi-objective optimisation problem. Zadeh (1965) had developed fuzzy set theory to solve a decision-making problem under fuzzy environment. Fuzzy set theory was designed specifically to represent uncertainty and vagueness mathematically. A fuzzy set is described as a category of elements with a continuum of grades of membership which range from zero to one. Its main function is to represent and manipulate fuzzy data that was not precise. Bellman and Zadeh (1970) later applied fuzzy theory in a decision-making problem to identify the preferred alternative by solving the fuzzy goal subjected to a set of fuzzy constraints. In their work, objective function was characterised as a fuzzy set in the space of alternatives, named as fuzzy goal. The solution, named as fuzzy decision, was obtained from an intersection between the fuzzy goal and constraints. Zimmermann (1978) further extended the Bellman-Zadeh principle to introduce fuzzy linear programming methods which involve multiple objectives by aggregating multiple objectives into a single objective. By solving the objective function subjected to the predefined fuzzy limits, an optimised solution can then be attained. However, in this model, both fuzzy goals

and fuzzy constraints were treated equivalently. This is not suitable for multi-objective CAMD problems when there is consideration of criteria belong to various categories. This is because the chosen design objectives may not be equally important. A weighted max-min fuzzy model utilising Analytic Hierarchy Process (AHP) approach was developed for supplier selection problem (Amid et al., 2011). This methodology aimed in effectively manage the uncertainty of input data and different weighting factor of criteria in supplier selection problem. Furthermore, when there is a need to allocate weighting factor to each objective using weighted sum method, the subjective opinions can also be managed through the application of AHP or Fuzzy Analytic Hierarchy Process (FAHP). These two methods systematically quantify the decision maker's subjective judgement to make a trade-off between target properties. The application of AHP or FAHP is dependent on the nature of the problem, which will be further discussed in Section 2.8 and 2.9.

2.8 Analytic Hierarchy Process (AHP)

Analytic hierarchy process (AHP) is a Multi-Criteria Decision Making (MCDM) method which was first introduced by Saaty (1977). It is a theory of relative measurement that can be used to model the complexity of the problem and sort out the personal judgement of individuals in decision making. AHP uses a decomposition strategy based on the principle that it is easier and more accurate for a human decision maker to compare two alternatives at a time, rather than a larger number simultaneously. The main advantage of AHP is that judgement on tangible and intangible criteria can be incorporated in the same analysis especially where the subjective judgements of different personnel account for a vital part in the decision making process (Mohanty and Deshmukh, 1993). To

perform trade-offs between many intangible criteria, the judgements which are normally expressed in qualitative terms are transformed into numerical term. AHP makes the pairwise comparison based on a fundamental 9-point scale. Since pairwise comparison is done through experts' evaluation, inconsistency is inherent in the judgement process. AHP has the ability to manage the judgement inconsistency by providing quantitative feedback on any discrepancies (Saaty, 2005). AHP incorporates the inconsistency into the process where decision makers can measure the degree of inconsistency in their judgements. If the degree of inconsistency is not tolerable, the decision maker must improve the consistency by repeating the judgement process.

AHP has been specially attractive as it can be easily integrated into multiple-objective programming formulations with iterative solution process (Yang and Lee, 1997). Due to its flexibility, simplicity and ease of use, AHP approach is widely applied in many areas of engineering design, including laboratory reactor selection (Hanratty and Joseph, 1992), optimal separation sequence for distillation process (Li et al., 2009), process safety assessment and design (Arslan, 2009), energy selection (Kahraman and Kaya, 2010) and HAZOP analysis of processes (Othman et al., 2016). Hanratty and Joseph (1992) utilized AHP approach to select laboratory reactor based on a number of criteria. For example, ease of sampling and analysis of product composition, isothermality, accuracy of residence time measurement, selectivity as well as construction cost and difficulty were the chosen criteria to evaluate the performance of reactor. The applicability of AHP on separation synthesis was demonstrated by Li et al., (2009). In their work, a novel method which combined AHP with thermodynamic insights and heuristic approaches was developed to

serve as a guide for the initial separation process design. AHP method was also used by Arslan (2009) to determine and prioritize environmental and safety precautions that should be applied by chemical tanker operations. Besides, Kahraman and Kaya (2010) developed a methodology based on AHP under fuzziness to identify the most appropriate energy policy for Turkey. In recent years, a methodology that integrated AHP for the prioritization process in HAZOP analysis was developed (Othman et al., 2016). The results showed that their developed methodology can determine and rank the most significant hazards when conducting process hazard analysis. In addition, the work of Leong et al., (2017) demonstrated their attempts in integrating AHP approach on synthesizing an optimal resource network in an eco-industrial parks (EIPs). Economic performance, network reliability, environmental impact and connectivity were the design criteria considered in their work. AHP was also applied for the selection of palm oil mill effluent (POME) treatment for the generation of biogas (Nasution et al., 2018). Their work aimed in identifying the best combination of open lagoon and existing wastewater technology for POME treatment based on the selected criteria such as opportunity, risk, cost and benefit.

Although AHP was widely used in various field of studies, the basic steps involved in these applications are similar. AHP methodology is made up of three key steps, starting with hierarchy construction, priority analysis and followed by consistency verification. In conclusion, AHP can be adequately applied to solve multi criteria decision-making problem if the information needed for the evaluation of relative importance between criterion is certain. However, if the information needed for assessing the relative importance between criterion is

complex and uncertain, a more powerful variant such as Fuzzy Analytic Hierarchy Process (FAHP) should be preferred (Ozdogoglu and Ozdogoglu, 2007).

2.9 Fuzzy Analytic Hierarchy Process (FAHP)

Fuzzy Analytic Hierarchy Process (FAHP) is a variant of the widely known AHP which was first developed by Saaty (1977). AHP approach has the advantage of allowing the judgement on both qualitative and quantitative criteria to be performed under the same analysis. However, it is often difficult to give exact numerical values which reflect the true character of human thinking in pairwise comparison (Chen and Fan, 2011). This happens when the information needed in eliciting the relative importance or preference between each criterion is complex and uncertain. As aforementioned, AHP approach utilises discrete numerical scales which makes it alone difficult to handle the fuzziness and ambiguity of subjective opinions occurred during pairwise comparisons. To overcome this limitation, FAHP method which is an integration of fuzzy set theory and AHP approach was developed.

Fuzzy set theory has proven benefits in dealing with the vagueness and uncertainty as it is capable to represent the uncertainty in the data. (Zadeh, 1965). It was developed to provide a framework that mimics human reasoning for many decision problems (Tseng et al., 2009). Triangular fuzzy numbers (TFNs) are often used due to their simplicity, since their membership functions can be characterized using only three numbers. The FAHP method translates linguistic judgements into TFNs, organized in fuzzy pairwise comparison matrices. FAHP has been widely applied in various fields of application. For example, the extend

analysis method proposed by Chang (1996) to derive the crisp weighting factor from TFNs had been applied by Yang et al., (2011) in prioritizing environmental issues in off shore oil and gas operations. Besides, Tan et al., (2014) have proposed a FAHP methodology for process engineering problems which involve multiple criteria and option. This methodology can determine a set of crisp weighting factors from scaled fuzzy judgements. In recent years, FAHP approach has also been applied in synthesizing inter-plant chilled and cooling water network (IPCCWN) (Leong et al., 2016). In this contribution, a two-stage procedure which involve fuzzy optimisation and FAHP method have been developed for generating alternative IPCCWN designs and selecting the most optimum network design based on qualitative and quantitative criteria. Moreover, FAHP approach had been utilised to determine the cumulative score for each renewable sources in India (Jha and Puppala, 2017). The total cumulative score, known as Energy Index, was obtained by evaluating each renewable alternative based on eleven environmental and techno-economic criteria. Based on their developed Energy Index, geothermal source was the most preferred alternatives among those available renewable energy in India. Another contribution applied FAHP approach to select the most suitable biomass sample for obtaining maximum bio-oil yield during pyrolysis (Madhu et al., 2018). Note that the above examples have shown that FAHP method is well suited to solving complex real-world decision-making problems which involve subjective evaluation.

2.10 Summary

To integrate the concept of environmental aspects into CAMD framework, various environmental indices had been critically reviewed and discussed in

Section 2.2. Based on the review, it shows that current environmental indices are more suitable for evaluating environmental performance of existing commercialised molecules or chemical processes. Hence, there is a need to fill in the research gap where systematic methodology must be developed for considering environmental aspects when performing solvent design and selection. Safety and health indices were also reviewed to determine suitable indices for evaluating the safety and health performance of molecules. It is important to consider SHE aspects during early design stage as it is often difficult and costly to retrofit the existing process in later stage. In addition, the current state of art of CAMD works were also reviewed. Although numerous research works on considering environmental aspects in molecular design, environmental properties were treated as constraints instead of design objective. There is no research that works on quantifying the effect of solvents on environmental impact of process. Besides, none of the CAMD framework can provide systematic method for integrating SHE elements into molecular design. There is no work reported on specifying the relative importance between SHE criteria. Thus, various multi-objective optimisation tools that can be used for solving multi-objective CAMD problems were reviewed. In this research, weighted sum method can be utilised in optimising multiple objective functions that belong to various categories such as physicochemical, safety, health and environmental properties. The overview of AHP and FAHP, tools that are normally used in multi-attribute decision making problem were also depicted in Section 2.8 and Section 2.9. The identified research gaps will be discussed in detail and addressed in the following chapters.

CHAPTER 3

RESEARCH SCOPES AND METHODOLOGIES

3.1 Research Gaps

Traditionally, the main focus of CAMD problems is on designing molecules with a set of targeted physical and thermodynamic properties. The effect of environmental impacts of molecules in decision making is often ignored during the early design stage. It is important to consider environmental aspects of molecules since product molecule with superior performance does not necessarily mean that they are safe to the environment. Although a significant amount of research has been done to address this issue, most of them only consider environmental properties as property constraints during design stage. The drawback of applying environmental properties as constraints is the generation of molecules that achieve targeted physicochemical properties but may exert major environmental impacts during the application. Thus, there is a need of a CAMD framework that consider both physicochemical and environmental properties as design objectives. This is to ensure that the designed molecules are environmental friendly and possess desirable functionalities. In order to optimise the physical and environmental properties of the molecule simultaneously, the CAMD problem needs to be formulated as a multi-objective optimisation problem. However, the relative importance of each property to be optimised in a multi-objective molecular design problem is not always definable. Without a proper procedure, it is difficult to assign the exact weighting factor to each property involved in multi-objective molecular design problem. For this

reason, there should be a methodology to quantify the weighting factor to each of the objective where subjectivity is involved in a multi-objective CAMD problem.

In addition to environmental aspects, it is also important to take safety and health aspects into consideration when designing a molecule. This is to ensure that the generated molecules serve their functions while being safe, environmental friendly and does not cause adverse health effects to human. Nevertheless, for this case, the complexity and uncertainty of CAMD problem increases as compared to the case where only physical and environmental properties were considered. This is mainly because the literature data needed for eliciting the relative importance between safety, health and environmental aspects are highly complex and uncertain. This issue must be addressed as large number of target properties are important for a molecular design problem. Besides, it is often difficult to assess their relative importance because different targeted properties are normally represented by different units. Thus, FAHP approach must be integrated into CAMD framework to capture the highly uncertain opinions of decision maker arising from ambiguity involved during value judgement elicitation.

By referring to the recent works, the performance of a process is greatly influenced by the choice of solvent applied in it (Papadopoulos and Linke, 2009). This is because the characteristics of a chemical solvent can indicate the degree of difficulty of the process. For example, the energy requirement of a solvent recovery process is heavily dependent on the physicochemical characteristics of the solvent. Since solvent recovery process is the most energy intensive among all the stages in a chemical industry (Luis et al., 2014), it is of vital importance

to evaluate the environmental impact during recovery process quantitatively. Nonetheless, no work has been found on reporting a method that generate a solvent that simultaneously meets predefined properties and improves the environmental aspects of its regeneration process. Hence, this leads to another research gap where there is a need to develop a more efficient strategy to identify solvents which achieve their targeted functionalities and reduce the environmental burden of its recovery process.

Normally, solvents can be recovered using various separation techniques. There are numerous solvent recovery technologies exist in literature, such as distillation, crystallisation, membrane technology, pervaporation etc. Distillation, being the most popular choice among the existing solvent recovery technologies, often requires excessive energy for separating a solvent from a mixture. Large energy consumption usually leads to higher utilities cost as well as pose a negative impact on environment. Although solvent treatment options were optimised based on environmental point of view, there is no work showing the effect of various solvent recovery processes on molecular design. It is particularly important to evaluate the effect of solvent recovery processes on solvent selection as the optimal solvent for an application will change accordingly to the chosen recovery process. This clearly leads to a major research gap where a systematic methodology is required to consider the effect of different solvent recovery alternatives on molecular design to design molecules that minimise pollution along with enhancement in economic performance.

3.2 Scopes of Research

Based on the identified research gaps, the research will concentrate on the following scopes:

3.2.1 Integrate physical property targets and environmental properties into CAMD framework

Both physical properties and environment-related properties can be estimated either through property prediction models or empirical correlations. CAMD problem is now formulated as multi-objective optimisation problem where performance is to be maximised and the environmental impact of molecules is to be minimised. When considering both physical and environmental-related properties as design objective, the major issue is the subjectivity involved in assigning the weighting factors to the multiple objectives. Hence, there is a need to develop mathematical model to quantify the subjectivity as distinct solutions will be generated due to different weighting factor of each property.

3.2.2 Manage the subjectivity arising from complex and uncertain information needed to incorporate safety, health and environmental (SHE) aspects into CAMD framework

In research scope 1, AHP approach has been utilised to quantify the subjectivity when only both physicochemical and environmental properties are integrated into multi-objective CAMD problem. However, additional problem

arises when SHE aspects are to be integrated into CAMD framework along with physicochemical properties. This is because the data needed for evaluating the relative importance between SHE properties are more uncertain and complex than comparing physical and environmental properties. Due to the uncertain and complex evaluation data, it is often difficult to assign exact numerical values when performing pairwise comparison. Besides, it also affects the confidence level of a decision maker when eliciting their value judgments. Thus, to address this issue, a better mathematical tool must be developed to handle the highly subjective nature occurred during performing pairwise comparison of SHE properties in CAMD problem.

3.2.3 Assess the environmental impact of solvent recovery process in which the designed solvent is applied

The use of solvents in industries have been found to cause numerous indirect environmental impacts (Capello et al., 2007). This is because the characteristic of chemical solvents can affect the overall performance as well as SHE hazards of a process. For examples, the volatility and stability of chemical solvent will affect the difficulty level in a separation process. A more difficult process indicates that the process will be more hazardous to human and the environment because larger amount of energy will be needed. Therefore, it is crucial to develop a single stage CAMD methodology for the systematic design of a solvent that achieves its functionality and reduce the environmental impact of its recovery process.

3.2.4 Evaluate the effect of different solvent recovery alternatives on molecular design

In conventional practice, after the solvent is applied in a chemical operation, the solvent is either being recovered for reuse or become a waste. There are a few technologies available in literature that can be used to regenerate the solvents. In the third research scope, it can be seen that high energy requirement is associated with negative environmental impact. Since different solvent recovery technologies will consume different amount of energy, it is important to regenerate solvent using technology that requires minimum energy. Besides, it should be noted that each solvent is associated with its own physicochemical properties that allow them to be recovered using different amount of energy. Thus, the suitability of the designed solvent for an application will also change according to the type of solvent recovery technology selected. To date, no work has been done on comparing the effect of solvent recovery alternatives on molecular design. Hence, there exists a need to simultaneously integrate both solvent application and its recovery technology into CAMD framework to assess their effects on solvent selections.

3.3 Research Objectives

The scopes identified previously will lead to the objectives of this research, which are stated as followings:

- i. To integrate physical property targets and environmental aspects into CAMD framework via Analytic Hierarchy Process
- ii. To integrate Fuzzy Analytic Hierarchy Process to incorporate safety, health and environmental aspects into CAMD framework
- iii. To integrate the quantitative assessment of environmental impact of solvent recovery process into a single stage CAMD framework
- iv. To develop a systematic CAMD framework that considers the entire cycle of solvent from its application to its recovery process

3.4 Overall Research Methodology

The overall methodology for this research work is presented. The methodology will be divided into five research stages. The research methodology proceeds with the following stages: early research stage, research scope 1, research scope 2, research scope 3 and ends with research scope 4.

In the early stage of research, extensive literature review on safety, health and environmental indexes, mathematical optimisation techniques and CAMD techniques is carried out. By using the information gathered from literatures, research gaps are identified. Thus, from the identified research gaps, new ideas on research direction can be generated. After knowing the research direction, it can be further divided into different scopes of research.

As the research progresses, safety, health and environmental indexes that are suitable for the application in molecular design are identified. Besides, multi-objective optimisation approaches will be utilised for the design of molecules that have favourable functionalities with low safety, health and environmental impacts. These approaches are targeted for CAMD problems where multiple target properties are to be considered and optimised simultaneously. Various CAMD techniques and mathematical optimisation approaches are utilised in addressing the proposed research scopes. The developed methodology for each research scope is discussed briefly in the following section 3.4.1 to 3.4.4. Figure 3.1 presents the flow diagram of the overall methodology developed for this research. The methodologies of all the four scopes are discussed in detail in the following chapters 4 to 7.

3.4.1 Integrate physical property targets and environmental properties into CAMD framework

To design a molecule that satisfies physical property targets as well as environmental properties, a multi-objective optimisation approach is proposed. As discussed previously, the major challenge faced in multi-objective CAMD problem is the subjectivity involved in assigning the weighting factors to the multiple objectives. To overcome this problem, Analytic Hierarchy Process (AHP) approach, which was developed based on the theory of relative measurement can be integrated into CAMD framework. Through AHP, molecular design problems can be approached as a hierarchical decision structure and dissimilar categories of target properties are combined in the same

analysis. AHP has the ability to generate numerical priorities from the subjective knowledge in evaluating the relative importance of properties using pairwise comparison. Besides being able to determine the weighting factor of each property systematically through pairwise comparison, the subjective weighting factors can be tested for their consistency to ensure that the identified solution reflects the decision-maker's true preferences. The methodology is discussed in detailed in chapter 4.

3.4.2 Manage the highly subjectivity nature arising from complex and uncertain information needed to incorporate safety, health and environmental aspects into CAMD framework

When target physicochemical targets as well as safety, health and environmental aspects are to be optimised simultaneously, the CAMD problem is formulated as multi-objective optimisation problem. As aforementioned, there is a need to develop a better mathematical tool to evaluate the relative importance of each property due to the nature of safety, health and environmental aspects. Thus, Fuzzy Analytic Hierarchy Process (FAHP), which is a variant of the widely known AHP, can be integrated into CAMD framework to design an optimal molecule that meets multiple target properties. FAHP approach can handle the fuzziness and ambiguity of subjective opinions occurred during pairwise comparison. Instead of using exact numerical values, FAHP uses triangular fuzzy numbers to express the pairwise comparison of decisions elements. Through triangular fuzzy number, the confidence level of decision maker can be quantified. Hence, the inability of classical AHP approach to deal

with the uncertainties arising from ambiguity involved during value judgement elicitation can be addressed by employing FAHP approach. Chapter 5 depicts this proposed methodology in detail.

3.4.3 Assess the environmental impact of solvent recovery process in which the designed solvent is applied

In order to instantly assess the environmental impact of solvent recovery process in which the designed solvent will be applied, the quantitative analysis of environmental impact of its recovery process has to be integrated into CAMD framework. The environmental indicator from IChemE Sustainability Metrics is applied to calculate the total environmental burden of a solvent recovery process. The molecular properties that affect the quantitative evaluation on the safety, health and environmental evaluation of a process will also be included in the CAMD formulation. The multi-objective model is then solved by using weighted sum method coupled with FAHP weighting approach. Through this approach, the total environmental burden and energy requirement of a process is known when a molecule is generated. Hence, a solvent that satisfies the predefined functionalities and improves the overall environmental performance of its recovery process can be generated. The proposed methodology for this research scope is discussed in detailed in chapter 6.

3.4.4 Evaluate the effect of different solvent recovery alternatives on molecular design

The importance of identifying the optimal solvent recovery route that is safe and environmental friendly is discussed in Section 3.2.4. In the previous developed approach, solvent design is performed based on only one chosen recovery route to regenerate the solvent. The proposed methodology for the third scope is further extended to simultaneously identify the optimal solvent as well as the cheapest and cleanest route to recover the solvent. This work focuses on comparing the effect of different separation techniques on solvent selection. Based on the design problem, preliminary screening on existing separation processes was first performed to identify suitable techniques that can be used to recover solvents. In addition to energy requirement, the utilities cost needed to recover the solvent is also considered along with physicochemical and SHE properties. Hence, molecular properties that will affect the cost and energy needed for solvent recovery process are included in CAMD formulation. Similarly, FAHP weighting approach is then integrated into CAMD framework to solve multi-objective solvent design problem. With this approach, the generated solvents can be recovered through a cheaper and cleaner process and give a better balance of performance for a set of predefined properties. The detailed method is shown in chapter 7.

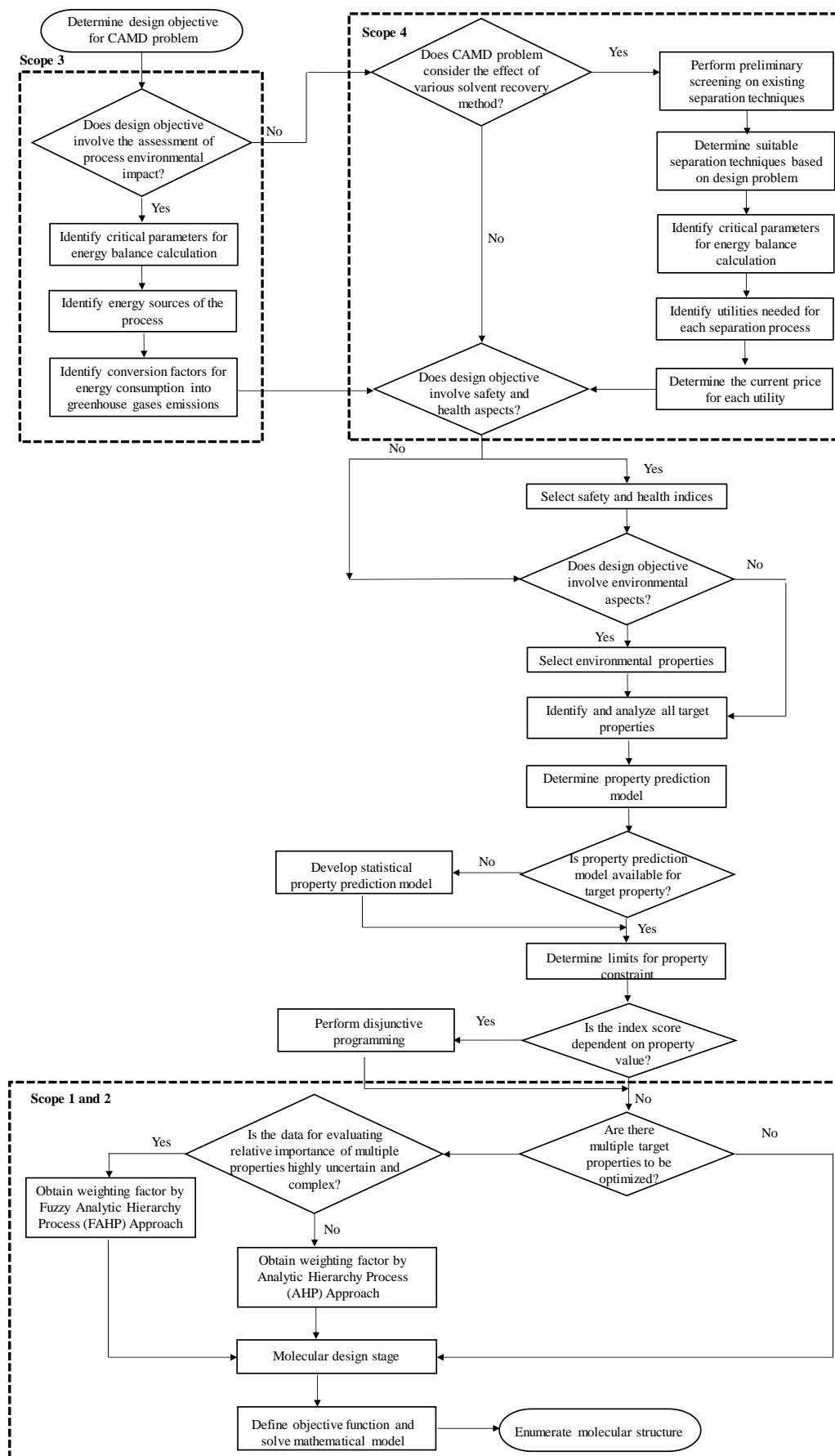


Figure 3.1: Overall methodology developed for this research

3.5 Summary

This chapter presents the research scopes and methodologies. Based on the research gaps discussed in section 3.1, there is a need to integrate environmental aspects into CAMD framework. Owing to the nature of safety, health and environmental aspects, the process in eliciting their relative importance will become more complex and difficult. Hence, mathematical models should be developed to address the ambiguity involved during value judgement. In addition, it is found out that the characteristic of chemical solvent may indicate the degree of difficulty of its recovery process, which will indirectly affect safety, health and environmental impact. Thus, a single stage methodology to integrate the quantitative assessment of the environmental impact of solvent recovery process into CAMD framework should be developed. Besides, different separation process will require different amount of energy to recover solvents. Therefore, the methodology should be further extended to include various solvent recovery techniques in CAMD framework to evaluate their effects on solvent selection.

CHAPTER 4

A SYSTEMATIC MULTI-OBJECTIVE MOLECULAR DESIGN

FRAMEWORK USING ANALYTIC HIERARCHY PROCESS

4.1 Introduction

This chapter presents the first research scope, which utilises CAMD techniques to design optimal molecules which are environmental friendly and fulfil the targeted physicochemical properties. During the early design stage, product needs from customers' requirements are determined to identify the design objective for molecular design problem. The product needs usually include the physical and thermodynamic properties which are responsible for the functionality of the product. In this work, environmental properties are also considered as design criteria to ensure that the generated molecules are safe to the environment. The CAMD problem is now formulated as multi-objective optimisation problem since physicochemical and environmental properties are to be optimised simultaneously. As all physicochemical and environmental properties have different units, it is difficult to define their relative importance. Without a proper methodology, it will inevitably result in subjectivity when weighting factor is allocated to each objective. Thus, AHP approach is integrated into multi-objective CAMD framework to deal with the ambiguities involved in assessing the relative importance between physicochemical and environmental properties. Through AHP, molecular design problems can be approached as a hierarchical decision structure and different categories of target properties are

combined in the same analysis. The multi-objective CAMD problem is then solved by weighted sum method, where the weighting factor of each objective is predetermined using AHP approach. A case study on solvent design for extracting residual oil from palm pressed fibre is performed to illustrate the application of this proposed methodology.

4.2 Problem Statement

The design objectives of a conventional CAMD problem usually defined by physical and thermodynamic properties. However, stricter environmental laws and regulations have prompted chemical industries to search for molecules that are environmental friendly and exert favourable product functionality. It is important to consider environmental aspects of molecules in early design phase because molecules that fulfil the targeted functionalities may not be environmental friendly. The integration of both physicochemical and environmental aspects into CAMD framework results in multiple target properties for a molecular design problem. Nevertheless, the step for determining weighting factors to describe trade-off among target properties is inherently subjective. For example, before fully understanding the trade-offs between different criteria, value judgements that reflect the relative importance or preferences among the criteria cannot be well elicited. The assigned relative weights to the property will then be subjective and provide no insight into the underlying multi-objective molecular design problem. Hence, it is important to address this issue as some good alternatives may have been eliminated due to the subjective weights assigned to the property. To solve this issue, a novel methodology must be developed to integrate environmental aspects into CAMD framework. The methodology must be able to provide a systematic way in

assigning the consistent weights to multiple target properties involved in CAMD formulation.

4.3 Methodology

The main objective of this work was to establish a multi-objective molecular design framework which provide numerical priorities of target properties from the subjective opinion in evaluating the relative importance of each target property. Weighted sum method was used to model the multiple target properties while AHP method was implemented to quantify the weights that reflect the value judgement from domain experts or literature review. By using the proposed framework, a molecule that fulfilled multiple target properties can be generated. The proposed design was summarised in the following steps:

The procedure started with the determination of objective for molecular design problem by identifying the product needs based on customers' requirements or from operating condition of industrial processes. The product needs were usually defined by physical and thermodynamic properties, which are responsible for the functionality of the product. Together with physicochemical properties, environmental properties were also considered to ensure that the molecules generated are safe to both human and environment. Once the product needs were determined, the desired properties will then be chosen as the design objectives to assure that the designed molecules simultaneously serve their functions and pose low environmental hazard levels. After determining the design objective, the qualitative product needs were translated into measurable quantitative target properties. These identified target

properties can either to be optimised or used as constraints during the design stage.

The next step was to identify the suitable property prediction models to estimate these target properties. One of the most commonly used property prediction models are group contribution method (GCM). This method estimates the property by adding up the frequency of each group appearing in the molecule multiplied by its contribution (Marrero and Gani, 2001). The GCM equation was expressed by Equation (4.1):

$$f(p) = \sum_i N_i C_i + y \sum_j M_j D_j + z \sum_k O_k E_k \quad (4.1)$$

where C_i represents the contribution of the first-order group of type- i that occurs N_i times, D_j the contribution of the second-order group of type- j that occurs M_j times and E_k the contribution of the third-order group of type- k that has O_k occurrences in a compound and $f(p)$ is a function of the target property p . In this work, first order groups were applied since only simple-structured molecules are considered. Correlations and empirical relationships can be used to estimate those properties with no GCM available.

For the target properties that were served as property constraints, it was important to identify their upper and lower limits to ensure that the designed molecules will have similar physical characteristics as conventional solvent. The target property ranges were determined based on product specification, which are normally given by process requirements or customer preferences. The product specification range can be represented by Equation (4.2):

$$v_p^L \leq V_p \leq v_p^U \quad \forall p \in P \quad (4.2)$$

where V_p is the value of target property p , v_p^L and v_p^U represents the lower and upper bound of product specification respectively.

4.3.1 Development of decision hierarchy

When multiple target properties were optimised simultaneously, AHP approach can be utilised to determine the weight of each property by assessing the relative importance between those identified properties. The initial step of AHP was to decompose the decision problem into a hierarchy framework. Generally, the overall objective was laid on the highest level, properties and/or sub properties in the intermediate level leaving the decision alternatives at the lowest level. By mean of a hierarchy framework, the relationship between elements of one level with those of the level below can be demonstrated.

4.3.2 Construction of pairwise comparison matrix

Human mind cannot simultaneously compare more than about seven objects without becoming inconsistent (Miller, 1956). This is one of the main limitations of multi-objective CAMD problem, as large numbers of target properties are usually involved in the formulation. There was a need to have a proper procedure to systematically define the relative importance of each property in CAMD problem. According to Saaty (1977), an individual may not be able to process huge amounts of data without showing the signs of inconsistent reasoning. However, it is simpler and more accurate to express one's opinion on only two properties at a time (Saaty, 1977; Ishizaka and Labib, 2011). AHP provides a mathematical framework that decomposes complex problems into pairwise comparisons, and then consolidates these judgements into a coherent decision rule.

Pairwise comparison was performed during the second step of AHP approach to evaluate the relative importance of properties of a particular level with respect to a specific property in the immediate upper level. For example, properties were compared pairwise with respect to the overall objective of the decision problem. The comparison between two properties was made by asking the question: “How much more important is property A compared to property B with respect to a satisfaction of the overall goal?” The relative importance between two properties can be deduced based on the information from literature review or based on expert’s judgement. The pairwise comparison matrices of size $(n \times n)$ was constructed as shown in Equation (4.3) below:

$$A = \begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ a_{n1} & a_{n2} & \cdots & a_{nn} \end{pmatrix}, \text{ For } i, j = 1, 2, \dots, n \quad (4.3)$$

where A is the positive reciprocal pairwise comparison matrix, $a_{ij} = \frac{w_i}{w_j}$,

$a_{ji} = \frac{1}{a_{ij}}$ and $a_{ij} > 0$. The ratio $\frac{w_i}{w_j}$ indicates the relative importance of element

in the i th row over the element in the j th column with respect to the specific element in the upper level. The total number of comparisons to be done can be identified with Equation (4.4):

$$\text{No of comparisons} = \left(\frac{n(n-1)}{2} \right) \quad (4.4)$$

where n is the matrix size.

Saaty's 9-point scale (Satty, 1980) was used to transform the verbal judgements into numerical quantities representing the values of a_{ij} . Table 4.1 shows the meaning of the comparison scale used in the weighting of two elements.

Table 4.1: Conventional AHP numerical scale for subjective judgements by Saaty (1980)

Intensity of importance	Linguistic equivalent for comparison of criteria
1	Equal important
3	Moderate more important
5	Strongly more important
7	Very strongly more important
9	Extremely more important

4.3.3 Sensitivity analysis

The assumption made in AHP was that the relative importance of one property over the others can be expressed exactly using the fundamental 9-point scale. However, the subjectivity involved in eliciting judgement when assigning a single number from the 9-point scales to the ratio must be analysed before a final decision is made. Based on expert's judgement or from literature review, such ratio which reflects the relative importance of one property over the other can be known but the intensity of importance is uncertain except for the case wherein the two properties are of equally important. Hence, there were uncertainties in the weighting of the properties due to the ambiguity occurred in generating the ratios for the pairwise comparison matrix. To determine the robustness of the proposed decision model, it was important to perform sensitivity analysis on the ratio scale given while the order of importance of elements which had been determined earlier is kept unchanged. By performing

sensitivity analysis, different sets of final weighting factors were produced which will result in the generation of different molecules.

In this work, a simplified sensitivity analysis was done by changing the intensity of importance of the base case by ± 1 . For example, if property A were slightly more important than property B, it was first assumed that property A was three times more important than property B. Nevertheless, property A may not be exactly three times more important than property B as there was ambiguity in assigning the intensity of importance to the verbal judgment. Accordingly, two cases of sensitivity analysis were performed, i.e., where property A was first assumed to be two times more important than property B followed by property A being four times more important than property B. An interval of ± 1 was chosen as it was assumed that the relative importance of two criteria will not deviate much from the base case. This was because literature review had been done while evaluating the relative importance of two properties for the base case. Thus, when there was uncertainty in assigning the intensity of importance, the sensitivity analysis was done by using Equation (4.5):

$$a_{ij_base} \pm 1 \tag{4.5}$$

where a_{ij_base} represents the intensity of importance given to the base case study

4.3.4 Synthesize the pairwise comparison

The relative importance weightage of each element was dictated by the principal eigenvector, w of the matrix A , which is given by Equation (4.6):

$$Aw = \lambda_{\max} w \tag{4.6}$$

where λ_{\max} is the principal eigenvalue. The principal eigenvalue, which is a constant, gives a measure of the consistency of the matrix. The greater the difference between the principal eigenvalue and the order of matrix, the more inconsistent is the matrix. The sum of w will be equal to 1. w can be solved using a spreadsheet by the following steps:

- i. Raise the pairwise comparison matrix to the power of two.
- ii. Calculate and normalize the sums of row.
- iii. Iterate the process until the value of eigenvector does not change from the previous section.

4.3.5 Perform the consistency verification

The consistency of the pairwise comparison can be determined by using consistency ratio (CR) as shown in Equation (4.7):

$$CR = \frac{CI}{RI} \quad (4.7)$$

where CI is the consistency index and RI is the random index.

CI can be calculated by using Equation (4.8):

$$CI = \frac{\lambda_{\max} - n}{n - 1} \quad (4.8)$$

where λ_{\max} represents the principal eigenvalue, n represents matrix size.

RI is the consistency index of a randomly generated reciprocal matrix from the 9-point scale and its value depends on n . Table 4.2 shows the random index table which is obtained by approximating random indices for matrices of order 1 to 10 (Satty, 1980). The inconsistency as considered acceptable if CR is

< 10% (Satty, 1980). However, if CR > 10%, it was necessary to elicit the judgement again.

Table 4.2: Random Index for AHP

Size of matrix (n)	1	2	3	4	5	6	7	8	9	10
Random index (RI)	0	0	0.52	0.89	1.11	1.25	1.35	1.4	1.45	1.49

Steps written in section 4.3.2 - 4.3.5 were repeated for all the levels in the hierarchy model determined earlier. After obtaining the relative importance weighting factor (principal eigenvector w) of each property and sub property, the weighting factor of each sub-property was multiplied by the weighting factor of its main property to obtain its final weightage in the overall system.

4.3.6 Molecular design stage

In this stage, potential molecular building blocks were chosen based on the nature of the target molecules. This step was important to ascertain that the molecular structure and properties of the designed molecules are similar to those of conventional product. For instance, molecular group –OH must be selected as one of the molecular building blocks while designing an alcohol solvent. Structural constraints were applied to ensure that the molecule formed is structurally feasible. To generate a molecule, the summation for the number of occurrences for all selected groups must be greater than zero as shown in Equation (4.9):

$$\sum_{i=1}^{G_r} N_i > 0 \quad (4.9)$$

where N_i is the number of occurrences of group i while G_r is the total number of groups selected to generate the molecules. In addition, to ensure that a

molecule has no free attachment, the octet rule of structural feasibility, which was dictated in Equation (4.10) was applied:

$$\sum_{i=1}^{G_T} N_i (2 - v_i) = 2g \quad (4.10)$$

where v_i is the valence of group i and g is 1, 0, -1 or -2 for acyclic, monocyclic, bicyclic and tricyclic compounds respectively. In this work, simple-structured acyclic compounds and monocyclic compounds were considered. Hence Equation (4.10) can be reduced to Equation (4.11) and Equation (4.12) for acyclic and monocyclic compound respectively:

$$\sum_{i=1}^{G_T} N_i (2 - v_i) = 2 \quad (4.11)$$

$$\sum_{i=1}^{G_T} N_i (2 - v_i) = 0 \quad (4.12)$$

Referring to the design objective identified earlier, the CAMD problem was formulated as multi-objective optimisation problem where target physicochemical, safety, health and environmental properties were to be optimised simultaneously together with the property and structural constraints. The optimisation model was solved by using weighted sum method and the overall objective function can be expressed by Equation (4.13).

$$F^{\text{weighted sum}} = w_1 \lambda_{p1} + w_2 \lambda_{p2} + \dots + w_m \lambda_{pm} \quad (4.13)$$

where $F^{\text{weighted sum}}$ is the overall objective function and w_m is the weighting factor for each normalised target property operator λ_{pm} .

Since the overall objective function was represented by different measurement units, all the target properties must be normalised to bring them to

the same magnitude. By performing normalisation, the normalised target property operators had values range from 0 to 1. Equation (4.14) was applied to normalise target property that needs to be maximized whereas Equation (4.15) was implemented on normalising target property that needs to be minimized.

$$\lambda_{pm} = \frac{\Omega_p - \Omega_{p\min}}{\Omega_{p\max} - \Omega_{p\min}} \quad (4.14)$$

$$\lambda_{pm} = \frac{\Omega_{p\max} - \Omega_p}{\Omega_{p\max} - \Omega_{p\min}} \quad (4.15)$$

where $\Omega_{p\min}$ and $\Omega_{p\max}$ are the minimum and maximum value of target property operator.

With such method, multiple objectives can be converted into an aggregated scalar objective function. This can be done by first allocating each objective function with a weighting factor, and then summing up all the contributors to obtain the overall objective function. The weighting factor was determined earlier from the AHP method (steps written in section 4.3.1 - 4.3.5). The design objective of this work was to maximize the value of $F^{weighted\ sum}$. After identifying a solution from the optimisation model, integer cut was performed to obtain a ranked list of optimal molecules. For cases where sensitivity analyses were performed, the overall objective function was re-written as there were changes in the final weighting factor of each objective. Using the proposed methodology, consistent weighting factor was assigned to each target property as the relative importance of each target property in molecular design can be systematically elicited. The proposed novel multi-objective molecular design framework is summarised in Figure 4.1.

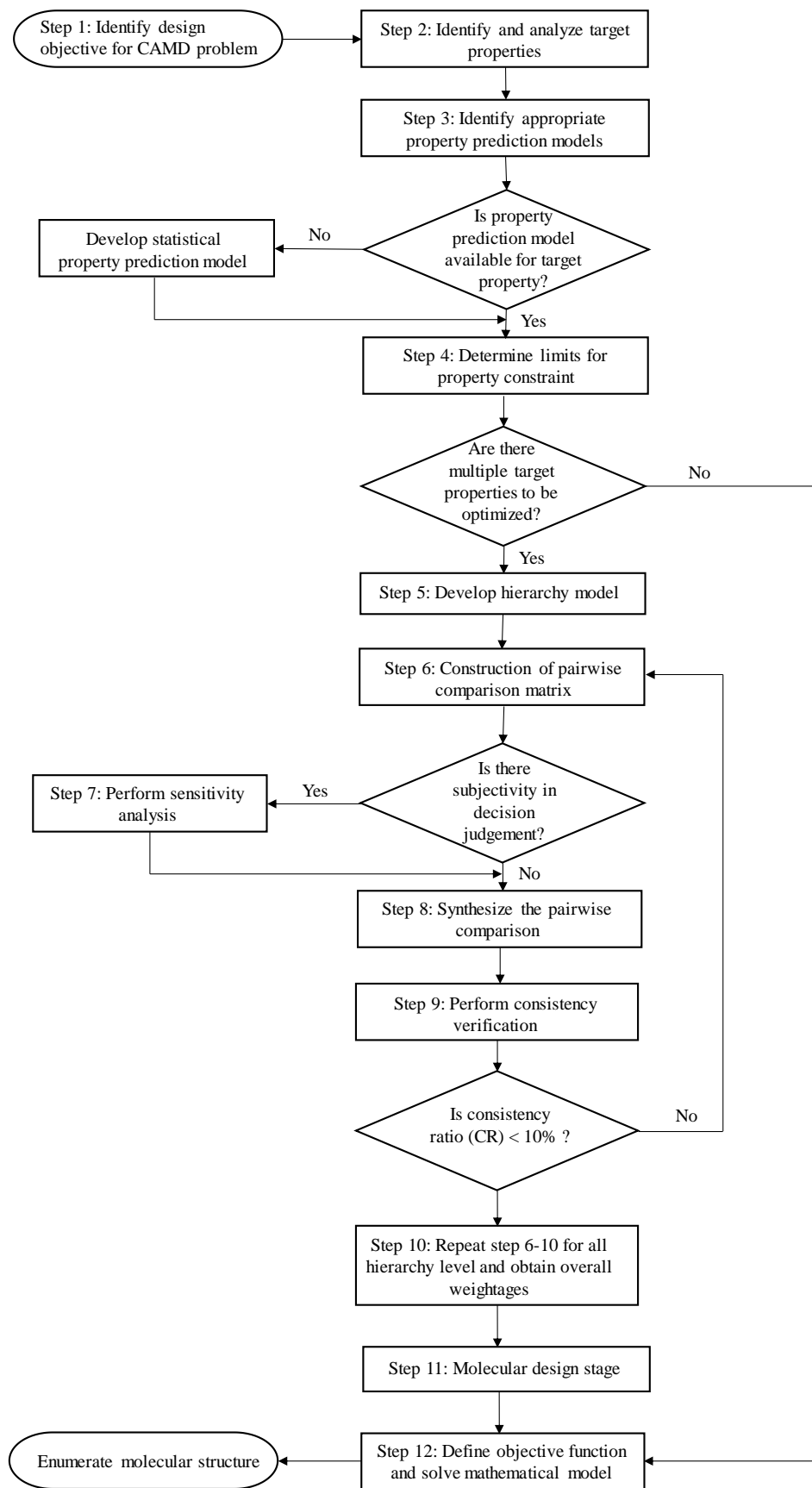


Figure 4.1: Procedures for research scope 1

4.4 Case study

4.4.1 Problem Statement

Southeast Asia is the most essential region for palm oil industry, as 90% of the worldwide palm oil production comes from Thailand, Indonesia and Malaysia (Colchester et al., 2011). Palm pressed fiber (PPF) is a by-product generated from palm oil milling process. In the process of extracting crude palm oil (CPO), 10.7 million tonnes of PPF are generated (Tabi et al., 2008). PPF is found out to retain 5-7 % of residual oil after extracting CPO using screw-press (Lik Nang Lau et al., 2008). In addition, it is well known that the residual oil retained in PPF is enriched with sterols, carotenoids and vitamin E. Based on Choo et al., (1996), there is 4500-8500 ppm of sterols, 4000-6000 ppm of carotenoids and 2400 – 3500 ppm of vitamin E found in residual oil extracted from PPF. Carotenoids and Vitamin E are usually used in food industry due to their antioxidant properties. Nowadays, solvent extraction is widely practised to extract the residual oil from PPF. Hexane is the solvent of choice for extracting the residual oil due to its low cost and high oil solubility in it (de Oliveira et al., 2013). However, there is a growing interest in identifying new solvents to replace hexane as hexane suffers from a number of major drawbacks. For instance, high boiling point of hexane has led to a higher degradation rate of carotenoids during oil recovery. Besides, hexane is highly flammable and prone to contribute to the formation of photochemical smog. Due to the abovementioned limitations of hexane, this work focused on improving the performance and environmental characteristics of solvent. Both solvent physicochemical and environmental properties were simultaneously considered as design criteria when designing the solvent.

4.4.2 Identification of design objective and target properties

This case study aimed to design alternate solvents for extracting residual oil from PPF. To prevent the degradation of carotenoids, boiling point (T_b) of the designed solvents should be kept low. Besides, solvent should exert low surface tension (σ) and viscosity (μ) to ensure higher rates of oil extraction. In addition, the difference of Hildebrand solubility parameter (δ) between solvent and carotene (R_{carotene}) should be small to make sure that the designed solvent is highly selective towards carotene and triglycerides (TAGs). Since δ values of carotene and TAGs are relatively close, it can be assumed that both carotene and TAGs will be soluble in the solvent when R_{carotene} was small. On the contrary, the unwanted free fatty acid (FFA) which mainly contains palmitic acid (PA), oleic acid (OA) and linoleic acid (LA) should have low solubility in the solvent.

It was important to ensure that the designed solvent will be less harmful to the environment while having favourable product functionality. Hence, the designed solvents should exert low aquatic and terrestrial toxicity potential, which were characterised by high fathead minnow LC_{50} toxicity and oral rat LD_{50} acute toxicity respectively. The designed solvent should also possess low photochemical oxidation potential (PCO) to minimise the formation of photochemical smog. Other than the abovementioned properties, the designed solvent should have minimum soil sorption coefficient ($\log K_{oc}$) to prevent the accumulation of the escaping solvent in one place, Moreover, bioconcentration factor (BCF) of the design solvent should be kept low to reduce the tendency of solvent to accumulate in aquatic organism. The abovementioned nine physicochemical and environmental properties were selected as the objective

functions to be optimised. Meanwhile, flashpoint (F_p) was chosen as property constraint to ensure that the designed solvent will have lower fire and explosion potential than that of hexane.

4.4.3 Determination of property prediction models

Following the proposed methodology, after determining the target properties for the design problem, property prediction models were identified. T_b , σ , μ , δ , F_p , M_w , LC_{50} , LD_{50} , PCO , $\log K_{ow}$ and BCF were properties that can be estimated using GCM equations whereas $\log K_{oc}$ can be calculated through empirical correlations. Both GCM equations and empirical correlations were shown in Table 4.3.

The next step was to identify the upper and lower bounds of property constraint for solvent design. For this case study, only lower bound was introduced to F_p as the higher the F_p , the lower the fire and explosion potential. Other than the property constraint, upper and lower limits were also introduced to target properties such as T_b , $R_{carotene}$ as well as $\log K_{oc}$ and BCF . This step was necessary to ensure that the designed molecules will have a better performance than hexane. Table 4.4 shows the property constraints ranges of the solvent at standard condition (298 K and 1 atm).

Table 4.3: GCM equations and empirical correlations for selected properties

Property	Equations/ Correlations	Universal constants	Reference
F_p (K)	$F_p - F_{p0} = \sum_i N_i F_{pli}$	$F_{p0} =$ 170.7058 K	(Hukkerikar et al., 2012b)
T_b (K)	$\exp\left[\frac{T_b}{T_{b0}}\right] = \sum_i N_i T_{bli}$	$T_{b0} = 244.5165$ K	(Hukkerikar et al., 2012b)
δ (MPA ^{1/2})	$\delta - \delta_0 = \sum_i N_i \delta_{li}$	$\delta_0 = 21.6654$ MPA ^{1/2}	(Hukkerikar et al., 2012b)
σ (mN/m)	$\sigma = \sum_i N_i \sigma_{li}$	-	(Conte et al., 2008)
μ (cP)	$\ln \mu = \sum_i N_i \mu_{li}$	-	(Conte et al., 2008)
M_w (g/mol)	$M_w = \sum_i N_i M_{wli}$	-	-
$\log K_{oc}$	$\log K_{oc} = 1.03 \log K_{ow} - 0.61$	-	(Seth et al., 1999)
$\log K_{ow}$	$\log K_{ow} - K_{ow0} = \sum_i N_i K_{owli}$	$K_{ow0} =$ 0.4876	(Hukkerikar et al., 2012b)
LD_{50} (mg/kg)	$-\log LD_{50} - A_{LD50} - B_{LD50} M_w = \sum_i N_i LD_{50li}$	$A_{LD50} =$ 1.9372 $B_{LD50} =$ 0.0016	(Hukkerikar et al., 2012a)
LC_{50}	$-\log LC_{50}(FM) + FM_0 = \sum_i N_i LC_{50li}$	$FM_0 =$ 2.1949	(Hukkerikar et al., 2012a)
PCO	$-\log PCO = \sum_i N_i PCO_{li}$	-	(Hukkerikar et al., 2012a)
BCF	$\log BCF = \sum_i N_i BCF_{li}$	-	(Hukkerikar et al., 2012a)

Table 4.4: Upper and lower bound of properties for solvent design

Property	Lower Bound	Upper Bound
F_p (K)	242	-
T_b (°C)	40	80
R_{carotene} (unit)	-	3.4
$\log K_{oc}$	-	4.5
$\log BCF$	-	3.3

4.4.4 Development of hierarchical structure

In this case study, a three-level hierarchy model was structured and shown in Figure 4.2. The decision problem aimed to design a solvent for extracting residual oil from palm pressed fibre. The designed solvent was expected to attain favourable physical and environmental characteristics. Hence, while designing the solvent for oil extraction, physical and environmental properties were the two main properties that needed to be satisfied by the solvent. There were four sub-properties under physical properties, such as boiling point (T_b), surface tension (σ), viscosity (μ) and Hildebrand solubility parameter (δ) difference between solvent and carotenoids (R_{carotene}). On the other hand, under environmental properties, there were five sub-properties naming aquatic toxicity (LC_{50}), terrestrial toxicity (LD_{50}), photochemical oxidation potential (PCO), soil sorption coefficient ($\log K_{oc}$) and bioconcentration factor (BCF).

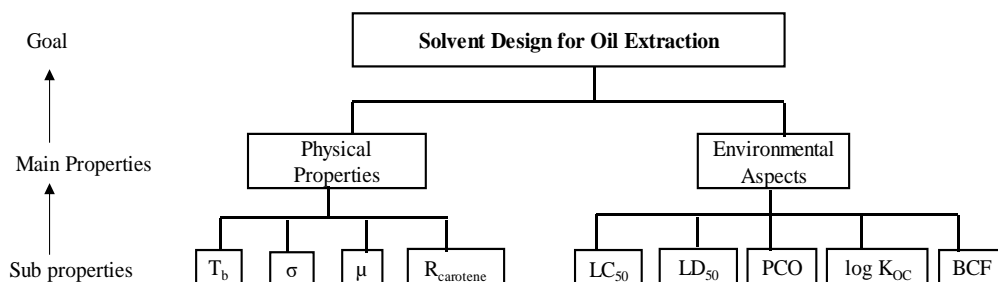


Figure 4.2: Hierarchy model for this case study

4.4.5 Computation of weights from Decision Maker's value judgement

Table 4.5, Table 4.6 and Table 4.7 show the assessment of relative importance of main properties with respect to goal as well as the relative importance of sub-properties with respect to each main property. In this work, the judgements were performed based on literature sources. For this case study,

the chosen literature sources must be related to the oil extraction process from either the PPF or the plant. The pairwise comparison between physical and environmental properties had been made by asking the question: “which property is more important and how much more important it is to satisfy the requirement in designing a solvent for oil extraction?” In this case study, physical property was given more priority compared to environmental property to ensure that the designed solvent will be simultaneously having better product functionality and does not bring harm to the environment. Furthermore, some constraints had been imposed on environmental properties to assure that the design solvent will not violate the environmental regulations. Thus, physical property was assumed to be strongly more important than environmental properties. Since the pairwise comparison matrix was only in the order of two, the judgement will always be consistent as the value of λ_{\max} was equal to n . As the physical and environmental properties were not equally important, there was subjectivity in assigning the intensity of importance while doing the pairwise comparison. Thus, sensitivity analysis was performed.

Table 4.5: Pairwise comparison matrix of main properties with respect to goal

	Physical properties	Environmental properties	Priority vector
Physical properties	1	5	0.8333
Environmental properties	1/5	1	0.1667
$\lambda_{\max}=2$			

The comparison between physical sub-properties was made by asking the question: “which is more important and how much more important it is with respect to a satisfaction of the physical properties of solvent?” Since the main objective of the case study was to reduce the degradation of carotene by lowering

the boiling point of solvent, T_b was strongly more important than R_{carotene} . μ and σ were slightly more important than R_{carotene} as it was crucial to ensure that the solvent was able to diffuse into the matrix of PPF to extract the residual oil. High surface tension can impede the penetration of designed solvent into the matrix of PPF, whereas solvent with low viscosity was favourable as part of the extraction process was governed by capillary flow (Johnson and Lusas, 1983). Moreover, the diffusion of residual oil from the matrix of PPF into the designed solvent can be modelled using Equation (4.16) (Tzia and Liadakis, 2003). Equation (4.16) clearly shows that diffusion of residual oil is dependent on the viscosity of solvent.

$$D_{AB} = \frac{117.3 \times 10^{-18} (\varphi M_B)^{0.5} T_{ext}}{\mu v_A^{0.6}} \quad (4.16)$$

where D_{AB} is the diffusivity of oil in solvent B, M_B is the molecular weight of solvent, T_{ext} is the temperature of the extraction unit, μ is the solution viscosity, v_A is the molar volume of oil and φ is the association factor for solvent. The intensity of importance allocated to each pairwise comparison is reported in Table 4.6. The inconsistency of the pairwise comparison was considered acceptable as the calculated CR is only 0.16% which was less than 10%. For physical sub-properties which were not equally important, sensitivity analysis was performed.

Table 4.6: Pairwise comparison matrix of sub-physical properties

	T_b	R_{carotene}	σ	μ	Priority vector
T_b	1	5	3	3	0.5320
R_{carotene}	1/5	1	1/2	1/2	0.0971
σ	1/3	2	1	1	0.1854
μ	1/3	2	1	1	0.1854
$\lambda_{\text{max}} = 4.004$; CI = 0.0013; CR = 0.0016					

The comparison between environmental sub properties was done by asking the question: “which one is more important and how much more important it is with respect to a satisfaction of the environmental properties of solvent?” Since the oil extraction process from plant or oilseed is similar, it can be assumed that the environmental impact caused by oil extraction from PPF using solvent will be similar to that from plant or oilseed. An environmental assessment of the extraction of essential oil from Oregano and Rosemary had been done by Moncada et al., (2016). Based on the environmental assessment reported by their work, solvent extraction technology with the use of hexane as choice of solvent had contributed significant impacts on aquatic toxicity and photochemical oxidation potential. From the point of view of environmental aspects, solvent extraction using hexane was the most harmful technology compared to supercritical fluid and water distillation technology. The results of potential environmental impact (PEI) per kilogram of essential oil extracted from both Oregano and Rosemary using hexane had shown similar trend. Referring to the result obtained for Rosemary oil, the PEI per kilogram of rosemary oil extracted for terrestrial toxicity, aquatic toxicity and photochemical oxidation potential were approximately 0.005, 0.03 and 0.07 respectively (Moncada et al., 2016). Thus, to design a solvent which will significantly reduce photochemical oxidation potential, it was assumed that photochemical oxidation potential was very strongly more important than terrestrial toxicity whereas aquatic toxicity was slightly more important than terrestrial toxicity. Besides, it was also important to ensure that the generated solvent will have low tendency to accumulate in one place as degradation products with low biodegradability may

persist in the environment. Since $\log K_{oc}$ is a measure of the tendency of solvent to accumulate in one place whereas BCF is a measure of tendency of solvent to accumulate in aquatic organism, both $\log K_{oc}$ and BCF were assumed to be equally important while designing the molecules. Moreover, upper limits had been imposed on both $\log k_{oc}$ and BCF to ensure that the designed solvent is not bio-accumulative.

Table 4.7 shows the intensity of importance assigned to each environmental property. CR of 3.4% showed that the inconsistency in decision judgement is acceptable. As stated in the methodology, sensitivity analysis was carried out when there as uncertainty in assigning the intensity of importance to the properties.

Table 4.7: Pairwise comparison matrix of sub-environmental properties

	LC ₅₀	LD ₅₀	PCO	K _{oc}	BCF	Priority vector
LC ₅₀	1	3	1/5	3	3	0.1869
LD ₅₀	1/3	1	1/7	2	2	0.0951
PCO	5	7	1	7	7	0.5943
$\log K_{oc}$	1/3	1/2	1/7	1	1	0.0618
BCF	1/3	1/2	1/7	1	1	0.0618

$\lambda_{max}= 5.15$; CI = 0.037; CR= 0.034

After obtaining the relative weighting factor of main properties and sub-properties, the final weighting factors of each sub property in the overall system was calculated by multiplying their weighting factor with the weighting factor of its main property. For this case study, the final weighting factors of target properties in the overall system was reported in Table 4.8.

Table 4.8: Final weighting factors of target properties in the overall system

Target Property	Final weighting factor
T_b	0.4433
R_{carotene}	0.0810
σ	0.1545
μ	0.1545
LC_{50}	0.0311
LD_{50}	0.0159
PCO	0.0991
BCF	0.0103
$\log K_{oc}$	0.0103

4.4.6 Molecular design stage

Next, molecular building blocks were selected based on the molecular structures of the conventionally used solvents for oil extraction. In this work, the chosen molecular groups include CH_3 , CH_2 , CH , C , OH , $COOH$, CH_3CO , CHO , CH_3O , NH_2 , $CH_2=CH$, CH_2O and $CH-O$. The structural constraints shown in Equation (4.9) and Equation (4.11) or Equation (4.12) were applied to ensure that a structurally feasible molecule can be formed without having any free bonds. After generating acyclic compounds using Equation (4.9) and Equation (4.11), monocyclic compounds were designed using Equation (4.9) and Equation (4.12).

4.4.7 Define objective function and solve the mathematical model

The target property models were first transformed into their property operators as shown in Table 4.9. The property operators were represented by the linear combinations of the number of occurrence for molecular group of type- i and its corresponding contribution. After determining the property operators, property operators were normalised using Equation (4.14) or Equation (4.15)

depending on whether the target property is to be minimised or maximised. The overall objective function for this case study can be expressed by Equation (4.17):

$$F^{weighted\ sum} = w_1\lambda_{T_b} + w_2\lambda_{\sigma} + w_3\lambda_{\mu} + w_4\lambda_{R_{carotene}} + w_5\lambda_{LC_{50}} + w_6\lambda_{LD_{50}} + w_7\lambda_{PCO} + w_8\lambda_{\log K_{oc}} + w_9\lambda_{BCF} \quad (4.17)$$

where w_1, w_2, \dots, w_9 are the weighting factors determined from AHP approach.

The optimisation model becomes a mixed-integer linear programming (MILP).

The design objective now was to maximise the value of $F^{weighted\ sum}$. Integer cuts were then introduced to produce alternate solutions.

Table 4.9: Property and property operator

Property, p	Property operator, Ω_p
T_b	$\exp(T_b / T_{b0})$
σ	σ
M_w	M_w
μ	$\ln \mu$
δ	$\delta - \delta_0$
F_p	$F_p - F_{p0}$
LC_{50}	$-\log LC_{50}(FM) + FM_0$
LD_{50}	$-\log LD_{50} - A_{LD50} - B_{LD50}M_w$
PCO	$-\log PCO$
BCF	$\log BCF$
$\log K_{oc}$	$\log K_{ow} - K_{ow0}$

4.4.8 Results and discussions

In this work, both acyclic and monocyclic solvents had been generated. Figure 4.3 and Figure 4.4 depict the molecular structures of the top ten acyclic and monocyclic solvents.

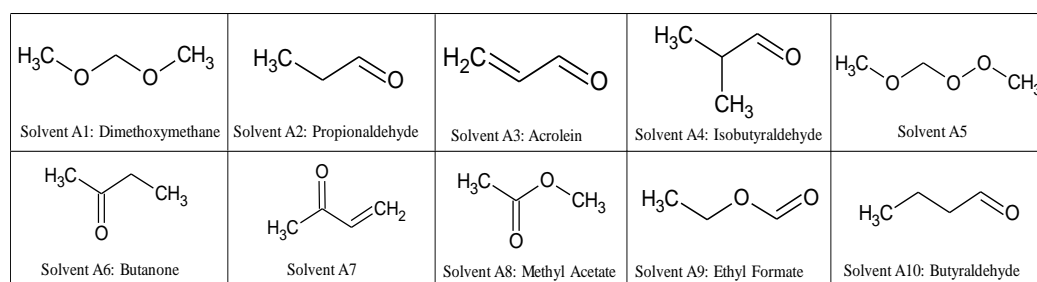


Figure 4.3: Molecular structure of the best ten acyclic solvents

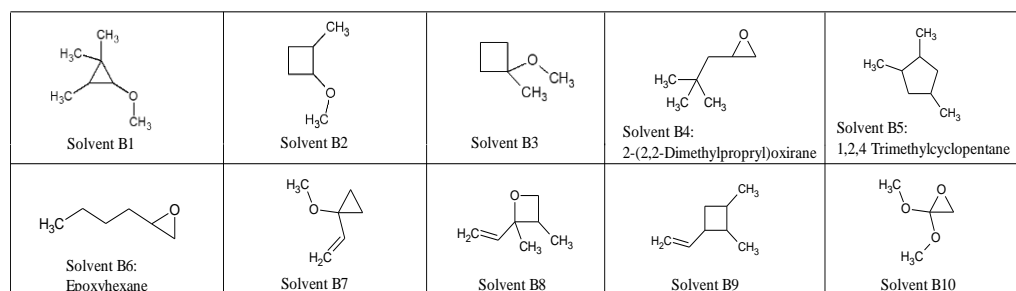


Figure 4.4: Molecular structures of the best ten monocyclic solvent

The MILP optimisation model was solved using LINGO 14.0 with global solver by a laptop with Intel® Core™ i7-6500U CPU @ 2.50GHz. Negligible computational time (0.1 second) was needed for the first generated solution. Table 4.10 and Table 4.11 show the properties of the top ten generated acyclic solvents whereas Table 4.12 and Table 4.13 report the properties of the best ten generated monocyclic solvents. By comparing the generated solutions with the existing literature, it was figured out that solvent A8 (methyl acetate) has been shown to be suitable solvent for extracting oil from oilseeds (Su et al., 2007). From the results, solvent A1 and solvent B1 had the highest $F^{weighted\ sum}$ values which made them rank the first among all the molecules generated. However, the generated ranking for each molecule was not absolute, as there will generally be uncertainties in prediction models and values of target properties. In this case, the rankings of molecules represented the identification of promising potential

candidates from a huge search space. A higher ranking denoted a greater possibility for a molecule to be useful for a specific application. After obtaining a ranked list of molecules, the potential solutions need to be further examined and verified through experiments.

The properties of the designed molecules were then analysed and compared with that of hexane. The properties of hexane were shown in Table 4.14. The generated results have shown that the T_b of top four acyclic solvents (solvent A1 to A4) and all the ten monocyclic solvents were lower than that of hexane. On top of that, R_{carotene} of both solvent A1 and B1 were significantly smaller than that of hexane. This was favourable as the result indicated that the mutual miscibility between carotenoids and solvent A1 or solvent B1 were higher than that of hexane. The mutual miscibility will decrease if the differences in δ vales between two solvents become larger (Giernoth, 2011). Besides, it was noticed that all acyclic and monocyclic solvents had lower $\log k_{oc}$ values than that of hexane. The generated acyclic solvent will have low soil sorption since $\log k_{oc}$ values were less than 1.5 (Allen and Shonnard, 2002). All the generated solvents were less likely to bioaccumulate as their BCF values were less than 250 (Allen and Shonnard, 2002). In addition, by looking at the values of $-\log LC_{50}$ of all the generated solvents, it can be concluded that the generated solvents were less likely to cause aquatic toxicity as the $-\log LC_{50}$ values were lower than that of hexane. In terms of safety aspects, the generated acyclic solvents will be less flammable than the generated monocyclic solvents by referring to their F_p values. However, both designed acyclic and monocyclic solvents were having better characteristic in safety aspects compared to that of hexane.

Table 4.10: The generated acyclic solvent with their respective properties

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	Solubility(mPA ^{1/2})	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)
A1	0.89	48.49	20.18	0.31	18.11	0.31	0.91	2.01	2.01	1.91
A2	0.67	42.30	23.23	0.41	20.37	2.57	3.17	4.27	4.27	4.17
A3	0.64	40.36	24.34	0.34	19.95	2.15	2.75	3.85	3.85	3.75
A4	0.46	61.69	22.86	0.44	19.54	1.74	2.34	3.44	3.44	3.34
A5	0.42	74.51	21.95	0.46	18.24	0.44	1.04	2.14	2.14	2.04
A6	0.40	71.34	23.98	0.37	19.25	1.45	2.05	3.15	3.15	3.05
A7	0.37	69.62	25.09	0.31	18.82	1.02	1.62	2.72	2.72	2.62
A8	0.26	77.57	25.10	0.42	19.81	2.01	2.61	3.71	3.71	3.61
A9	0.20	68.95	25.00	0.61	20.50	2.70	3.30	4.40	4.40	4.30
A10	0.18	78.60	23.85	0.51	20.22	2.42	3.02	4.12	4.12	4.02

Table 4.11: The generated acyclic solvent with their respective properties (continued)

Solvent	M _w (g/mol)	F _p (°C)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	log k _{oc}	BCF
A1	76.10	-7.00	-2.95	711.06	0.45	-0.28	3.99
A2	58.08	-6.85	-1.21	831.00	1.04	-0.16	2.54
A3	56.06	-8.01	-0.56	558.31	2.77	-0.40	2.60
A4	72.11	-1.74	-1.16	899.72	1.04	0.10	3.83
A5	92.09	14.40	-3.45	682.47	0.66	-0.88	2.51
A6	72.11	1.76	-1.73	749.04	0.49	0.26	26.66
A7	70.09	0.60	-1.08	506.77	1.30	0.02	27.33
A8	74.08	10.46	-2.63	719.56	0.51	-0.81	8.29
A9	74.08	14.54	-1.71	840.56	1.53	-0.76	1.60
A10	72.11	4.67	-0.92	930.69	0.93	0.29	3.16

Table 4.12: The generated monocyclic solvents with their respective properties

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	Solubility (mPA ^{1/2})	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)
B1	0.85	48.21	1.92	5.35	17.84	0.04	0.64	1.74	1.74	1.64
B2	0.83	40.93	3.49	3.83	19.78	1.98	2.58	3.68	3.68	3.58
B3	0.78	47.00	3.29	5.66	19.36	1.56	2.16	3.26	3.26	3.16
B4	0.77	49.05	2.94	6.52	18.24	0.44	1.04	2.14	2.14	2.04
B5	0.77	53.74	1.99	3.65	18.39	0.59	1.19	2.29	2.29	2.19
B6	0.76	41.81	4.50	4.67	20.19	2.39	2.99	4.09	4.09	3.99
B7	0.75	45.10	4.40	4.72	18.93	1.13	1.73	2.83	2.83	2.73
B8	0.75	47.17	4.05	5.44	17.82	0.02	0.62	1.72	1.72	1.62
B9	0.74	51.89	3.10	3.05	17.97	0.17	0.77	1.87	1.87	1.77
B10	0.72	43.18	5.56	7.75	20.19	2.39	2.99	4.09	4.09	3.99

Table 4.13: The generated monocyclic solvent with their respective properties (continued)

Solvent	M _w (g/mol)	F _p (°C)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	log k _{oc}	BCF
B1	114.19	-25.24	-2.32	451.98	0.48	1.95	3.57
B2	100.16	-25.94	-1.55	491.75	0.62	1.58	2.11
B3	100.16	-23.93	-2.14	470.26	0.43	1.89	1.95
B4	114.19	-17.65	-1.97	439.56	0.68	2.17	4.79
B5	112.22	-29.53	-0.59	513.82	0.60	2.90	10.24
B6	100.16	-18.35	-1.20	478.23	0.87	1.79	2.83
B7	98.14	-25.09	-1.49	320.73	1.14	1.65	2.00
B8	112.17	-18.80	-1.32	300.54	1.81	1.93	4.91
B9	110.20	-30.69	0.05	351.20	1.59	2.67	10.50
B10	104.11	-5.36	-3.83	401.79	0.73	-0.23	0.31

Table 4.14: Properties of hexane

Property	Property value
T _b (°C)	68.7
σ (mN/m)	17.91
μ (cp)	0.297
R _{carotene} (unit)	2.9
R _{TAG} (unit)	2.3
R _{LA} (unit)	1.2
R _{PA} (unit)	1.2
R _{OA} (unit)	1.3
F _p (°C)	-30.9
-log LC ₅₀	4.54
LD ₅₀ (mg/kg)	28000
PCO	0.4306
log k _{oc}	3.62
BCF	51.357

Sensitivity analysis is performed when there are subjectivities in assigning the intensity of importance to the properties. All the sensitivity analysis results showed that the first molecule generated is having the same properties as that of the original case study. Thus, it can be concluded that the first molecule generated for both acyclic and monocyclic solvent is robust as the molecule still ranks the first even though there are variations in weighting factors between physical and environmental properties. For the case where acyclic solvents are generated, there are no changes found in the ranking order unless T_b is assumed to be only two times more important than μ and σ. When T_b is assumed to be only two times more important than μ and σ, solvent A9 and solvent A10 have swapped their rankings with each other. However, for the cases where monocyclic solvents are generated, there are usually some minor changes in the ranking order within the molecules generated when the sensitivity analysis is performed. In this work, only cases where there is an abrupt change in the molecule ranking are chosen to be reported and discussed. For example, for case study “a” where physical property is assumed to be four times more important

than environmental property, monocyclic solvent B9 in the original case study has fallen out of the top ten ranking. On the contrary, monocyclic solvent C3 which originally does not fall within the top ten ranking has turned out to be the third best molecule in case study 'a'. Table 4.15 and Table 4.16 show the best ten monocyclic solvents generated for case study 'a'. In case study 'b', T_b is assumed to be twice more important than μ and σ . The sensitivity analysis result shows that there are a few changes on the solvent ranking. Monocyclic solvent B5 and B9 in the original case study are ranked at the third and sixth position respectively for case study 'b'. In addition, monocyclic D10 which falls out of the top ten ranking has successfully ranked at the tenth position in case study 'b'. The properties of the molecules generated for case study 'b' are clearly shown in Table 4.17 and Table 4.18 respectively.

Table 4.15: Top ten monocyclic solvent generated for case study 'a'

Solvent	T _b (°C)	σ (mN/m)	μ (cp)	Solubility (mPA ^{1/2})	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)
C1	48.21	1.92	5.35	17.84	0.04	0.64	1.74	1.74	1.64
C2	40.93	3.49	3.83	19.78	1.98	2.58	3.68	3.68	3.58
C3	43.04	3.14	4.41	18.67	0.87	1.47	2.57	2.57	2.47
C4	47.00	3.29	5.66	19.36	1.56	2.16	3.26	3.26	3.16
C5	49.05	2.94	6.52	18.39	0.44	1.19	2.29	2.29	2.19
C6	53.74	1.99	3.65	18.39	0.59	1.19	2.29	2.29	2.19
C7	41.81	4.50	4.67	20.19	2.39	2.99	4.09	4.09	3.99
C8	45.10	4.40	4.72	18.93	1.13	1.73	2.83	2.83	2.73
C9	47.17	4.05	5.44	17.82	0.02	0.62	1.72	1.72	1.62
C10	43.18	5.56	7.75	20.19	2.39	2.99	4.09	4.09	3.99

Table 4.16: Top ten monocyclic solvent generated for case study 'a' (continued)

Solvent	M _w (g/mol)	F _p (°C)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	log k _{oc}	BCF
C1	114.19	-25.24	-2.32	451.98	0.48	1.95	3.57
C2	100.16	-25.94	-1.55	491.75	0.62	1.58	2.11
C3	114.19	-19.65	-1.39	459.64	0.98	1.86	5.19
C4	100.16	-23.93	-2.14	470.26	0.43	1.89	1.95
C5	112.22	-29.53	-1.97	435.12	0.68	2.17	4.79
C6	112.22	-29.53	-0.59	513.82	0.60	2.90	10.24
C7	100.16	-18.35	-1.20	478.23	0.87	1.79	2.83
C8	98.14	-25.09	-1.49	320.73	1.14	1.65	2.00
C9	112.17	-18.80	-1.32	300.54	1.81	1.93	4.91
C10	104.11	-5.36	-3.83	401.79	0.73	-0.23	0.31

Table 4.17: Top ten monocyclic solvent generated for case study 'b'

Solvent	T _b (°C)	σ (mN/m)	μ (cp)	Solubility (mPA ^{1/2})	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)
D1	48.21	1.92	5.35	17.84	0.04	0.64	1.74	1.74	1.64
D2	40.93	3.49	3.83	19.78	1.98	2.58	3.68	3.68	3.58
D3	53.74	1.99	3.65	18.39	0.59	1.19	2.29	2.29	2.19
D4	47.00	3.29	5.66	19.36	1.56	2.16	3.26	3.26	3.16
D5	49.05	2.94	6.52	18.39	0.44	1.19	2.29	2.29	2.19
D6	51.89	3.10	3.05	17.97	0.17	0.77	1.87	1.87	1.77
D7	45.10	4.40	4.72	18.93	1.13	1.73	2.83	2.83	2.73
D8	41.81	4.50	4.67	20.19	2.39	2.99	4.09	4.09	3.99
D9	47.17	4.05	5.44	17.82	0.02	0.62	1.72	1.72	1.62
D10	52.56	3.36	3.87	19.91	2.11	2.71	3.81	3.81	3.71

Table 4.18: Top ten monocyclic solvent generated for case study 'b' (continued)

Solvent	M _w (g/mol)	F _p (°C)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	log k _{oc}	BCF
D1	114.19	-25.24	-2.32	451.98	0.48	1.95	3.57
D2	100.16	-25.94	-1.55	491.75	0.62	1.58	2.11
D3	112.22	-29.53	-0.59	513.82	0.60	2.90	10.24
D4	100.16	-23.93	-2.14	470.26	0.43	1.89	1.95
D5	112.22	-29.53	-1.97	435.12	0.68	2.17	4.79
D6	110.20	-30.69	0.05	351.20	1.59	2.67	10.50
D7	98.14	-25.09	-1.49	320.73	1.14	1.65	2.00
D8	100.16	-18.35	-1.20	478.23	0.87	1.79	2.83
D9	112.17	-18.80	-1.32	300.54	1.81	1.93	4.91
D10	98.19	-28.22	-0.41	533.29	0.53	2.84	5.59

4.5 Summary

A novel CAMD methodology utilizing AHP approach for criterion weighting had been developed to address the subjectivity issue involved in multi-objective molecular design problems. With the developed approach, the process of eliciting relative importance between each property can be done systematically and consistently using pairwise comparisons. Besides, the developed methodology allowed the quantification of decision maker's subjective judgement to make a trade-off between target properties. Thus, consistent relative weighting factors, which reflected the preference of decision maker, can be assigned to each target property. A case study on the solvent design for oil extraction from palm pressed fibre was solved to illustrate the proposed methodology. In this case study, environmental aspects of the molecule together with the physicochemical properties were considered during the decision-making stage. Based on the results obtained from sensitivity analysis, it can be concluded that the proposed decision model was robust as the first molecule generated for the original case study still ranks the first for all other cases despite of the changes in weighting factors between physical and environmental properties. However, it was to be noted that when the information required to assess the relative importance between the multiple properties are uncertain and complex, it was rather difficult for a decision maker to assign exact numerical values while eliciting the comparison judgement. This situation may occur when comparing the relative importance between safety, health, environmental and physicochemical properties because literature data that supported their relative important may not be available. AHP approach alone was no longer to sufficient to manage the uncertainty of subjective opinions

involved in pairwise comparison. Hence, there exists a need to revise the current CAMD methodology to capture the uncertainty and vagueness of decision makers' opinion when performing judgement in pairwise comparison. This novel approach in addressing the uncertainties arising from ambiguity involved during value judgement elicitation in multi-objective molecular design problems will be presented in the next chapter.

CHAPTER 5

INTEGRATION OF FUZZY ANALYTIC HIERARCHY PROCESS

INTO MULTI-OBJECTIVE COMPUTER AIDED MOLECULAR

DESIGN

5.1 Introduction

This chapter presents the integration of Fuzzy Analytic Hierarchy Process (FAHP) into CAMD framework to design optimal molecules that satisfy multiple target properties including physicochemical and SHE properties. In addition to physicochemical and environmental properties, safety and health aspects of molecules were considered to ensure that the generated molecules are safe and do not cause adverse health impacts to consumers. Similar to the previous chapter, the CAMD problem was formulated as a multi-objective optimisation problem. For the previous case, there is literature data available for evaluating the relative importance of both physicochemical and environmental properties. Hence, AHP approach was sufficient to quantify the subjectivity since decision maker can easily allocate exact value of weighting factors based on the information available. Nonetheless, in this case, literature data needed to assess the relative importance between some properties, especially safety and health properties, may not be available. In such situation, it will be harder for a decision maker to allocate an exact numerical value when performing pairwise comparison. AHP alone can no longer manage the highly uncertain opinions when eliciting the value judgement. Hence, FAHP approach was applied to

quantify the highly subjective opinions of decision maker in eliciting the value judgement. A case study on solvent design for extracting residual oil from palm pressed fibre was performed to illustrate the proposed methodology.

5.2 Problem statement

The design objective of this CAMD problem was to identify optimal molecules that achieve good functionalities and fulfil safety, health and environmental (SHE) criteria. The incorporation of SHE aspects together with physicochemical properties into CAMD framework brings up an additional issue. For example, the information needed to elicit the relative importance or preference between SHE criteria and physicochemical properties may not exist. This added the uncertainty and complexity of the process in performing the value judgement. For such situation, it is often difficult to assign exact numerical values that truly reflect decision maker's thought during pairwise comparison. Besides, the uncertain and complex evaluation data affects the confidence level of a person when making decisions. As previously mentioned, AHP approach utilises discrete numerical scales which were not sufficient to handle the fuzziness and ambiguity of subjective opinions occurred during pairwise comparison. Hence, a better mathematical tool must be developed to address this issue. The methodology must be able to offer a more systematic decision-making procedure in aiding the decision maker to decide their judgement in a more precise manner when doing pairwise comparison.

5.3 Methodology

The main purpose of this work was to develop a novel multi-objective CAMD methodology for systematic allocation of weighting factors to each target property the problem. The integration of FAHP approach into multi-objective molecular design framework can account for the inherent vagueness and uncertainty arising from the determination of weighting factor of each property under fuzzy surrounding. By using the proposed methodology, a molecule that gave the best balance of performance in terms of physicochemical properties as well as SHE aspects can be designed. The proposed framework was summarised in the following steps:

5.3.1 Identification of design objective

In the first step, the identification of design objective for CAMD problem was done by determining the needs of chemical product based on customers' preferences or from operating condition of industrial processes. Other than physical and thermodynamic properties, safety, health and environmental criteria were considered to ensure that the designed molecule achieves favourable safety, health and environmental performance. Safety and health performance of molecules can be characterised by appropriate indices, which will be further illustrated in Section 5.3.3. The desired target properties and criteria were then selected as design objectives to ensure that the designed molecules simultaneously achieve the functionality and pose low safety, health and environmental hazard levels.

5.3.2 Determination of property prediction model

Once the product specifications and SHE targets were identified, the next step was the estimation of all identified target properties via property prediction models. Most of the targeted properties can be estimated by using GCM equation. For properties with no GCM available, empirical relationships and correlations can be applied to estimate the properties. Next, the ranges of targeted properties were defined to ensure that the generated molecules can behave and function like the conventional molecule.

5.3.3 Identification of safety and health indices

Due to the growing number of industrial accidents, there is an increased emphasis on process safety in chemical industries. Safety hazards can be minimized by having milder process operating condition and replacing those hazardous materials with less harmful substances. Besides, occupational health should not be neglected as health hazards will often lead to chronic diseases after a prolonged exposure. The safety and health impact of chemical product can be assessed by safety and health indices.

Under safety aspects, two safety indices were applied to evaluate the safety characteristics of the molecules, namely explosiveness based index (I_{EX}) and flammability based index (I_{FL}). The scores for I_{EX} were obtained from ISI (Heikkilä, 1999) whereas the scores for I_{FL} were taken from NFPA flammability rating (National Fire Protection Association, 2007). On the other hand, health indices such as exposure limit based index (I_{EL}) and acute health hazards (I_{AH}) were selected to assess the health performance of designed molecules. The index

score for I_{EL} was taken from IOHI (Hassim and Hurme, 2010) whereas the index score for I_{AH} was obtained from the NFPA health hazard rating (National Fire Protection Association, 2007). The penalty score for both safety indices were presented in Table 5.1 and Table 5.2 whereas penalty score for health indices were presented in Table 5.3 and Table 5.4. The total weighted penalty score for safety and health aspects of molecules ($I_{SHI,w}$) can be calculated by summing up all the sub-index values assigned to it, which was dictated in Equation (5.1). The weighting factor for each sub index was determined using FAHP approach.

$$I_{SHI,w} = w_{FL}I_{FL} + w_{EX}I_{EX} + w_{EL}I_{EL} + w_{AH}I_{AH} \quad (5.1)$$

where w_{FL} represents weighting factor for sub-index I_{FL} ; w_{EX} represents weighting factor for sub-index I_{EX} ; w_{EL} represents weighting factor for sub-index I_{EL} ; w_{AH} represents weighting factor for sub-index I_{AH} .

Table 5.1: Flammability (I_{FL}) based index (NFPA)

Flammability, I_{FL}	Penalty scores
Non-flammable	0
$F_p \geq 93.4$ °C	1
$F_p < 93.4$ °C	2
$F_p < 37.8$ °C	3
$F_p < 22.8$ °C & $T_b < 37.8$ °C	4

Table 5.2: Explosiveness (I_{EX}) based index (modified from ISI)

Explosiveness, I_{EX}	Penalty scores
Non-explosive	0
$0 \leq S$ (vol %) ≤ 20	1
$20 \leq S$ (vol %) ≤ 45	2
$45 \leq S$ (vol %) ≤ 70	3
$70 \leq S$ (vol %) ≤ 100	4
where S = Upper Explosion Limit (UEL) – Lower Explosion Limit (LEL)	

Table 5.3: Exposure limit (I_{EL}) based index (modified from IOHI)

Exposure limit, I_{EL}	Penalty scores
PEL > 1000 ppm	0
PEL \leq 1000 ppm	1
PEL \leq 100 ppm	2
PEL \leq 10 ppm	3
PEL \leq 1 ppm	4

Table 5.4: Acute health hazard (I_{AH}) based index (NFPA)

Acute health hazard, I_{AH}	Penalty scores
LD_{50} (mg/kg) > 2000	0
$500 < LD_{50}$ (mg/kg) \leq 2000	1
$50 < LD_{50}$ (mg/kg) \leq 500	2
$5 < LD_{50}$ (mg/kg) \leq 50	3
LD_{50} (mg/kg) \leq 5	4

5.3.4 Disjunctive programming on allocation of index score

Since the assignation of penalty score to the molecule was dependent on the property value, disjunctive programming can be applied to translate the molecular properties into index score which implied the hazard level of molecules (Ten et al., 2016b). Disjunctive programming is a modelling approach which applies discontinuous functions to trace the abrupt changes over a certain decision variable (El-Halwagi, 2011). For example, a score of I_A was assigned to a sub-index score if the corresponding property, p value was smaller than a certain property value whereas a score of I_B was allocated when p value was equal to or larger than p_{switch} . The sub-index score model was shown by Equation (5.2):

$$I_p = \begin{cases} I_A & p < p_{switch} \\ I_B & p \geq p_{switch} \end{cases} \quad (5.2)$$

Binary integer variables are normally introduced to develop models for such cases which involve discontinuous function. Discontinuous functions can be transformed to the following mixed-integer formulation using a binary integer variable (I):

$$I_p = I_A * I + I_B * (I - 1) \quad (5.3)$$

subjected to the following condition:

$$I = \begin{cases} 0 & p < p_{switch} \\ 1 & p \geq p_{switch} \end{cases} \quad (5.4)$$

To ascertain that the model allocated the correct value to I to fulfil condition (5.4), the constraints written in Equation (5.5) must be included:

$$(p_L - p_{switch}) * I < p - p_{switch} \leq (p_U - p_{switch}) * (1 - I) \quad I \in \{0, 1\} \quad (5.5)$$

where p_L and p_U are lower and upper limits respective to any feasible value of p . When $p < p_{switch}$, the term $p - p_{switch}$ becomes negative, forcing I to have value 1 to satisfy both equalities in the constraint (5.4). On the contrary, when $p > p_{switch}$, I is forced to be 0 to again fulfil both equalities in constraint (5.4). The illustrative example for the formulation of disjunctive programming will be further discussed in section 5.4.4.

5.3.5 Development of hierarchical decision structure

Next, FAHP approach was utilised to systematically allocate a weighting factor for each property. The first step in the FAHP approach was analogous to that of AHP method, which was stated in section 4.3.1.

5.3.6 Computation of weights from Decision Maker's value judgement

The step was then followed by performing pairwise comparisons based on expert judgement to derive the relative importance of criteria at a particular level. For example, the comparison between two main properties was carried out by asking the question: "How much more important was property A compared to property B with respect to a satisfaction of the goal of decision problem?" The intensity of importance of one property over the other property within the same level with respect to a common property in the upper level was represented in the form of solution ratios ($\frac{w_i}{w_j}$). The solution ratio $\frac{w_i}{w_j}$ denotes the relative importance of property in the i^{th} row over the property in the j^{th} column with respect to the specific element in the upper level.

In a conventional AHP problem, the 9-point scale (Satty, 1980), shown in Table 4.1, was used to translate a linguistically expressed judgement into a numerical ratio $\frac{w_i}{w_j}$. However, to capture the uncertainty and vagueness of judgement during pairwise comparison, triangular fuzzy number (TFN) was used to extend the standard AHP 9-point scale. Thus, instead of using the exact numerical value to approximate the solution ratio $\frac{w_i}{w_j}$, a fuzzy scale was used to

represent the value judgement \hat{a}_{ij} as TFN. The general form of a FAHP pairwise comparison matrix can be expressed by Equation (5.6).

$$A = \begin{pmatrix} \langle 1,1,1 \rangle & \hat{a}_{12} & \cdots & \hat{a}_{1n} \\ \hat{a}_{21} & \langle 1,1,1 \rangle & \cdots & \hat{a}_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ \hat{a}_{n1} & \hat{a}_{n2} & \cdots & \langle 1,1,1 \rangle \end{pmatrix} \quad \text{where } \hat{a}_{ji} = \frac{1}{\hat{a}_{ij}} = \left(\frac{1}{\hat{L}_{ij}}, \frac{1}{\hat{M}_{ij}}, \frac{1}{\hat{U}_{ij}} \right) \quad (5.6)$$

where A is the fuzzy pairwise comparison matrix, \hat{a}_{ij} is the fuzzy judgement which is represented by TFN (lower bound \hat{L}_{ij} , modal value \hat{M}_{ij} and upper bound \hat{U}_{ij}). For instance, if \hat{a}_{ij} was identified to be more or less equally important, it will be represented by the TFN $\langle \frac{1}{1+\delta_c}, 1, 1 + \delta_c \rangle$ whereas if \hat{a}_{ij} was identified to be more important over the other, it will be represented using the fuzzy scale written in Table 5.5. Note that δ_c is the degree of confidence of the decision maker, with a lower value suggests higher degree of confidence, and vice-versa. δ_c value of one, two and three indicate the high, moderate and low degree of confidence while eliciting the value judgement (Tan et al., 2014).

Table 5.5: Summary of fuzzy scale (Tan et al., 2016)

Fuzzy number, \hat{a}_{ij}	Linguistic scale for comparison of criteria
$\langle \frac{1}{1 + \delta_c}, 1, 1 + \delta_c \rangle$	More or less equally important
$\langle \max(1, 3 - \delta_c), 3, \min(9, 3 + \delta_c) \rangle$	Moderately more important
$\langle \max(1, 5 - \delta_c), 3, \min(9, 5 + \delta_c) \rangle$	Strongly more important
$\langle \max(1, 7 - \delta_c), 3, \min(9, 7 + \delta_c) \rangle$	Very strongly more important
$\langle \max(1, 9 - \delta_c), 3, \min(9, 9 + \delta_c) \rangle$	Extremely more important

The w that approximated the solution ratio in pairwise comparison matrix were then computed using the nonlinear programming (NLP) formulation proposed by Promentilla et al., (2014), which was shown in Equation (5.7):

$$\max \lambda; \tag{5.7a}$$

subject to:

$$\lambda(M_{ij} - L_{ij})(w_j) - w_i + w_j L_{ij} \leq 0; \tag{5.7b}$$

$$\lambda(M_{ji} - L_{ji})(w_i) - w_j + w_i L_{ji} \leq 0; \tag{5.7c}$$

$$\lambda(U_{ij} - M_{ij})(w_j) - w_i + w_j U_{ij} \leq 0; \tag{5.7d}$$

$$\lambda(U_{ji} - M_{ji})(w_i) - w_j + w_i U_{ji} \leq 0; \tag{5.7e}$$

$$\sum_{m=1}^n w_m = 1; w_m > 0 \tag{5.7f}$$

where L_{ij} is the lower bound, M_{ij} is the modal value lambda, U_{ij} is the upper bound and λ is the consistency index, which indicate the degree of satisfaction of all computed weight ratios that would satisfy the initial fuzzy judgments. λ value shall range from 0 to 1. λ value of 0 denoted that the judgements were fulfilled at the boundaries whereas a value of 1 indicated perfect consistency (Tan et al., 2014). Therefore, by maximising λ , the most consistent set of weighting factors within the fuzzy bounds elicited from decision maker can be determined. However, if λ value fell out of the range, it implied a completely inconsistent pairwise comparison and there will be no solution. In such case, it was necessary to elicit the judgement again. After obtaining the weighting factor for each property and sub property, the final weighting factor of each sub property, w_m in the overall system were calculated by multiplying the weighting factor of sub property with that of its main property.

5.3.7 Molecular design stage

The subsequent step included the selection of potential molecular building blocks based on the nature of the target molecules. Structural constraints dictated in Section 4.3.6 were applied to design structurally feasible acyclic and monocyclic compounds respectively.

5.3.8 Optimisation model

Based on the identified design objective, the CAMD problem was formulated as multi-objective optimisation problem. The chosen targeted properties were first transformed into their respective target property operators (Ω_p) to reduce the non-linearity equations in the model. Weighted sum method was then applied to solve this multi-objective optimisation model. However, all the target properties and sub-indices were depicted by different measurement units and scales. Thus, normalisation step was important in bringing them to the same magnitude. Equation (5.8) and Equation (5.9) were applied to normalise target property or sub-indices that needs to be maximized and minimized respectively.

$$\lambda_{pm} = \frac{\Omega_p - \Omega_{p\min}}{\Omega_{p\max} - \Omega_{p\min}} \quad (5.8)$$

$$\lambda_{pm} = \frac{\Omega_{p\max} - \Omega_p}{\Omega_{p\max} - \Omega_{p\min}} \quad (5.9)$$

where $\Omega_{p\min}$ and $\Omega_{p\max}$ are the minimum and maximum value of target property operator. The normalised target property operators, λ_{pm} will now have values range from 0 to 1. The consistent set of weighting factor computed from FAHP

approach together with λ_{pm} can then be used to represent the overall objective function, which is shown in Equation (5.10):

$$F^{weighted\ sum} = w_1\lambda_{p1} + w_2\lambda_{p2} + \dots + w_m\lambda_{pm} \quad (5.10)$$

where $F^{weighted\ sum}$ is the overall objective function and w_m is the weighting factor for each normalised target property operator λ_{pm} . The design objective of this work was to maximize the value of $F^{weighted\ sum}$. After identifying a solution from the optimisation model, integer cut was performed to obtain a ranked list of optimal molecules. Using the proposed methodology, a more precise and consistent weighting factor was assigned to each target property as the relative importance of each target property in molecular design can be systematically elicited. The proposed methodology was summarised in Figure 5.1.

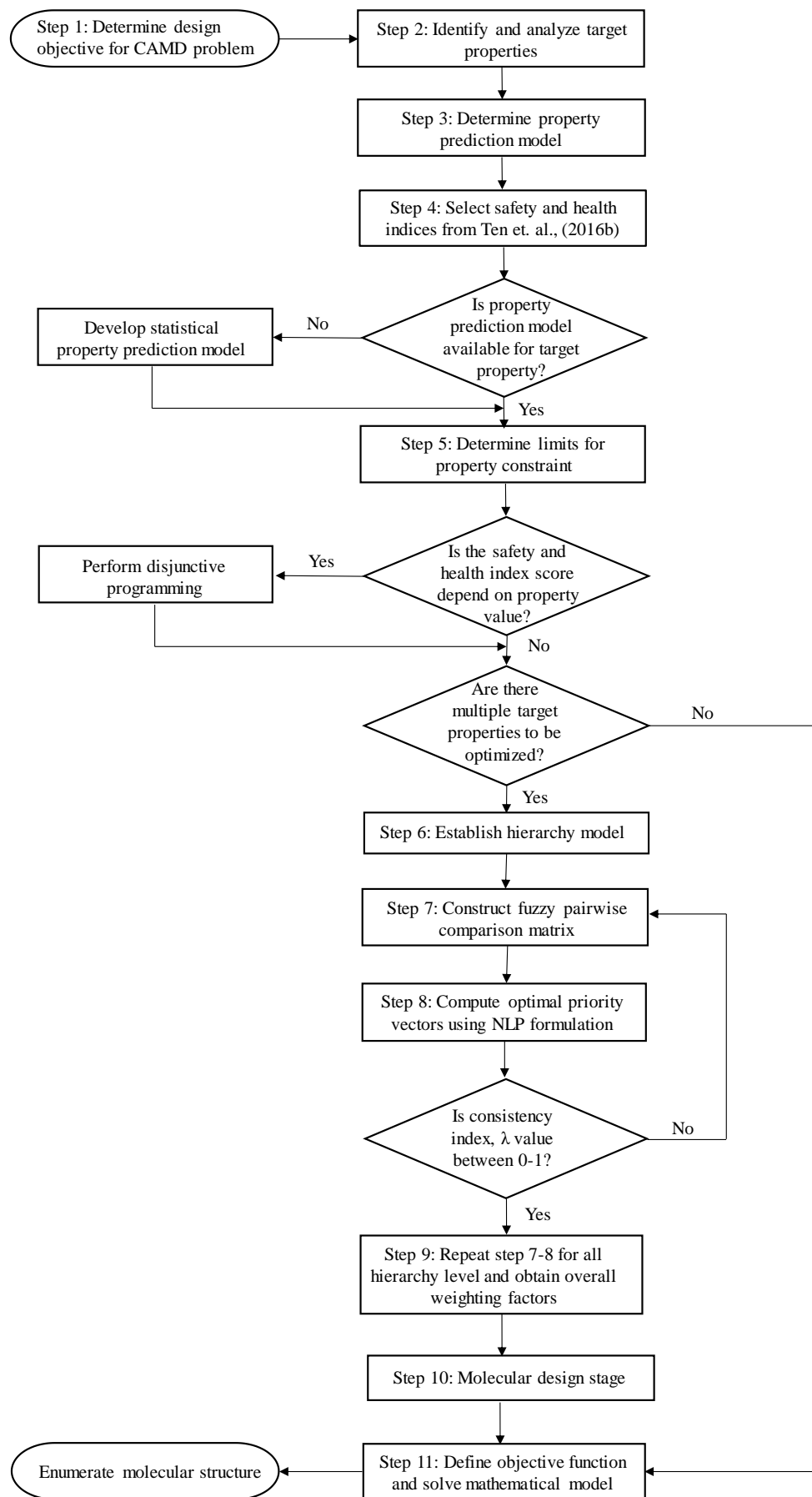


Figure 5.1: Methodology for research scope 2

5.4 Case study

5.4.1 Problem statement

The same case study stated in Section 4.4.1 was used to illustrate the proposed methodology. In addition to the aforementioned limitations of hexane in section 4.4.1, it is realized that hexane is not suitable for edible oil extraction due to its adverse effects on human health after a long-term exposure. Moreover, its high flammability characteristic leads to higher operating cost as additional layers of protection must be installed in the plant. Hence, besides physical and environmental properties, this work also focused on improving safety and health performance of the designed molecules.

5.4.2 Determination of design objective

The main objective of this case study was to design alternate solvents to replace hexane for residual oil extraction from PPF. The designed solvents should have desirable characteristics in terms of physical attributes as well as safety, health and environmental aspects. Table 5.6 shows the summary of desirable qualitative attributes of the designed solvents and their respective translated quantitative properties

Table 5.6 The desirable qualitative attributes of designed solvent with their respective translated quantitative properties

	Desirable qualitative attributes	Quantitative properties
Physical attributes	Reduce the degradation rates of carotene	Low boiling point (T_b)
	Ensure good percolation and surface wetting which will lead to high rates of oil extraction (Bockisch, 1998)	low viscosity (μ) and surface tension (σ)
	Ensure both carotene and triglycerides (TAGs) has high solubility in designed solvents	Small difference of Hildebrand solubility parameter (δ) between solvent and carotene (R_{carotene})

Safety aspects	Low flammability sub index I_{FL}	High flash point (F_p)
	Low explosiveness sub index I_{EX}	Small difference between lower explosion limit (LEL) and upper explosion limit (UEL)
Health Aspects	Low exposure limit sub index I_{EL}	High permissible exposure limit (PEL)
	Low acute health hazard index I_{AH}	High oral rat LD_{50}
Environmental Aspects	Low aquatic toxicity	High fathead minnow LC_{50}
	Minimise the formation of photochemical smog	Low photochemical oxidation potential (PCO)
	Reduce accumulation of solvent in one place	Low soil sorption coefficient ($\log K_{oc}$)
	Reduce the tendency of solvent to concentrate in aquatic organism	Low bioconcentration factor (BCF)

5.4.3 Identification of property prediction models

The following step included the determination of property prediction models for the identified target properties for the design problem. T_b , σ , μ , δ , F_p , M_w , LC_{50} , LD_{50} , PCO , $\log K_{oc}$ and BCF were properties that can be estimated using the same GCM equations and/or correlation stated in Table 4.3. Additional safety and health properties such as PEL , UEL and LEL can be estimated through a series of equations expressed below. PEL was calculated using Equation (5.11)(Hukkerikar et al., 2012a):

$$-\log PEL = \sum_i N_i PEL_i \quad (5.11)$$

The value of PEL calculated using Equation (5.11) had a unit of mol/m^3 . However, the value of PEL used for penalty score calculation had the unit of ppm. Thus, Equation (5.12) can be used to convert the unit of PEL into ppm.

$$PEL' = V_{gas, std} \times PEL \times 1000 \quad (5.12)$$

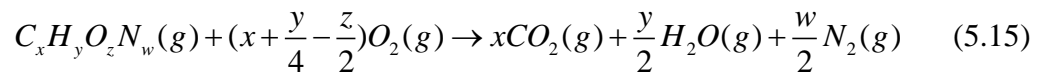
where PEL' has the unit of ppm whereas $V_{gas, std}$ is the molar volume of gas or vapour at standard condition (1 atm and 298 K), which has the value of 24.45 dm³/mol. From Table 5.2, the difference between UEL and LEL , which was denoted as S , can be used to calculate the I_{EX} . Both UEL and LEL were used interchangeably with upper flammability limit (UFL) and lower flammability unit (LFL). They can be calculated using Equation (5.13) and Equation (5.14) respectively.

$$LFL = \frac{100\%}{1 + 9.0454C_o} \quad (5.13)$$

$$UFL = \frac{100\%}{1 + 1.1843C_o} \quad (5.14)$$

where C_o is the oxygen stoichiometric coefficient in a reaction (Ma et al., 2013).

Consider a general compound $C_xH_yO_zN_w$ undergoes a complete combustion in air:



C_o can then be calculated using Equation (5.16).

$$C_o = x + \frac{y}{4} - \frac{z}{2} \quad (5.16)$$

The following step was to identify the upper and lower limits of property constraints for solvent design. The same property constraints ranges shown in Section 4.4.3 (Table 4.4) were applied.

5.4.4 Disjunctive optimisation

In this section, the application of disjunctive programming on the index scoring was demonstrated for I_{EX} . Consider the following criteria:

$$I_{EX} = \begin{cases} 1 & 0 \leq S < 20 \\ 2 & 20 \leq S < 45 \\ 3 & 45 \leq S < 70 \\ 4 & 70 \leq S < 100 \end{cases} \quad (5.17)$$

The I_{EX} score may be one, two, three or four depending on the S value of molecule. Binary integer variables had been used to model these functions. The I_{EX} functions were translated to the following mixed-integer formulation using three integer variables (I_{EX1} , I_{EX2} and I_{EX3}):

$$I_{EX} = I_{EX1} + I_{EX2} + I_{EX3} + 1 \quad (5.18)$$

Subjected to the following conditions:

$$I_{EX1} = \begin{cases} 0 & S < 20 \\ 1 & S \geq 20 \end{cases} \quad (5.19)$$

$$I_{EX2} = \begin{cases} 0 & S < 45 \\ 1 & S \geq 45 \end{cases} \quad (5.20)$$

$$I_{EX3} = \begin{cases} 0 & S < 70 \\ 1 & S \geq 70 \end{cases} \quad (5.21)$$

In order to model conditions stated in Equation (5.19), (5.20) and (5.21) which allocated the values of I_{EX1} , I_{EX2} and I_{EX3} to be either 0 or 1 based on S value of molecule, the following constraints were considered:

$$(0 - 20) * (1 - I_{EX1}) < S - 20 \leq (100 - 20) * I_{EX1} \quad I_{EX1} \in \{0, 1\} \quad (5.22)$$

$$(0-45) * (1 - I_{EX2}) < S - 45 \leq (100 - 45) * I_{EX2} \quad I_{EX2} \in \{0,1\} \quad (5.23)$$

$$(0-70) * (1 - I_{EX3}) < S - 70 \leq (100 - 70) * I_{EX3} \quad I_{EX3} \in \{0,1\} \quad (5.24)$$

5.4.5 Development of hierarchy model

A three-level hierarchical decision structure was constructed for this case study and shown in Figure 5.2. The main goal of this decision problem was to design a solvent for extracting the residual oil from palm pressed fibre. The designed solvents should attain its functionalities while having favourable safety, health and environmental characteristics. Thus, physicochemical properties as well as SHE criteria were the main elements that need to be fulfilled by the designed solvent. Under physicochemical properties, there were four sub-properties naming boiling point (T_b), surface tension (σ), viscosity (μ) and Hildebrand solubility parameter (δ) difference between solvent and carotenoids (R_{carotene}). I_{FL} and I_{EX} were the sub-indices chosen for safety aspects whereas I_{EL} and I_{AH} were the sub-indices selected for assessing health criterion. There were four sub-properties under environmental criteria, such as aquatic toxicity (LC_{50}), photochemical oxidation potential (PCO), soil sorption coefficient ($\log K_{oc}$) and bioconcentration factor (BCF).

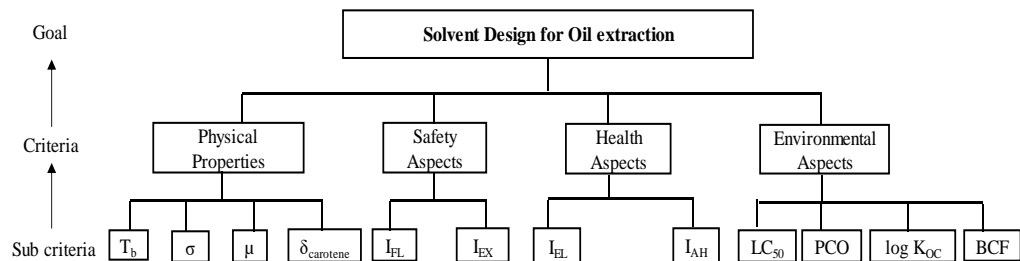


Figure 5.2: Hierarchical decision structure for this case study

5.4.6 Computation of weighting factor

The judgement in eliciting the relative importance of each criterion was identified from supporting literature or theory, which will be discussed in this section. The pairwise comparison between each criterion had been made in standard AHP form. However, the degree of confidence was also being taken into account while eliciting the judgements. For instance, when comparing the relative importance between physical properties and safety aspects, questions asked were: “which criteria is more important and how much more important it is to satisfy the requirement in designing a solvent for extracting residual oil from PPF?” In addition, decision maker can choose the degree of confidence when eliciting judgement, such as having high, moderate or low confidence while assigning the intensity of importance to the criteria.

In this case study, safety aspect was given the most priority compared to the other aspects. This ensured that the designed solvents were inherently safe and did not bring much adverse effects to the surrounding community if there were any unintentional release. Moreover, by using a less hazardous material in a process, the operational cost can be reduced as number of protection layer used in a plant can be minimised. Thus, the safety aspect of a molecule was assumed to be moderately more important than physical properties taken together; it was also considered to be strongly more important than environmental and health aspects of the molecule. On the other hand, physical properties were assumed to be strongly more important than environmental and health aspects of the molecules. In order to assure that the designed solvent will meet the environmental specification, constraints were imposed on the environmental properties. Table 5.7 shows the assessment of relative importance of main

criteria with respect to the main objective using fuzzy scale. Note that the λ value was larger than zero denoting that the judgement was consistent in this pairwise comparison matrix.

Table 5.7: Fuzzy pairwise comparison matrix of main criteria for solvent design on oil extraction

	Physical Properties	Environmental Aspects	Safety Aspects	Health Aspects	Priority Vector
Physical Properties	1	(3, 5, 7)	(1/5, 1/3, 1)	(3, 5, 7)	0.3105
Environmental Aspects		1	(1/7, 1/5, 1/3)	(1/2, 1, 2)	0.0844
Safety Aspects			1	(3, 5, 7)	0.5206
Health Aspects				1	0.0844
$\lambda = 0.3384$					

Table 5.8 and Table 5.9 reported the fuzzy pairwise comparison matrix of physical and environmental sub properties respectively. The comparative judgements for all these physical and environmental sub-properties had been elicited in the previous chapter stated in Section 4.4.5. Hence, all the modal value of these sub-properties followed the same intensity of importance assigned in Section 4.4.5. However, decision makers had to perform additional step which was to dictate their degree of confidence while eliciting their judgments. The elicited judgement was consistent since λ value is bigger than zero.

Table 5.8: Fuzzy pairwise comparison of physical sub properties for solvent design on oil extraction

	T_b	$R_{carotene}$	σ	μ	Priority Vector
T_b	1	(3, 5, 7)	(1, 3, 5)	(1, 3, 5)	0.5213
$R_{carotene}$		1	(1/3, 1/2, 1)	(1/3, 1/2, 1)	0.1006
σ			1	(1/2, 1, 2)	0.1891
μ				1	0.1891
$\lambda = 0.8786$					

Table 5.9: Fuzzy pairwise comparison of environmental sub properties for solvent design on oil extraction

	LC ₅₀	PCO	log K _{oc}	BCF	Priority Vector
LC ₅₀	1	(1/7, 1/5, 1/3)	(2, 3, 4)	(2, 3, 4)	0.1827
PCO		1	(5, 7, 9)	(5, 7, 9)	0.6583
log K _{oc}			1	(1/2, 1, 2)	0.0794
BCF				1	0.0794
$\lambda = 0.3009$					

When comparing the relative importance between flammability and explosiveness index, both indices were assumed to be more or less equally important. This was because the flammable range of a material was indicated by *LEL* and *UEL*. The terms *LFL* and *UFL* are used interchangeably with *LEL* and *UEL* (National Fire Protection Association, 2007). It is equally important to prevent fire and explosion hazards in a plant. Table 5.10 shows that both flammability and explosiveness had equal relative weights after carrying out the fuzzy pairwise comparison which considered the degree of confidence of decision maker.

Table 5.10: Fuzzy pairwise comparison of safety sub index for solvent design on oil extraction

	Flammability	Explosiveness	Priority Vector
Flammability	1	(1/3, 1, 3)	0.5
Explosiveness		1	0.5
$\lambda = 1$			

Exposure limit and acute health hazard indices were assumed to be equally important with moderate confidence. The permissible exposure limit for hexane in Malaysia is relatively low, which is only 50ppm TWA is allowed (Department of Occupational Safety and Health, 2001). Since hexane has high volatility, it is easily inhaled by human. There is an increasing risk of nerve damage from inhaling hexane when there is an increase in exposure time and level. Thus, while designing the alternative solvent to replace hexane, it aimed

to reduce the penalty score for exposure limit. Hexane has relatively low acute toxicity towards rat through ingestion where their oral rat LD₅₀ is 28000 mg/kg. However, it is also important to consider acute health hazard of a molecule during the design stage to ensure that the designed molecule has low acute toxicity when being accidentally swallowed. The intensity of importance assigned to each health sub index along with degree of confidence was shown in Table 5.11.

Table 5.11: Fuzzy pairwise comparison of health sub index for solvent design on oil extraction

	Exposure limit	Acute health hazard	Priority Vector
Exposure limit	1	(1/3, 1, 3)	0.5
Acute health hazard		1	0.5

$\lambda = 1$

The following step included the calculation of final weighting factors of each sub property in the overall system. It can be calculated by multiplying weighting factor of sub property with the weighting factor of its main property. The final weighting factors of target properties in the overall system for this case study were reported in Table 5.12.

Table 5.12: Final weighting factors of target properties in the overall system

Target Property	Final weighting factor
T_b	0.1618
R_{carotene}	0.0312
σ	0.0587
μ	0.0587
LC_{50}	0.0154
PCO	0.0556
$\log K_{oc}$	0.0067
BCF	0.0067
I_{FL}	0.2603
I_{EX}	0.2603
I_{EL}	0.0507
I_{AH}	0.0507

5.4.7 Molecular design stage

The following step included the selection of molecular building block based on the molecular structure of the conventionally used solvents in oil extraction process. The chosen molecular groups for this case study included C, CH, CH₂, CH₃, OH, COOH, CHO, CH-O, CH₃CO, CH₃O, CH₂O, NH₂ and CH₂=CH. To ensure the formation of a structurally feasible molecule without having any free bonds, structural constraints expressed Section 4.3.6 were implemented for the design of acyclic and monocyclic compounds respectively.

5.4.8 Optimisation model

The target property models as well as safety and health indices were first transformed into their property operators as shown in Table 5.13. After determining the property operators, property operators are normalised using Equation (5.8) or Equation (5.9) depending on whether the target property was to be minimised or maximised. The overall objective function for this case study can be expressed by Equation (5.25):

$$F^{weighted\ sum} = w_1\lambda_{T_b} + w_2\lambda_{\sigma} + w_3\lambda_{\mu} + w_4\lambda_{R_{carotene}} + w_5\lambda_{LC_{50}} + w_6\lambda_{PCO} + w_7\lambda_{\log K_{oc}} + w_8\lambda_{BCF} + w_9\lambda_{I_{FL}} + w_{10}\lambda_{I_{EX}} + w_{11}\lambda_{I_{EL}} + w_{12}\lambda_{I_{AH}} \quad (5.25)$$

where w_1, w_2, \dots, w_{12} were the weighting factors determined from FAHP approach. The design objective was to maximise the value of $F^{weighted\ sum}$. This optimisation model was a mixed integer non-linear programming (MINLP). Integer cuts were then introduced to produce alternate solutions.

Table 5.13: Property and property operator

Property, p	Property operator, Ω_p
T_b	$\exp(T_b/T_{b0})$
σ	σ
M_w	M_w
μ	$\ln \mu$
δ	$\delta - \delta_0$
F_p	$F_p - F_{p0}$
LC_{50}	$-\log LC_{50}(FM) + FM_0$
LD_{50}	$-\log LD_{50} - A_{LD50} - B_{LD50} M_w$
PCO	$-\log PCO$
BCF	$\log BCF$
$\log K_{oc}$	$\log K_{ow} - K_{ow0}$
PEL	$-\log PEL$
I_{FL}	I_{FL}
I_{EX}	I_{EX}
I_{EL}	I_{EL}
I_{AH}	I_{AH}

5.4.9 Results and discussions

Both acyclic and monocyclic solvents were generated for this case study. The ten acyclic solvents were listed as solvent A1 - A10 whereas the ten monocyclic solvents were displayed as solvent B1 - B10. The molecular structures of the top ten acyclic and monocyclic solvents were displayed in Figure 5.3. The MINLP optimisation model was solved using LINGO 14.0 with global solver by a laptop with Intel® Core™ i7-6500U CPU @ 2.50GHz. Negligible computational time (8 second) was needed for the first generated solution.

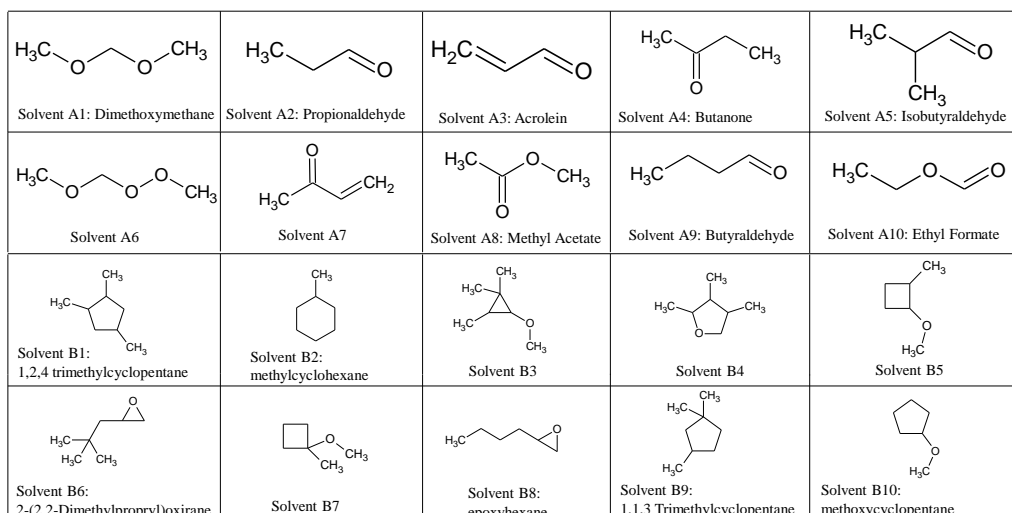


Figure 5.3: Molecular structure of the best ten acyclic and monocyclic solvents

Table 5.14 and Table 5.15 show the properties of the best ten generated acyclic solvents whereas Table 5.16 and Table 5.17 depict the properties of the best ten monocyclic solvents. The generated solutions were selected based on their rankings. Nevertheless, it should be noted that the generated ranking for each molecule was not absolute, since there will generally be uncertainties in values of target properties and prediction models. In this case, the rankings of molecules represented the potential solutions from a huge search space. When a molecule was positioned at a higher ranking, it meant that the molecule had a better potential for a specific application. Thus, in a later stage, the molecule can be selected for further verification through experiments.

From the results, solvents A1 and B1 had the highest $F^{weighted\ sum}$ values which made them ranked the first among all the generated acyclic and monocyclic solvents. Besides, the designed acyclic and monocyclic solvents with their sub-index scores were reported in Table 5.18 and Table 5.19. The properties of the designed molecules were then compared with that of hexane. The properties of hexane were shown in Table 5.20.

Table 5.14: The generated acyclic solvents with their respective properties [with FAHP approach]

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	Solubility (mPA ^{1/2})
A1	0.941	48.49	20.18	0.31	0.31	0.91	2.01	2.01	1.91	76.10	18.11
A2	0.860	42.30	23.23	0.41	2.57	3.17	4.27	4.27	4.17	58.08	20.37
A3	0.810	40.36	24.34	0.34	2.15	2.75	3.85	3.85	3.75	56.06	19.95
A4	0.788	71.34	23.98	0.37	1.45	2.05	3.15	3.15	3.05	72.11	19.25
A5	0.786	61.69	22.86	0.44	1.74	2.34	3.44	3.44	3.34	72.11	19.54
A6	0.752	74.51	21.95	0.46	0.44	1.04	2.14	2.14	2.04	92.09	18.24
A7	0.738	69.62	25.09	0.31	1.02	1.62	2.72	2.72	2.62	70.09	18.82
A8	0.707	77.57	25.10	0.42	2.01	2.61	3.71	3.71	3.61	74.08	19.81
A9	0.681	78.60	23.85	0.51	2.42	3.02	4.12	4.12	4.02	72.11	20.22
A10	0.670	68.95	25.00	0.61	2.70	3.30	4.40	4.40	4.30	74.08	20.50

Table 5.15: The generated acyclic solvent with their respective properties [with FAHP approach] (continued)

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}
A1	-7.00	14.74	1.16	-2.95	711.06	0.45	3.99	-0.28
A2	-6.85	14.74	15.03	-1.21	831.00	1.04	2.54	-0.16
A3	-8.01	16.37	0.57	-0.56	558.31	2.77	2.60	-0.40
A4	1.76	11.34	138.57	-1.73	749.04	0.49	26.66	0.26
A5	-1.74	11.34	13.59	-1.16	899.72	1.04	3.83	0.10
A6	14.40	16.37	0.16	-3.45	682.47	0.66	2.51	-0.88
A7	0.60	12.28	5.28	-1.08	506.77	1.30	27.33	0.02
A8	10.46	16.37	7.27	-2.63	719.56	0.51	8.29	-0.81
A9	4.67	11.34	12.72	-0.92	930.69	0.93	3.16	0.29
A10	14.54	16.37	2.10	-1.71	840.56	1.53	1.60	-0.76

Table 5.16: The generated monocyclic solvent with their respective properties [with FAHP approach]

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	Solubility (mPA ^{1/2})
B1	0.920	53.74	1.99	3.65	0.59	1.19	2.29	2.29	2.19	112.22	18.39
B2	0.895	52.56	3.36	3.87	2.11	2.71	3.81	3.81	3.71	98.19	19.91
B3	0.891	48.21	1.92	5.35	0.04	0.64	1.74	1.74	1.64	114.19	17.84
B4	0.889	43.04	3.14	4.41	0.87	1.47	2.57	2.57	2.47	114.19	18.67
B5	0.882	40.93	3.49	3.83	1.98	2.58	3.68	3.68	3.58	100.16	19.78
B6	0.873	49.05	2.94	6.52	0.44	1.04	2.14	2.14	2.04	114.19	18.24
B7	0.866	47.00	3.29	5.66	1.56	2.16	3.26	3.26	3.16	100.16	19.36
B8	0.864	41.81	4.50	4.67	2.39	2.99	4.09	4.09	3.99	100.16	20.19
B9	0.854	59.51	1.79	5.40	0.16	0.76	1.86	1.86	1.76	112.22	17.96
B10	0.841	59.29	4.48	4.38	2.66	3.26	4.36	4.36	4.26	100.16	20.46

Table 5.17: The generated monocyclic solvent with their respective properties [with FAHP approach] (continued)

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}
B1	-29.53	5.66	7817.70	-0.59	513.82	0.60	10.24	2.90
B2	-28.22	6.40	8094.29	-0.41	533.29	0.53	5.59	2.84
B3	-25.24	6.69	396.35	-2.32	451.98	0.48	3.57	1.95
B4	-19.65	6.69	1290.86	-1.39	459.64	0.98	5.19	1.86
B5	-25.94	7.75	453.82	-1.55	491.75	0.62	2.11	1.58
B6	-17.65	6.69	1167.29	-1.97	439.56	0.68	4.79	2.17
B7	-23.93	7.75	410.37	-2.14	470.26	0.43	1.95	1.89
B8	-18.35	7.75	1336.53	-1.20	478.23	0.87	2.83	1.79
B9	-27.52	5.66	7069.34	-1.18	491.37	0.41	9.46	3.21
B10	-19.52	7.75	424.70	-1.32	508.68	0.55	1.74	1.77

Table 5.18: The generated acyclic solvents with their sub-index scores [with FAHP approach]

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI,w
A1	3	1	3	1	1.998
A2	3	1	2	1	1.917
A3	3	1	4	1	2.080
A4	3	1	1	1	1.835
A5	3	1	2	1	1.917
A6	3	1	4	1	2.080
A7	3	1	3	1	1.998
A8	3	1	3	1	1.998
A9	3	1	2	1	1.917
A10	3	1	3	1	1.998

Table 5.19: The generated monocyclic solvent with their sub-index scores [with FAHP approach]

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI,w
B1	3	1	0	1	1.754
B2	3	1	0	1	1.754
B3	3	1	1	2	1.917
B4	3	1	0	2	1.835
B5	3	1	1	2	1.917
B6	3	1	0	2	1.835
B7	3	1	1	2	1.917
B8	3	1	0	2	1.835
B9	3	1	0	2	1.835
B10	3	1	1	1	1.835

Table 5.20: Properties of hexane

Property	Property value
T _b (°C)	68.7
σ (mN/m)	17.91
μ (cp)	0.297
R _{carotene} (unit)	2.9
R _{TAG} (unit)	2.3
R _{LA} (unit)	1.2
R _{PA} (unit)	1.2
R _{OA} (unit)	1.3
F _p (°C)	-30.9
-log LC ₅₀	4.54
LD ₅₀ (mg/kg)	28000
PCO	0.431
log k _{oc}	3.62
BCF	51.36
PEL (ppm)	50
S (%)	7.013
I _{FL}	3
I _{EX}	1
I _{EL}	2
I _{AH}	0
I _{SHI}	1.835

The results showed that T_b of top three acyclic solvents (solvent A1 to A3) and solvent A5 as well as all the ten monocyclic solvents were lower than that of hexane. Besides, R_{carotene} of all generated solvents were smaller than that of hexane which means that carotenoids can dissolve better in those generated solvents compared to that of hexane. Based on the results, Solvent A1 and solvent B3 had the lowest R_{carotene} values among the generated acyclic and monocyclic solvent. When compared the generated solutions with the existing solution in literature, it was found out that solvent A8 (methyl acetate) has been shown to be a suitable solvent for extracting oil from oilseeds. In addition, all the generated solvents had improved properties in terms of soil sorption as their

$\log k_{oc}$ values were lower than that of hexane. In terms of safety aspects, although all the generated solvents are carrying the same safety sub index (I_{FL} and I_{EX}) scores as that of hexane, their flash point properties especially for acyclic solvents were better than that of hexane. Solvent A6 and solvent A10 were the least flammable compared to the other generated solvents as their F_p values were significantly higher. From the point of view of health aspects, the generated monocyclic solvents exerted a better characteristic in terms of the permissible exposure limit. All the generated monocyclic solvents obtained a better I_{EL} score compared to that of hexane. Besides, by comparing the overall $I_{SHI,w}$ scores, solvent B1 and solvent B2 exhibited better safety and health performance compared to all the generated solvents and hexane.

Table 5.21: The generated acyclic solvents with their respective properties [without FAHP approach]

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	Solubility (mPA ^{1/2})
C1	0.843	48.49	20.18	0.31	0.31	0.91	2.01	2.01	1.91	76.10	18.11
C2	0.727	74.51	21.95	0.46	0.44	1.04	2.14	2.14	2.04	92.09	18.24
C3	0.640	42.30	23.23	0.41	2.57	3.17	4.27	4.27	4.17	58.08	20.37
C4	0.603	77.57	25.10	0.42	2.01	2.61	3.71	3.71	3.61	74.08	19.81
C5	0.594	71.34	23.98	0.37	1.45	2.05	3.15	3.15	3.05	72.11	19.25
C6	0.593	61.69	22.86	0.44	1.74	2.34	3.44	3.44	3.34	72.11	19.54
C7	0.561	40.36	24.34	0.34	2.15	2.75	3.85	3.85	3.75	56.06	19.95
C8	0.524	68.95	25.00	0.61	2.70	3.30	4.40	4.40	4.30	74.08	20.50
C9	0.515	69.62	25.09	0.31	1.02	1.62	2.72	2.72	2.62	70.09	18.82
C10	0.489	78.60	23.85	0.51	2.42	3.02	4.12	4.12	4.02	72.11	20.22

Table 5.22: The generated acyclic solvents with their respective properties [without FAHP approach] (continued)

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}
C1	-7.00	14.74	1.16	-2.95	711.06	0.45	3.99	-0.28
C2	14.40	16.37	0.16	-3.45	682.47	0.66	2.51	-0.88
C3	-6.85	14.74	15.03	-1.21	831.00	1.04	2.54	-0.16
C4	10.46	16.37	7.27	-2.63	719.56	0.51	8.29	-0.81
C5	1.76	11.34	138.57	-1.73	749.04	0.49	26.66	0.26
C6	-1.74	11.34	13.59	-1.16	899.72	1.04	3.83	0.10
C7	-8.01	16.37	0.57	-0.56	558.31	2.77	2.60	-0.40
C8	14.54	16.37	2.10	-1.71	840.56	1.53	1.60	-0.76
C9	0.60	12.28	5.28	-1.08	506.77	1.30	27.33	0.02
C10	4.67	11.34	12.72	-0.92	930.69	0.93	3.16	0.29

Table 5.23: The generated monocyclic solvents with their respective properties [without FAHP approach]

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	Solubility (mPA ^{1/2})
D1	0.717	53.74	1.99	3.65	0.59	1.19	2.29	2.29	2.19	112.22	18.39
D2	0.710	48.21	1.92	5.35	0.04	0.64	1.74	1.74	1.64	114.19	17.84
D3	0.670	49.05	2.94	6.52	0.44	1.04	2.14	2.14	2.04	114.19	18.24
D4	0.669	52.56	3.36	3.87	2.11	2.71	3.81	3.81	3.71	98.19	19.91
D5	0.662	54.90	5.59	11.82	2.43	3.03	4.13	4.13	4.03	98.15	20.23
D6	0.661	43.04	3.14	4.41	0.87	1.47	2.57	2.57	2.47	114.19	18.67
D7	0.661	47.00	3.29	5.66	1.56	2.16	3.26	3.26	3.16	100.16	19.36
D8	0.660	59.29	4.48	4.38	2.66	3.26	4.36	4.36	4.26	100.16	20.46
D9	0.659	43.18	5.56	7.75	2.39	2.99	4.09	4.09	3.99	104.11	20.19
D10	0.652	40.93	3.49	3.83	1.98	2.58	3.68	3.68	3.58	100.16	19.78

Table 5.24: The generated monocyclic solvents with their respective properties [without FAHP approach] (continued)

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}
D1	-29.53	5.66	7817.70	-0.59	513.82	0.60	10.24	2.90
D2	-25.24	6.69	396.35	-2.32	451.98	0.48	3.57	1.95
D3	-17.65	6.69	1167.29	-1.97	439.56	0.68	4.79	2.17
D4	-28.22	6.40	8094.29	-0.41	533.29	0.53	5.59	2.84
D5	-14.39	8.18	243.21	-2.07	531.91	0.80	0.65	1.32
D6	-19.65	6.69	1290.86	-1.39	459.64	0.98	5.19	1.86
D7	-23.93	7.75	410.37	-2.14	470.26	0.43	1.95	1.89
D8	-19.52	7.75	424.70	-1.32	508.68	0.55	1.74	1.77
D9	-5.36	13.40	3.56	-3.83	401.79	0.73	0.31	-0.23
D10	-25.94	7.75	453.82	-1.55	491.75	0.62	2.11	1.58

Table 5.25: The generated acyclic solvents with their sub index score [without FAHP approach]

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI,w
C1	3	1	3	1	2.000
C2	3	1	4	1	2.250
C3	3	1	2	1	1.750
C4	3	1	3	1	2.000
C5	3	1	1	1	1.500
C6	3	1	2	1	1.750
C7	3	1	4	1	2.250
C8	3	1	3	1	2.000
C9	3	1	3	1	2.000
C10	3	1	2	1	1.750

Table 5.26: The generated monocyclic solvents with their sub index score [without FAHP approach]

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI,w
D1	3	1	0	1	1.250
D2	3	1	1	2	1.750
D3	3	1	0	2	1.500
D4	3	1	0	1	1.250
D5	3	1	1	1	1.500
D6	3	1	0	2	1.500
D7	3	1	1	2	1.750
D8	3	1	1	1	1.500
D9	3	1	3	2	2.250
D10	3	1	1	2	1.750

On top of that, the results were compared to the case where FAHP method was not used for assigning the weightage for each property. In such case, each property was assumed to carry the same weighting factor and the results were displayed from Table 5.21 to Table 5.26. From the obtained results, it showed that there was an abrupt change in the ranking of molecules for both acyclic and monocyclic solvents. For acyclic solvents, solvent A6 and solvent A8 which ranked at the 6th and 8th place had become the 2nd and 4th best solution respectively in the case where all the property was assumed to carry the same weighting factor. This was because the weighting factor assigned to T_b in both cases were significantly different. When using the proposed FAHP method, T_b was carrying a weighting factor of 0.1618. On the other hand, when assuming all the properties were having equal weightage, a weighting factor of 0.08333 was assigned to T_b . This was the reason why solvent A6 and A8 which were having significantly higher T_b values were ranked the 2nd and 4th place. For monocyclic solvents, solvent D5 and D9 had dropped out of top ten solvents when proper weighting factor was assigned by using FAHP approach. Thus, it showed that the molecular ranking is sensitive to the weighting factor of each property. The good alternatives may be eliminated due to faulty weighting factors. Hence, it is important to evaluate the relative importance of each property to assign a more precise weighting factor to each property.

5.5 Summary

A systematic multi-objective molecular design framework embedded with FAHP approach had been developed for optimal design of molecules with multiple properties. Through this approach, the highly subjectivity nature arise from complex and uncertain data required to integrate SHE aspects into CAMD framework was managed. This proposed methodology quantified the subjective judgement of decision maker through fuzzy scale and considered their degree of confidence when eliciting the relative importance between each property. Hence, a more precise relative weighting factor which reflects the preference of decision makers can be assigned to each criterion. A case study on the solvent design for extracting residual oil from palm pressed fibre was solved to illustrate the proposed methodology. The results obtained showed the best balance of performance for criteria from different categories such as physicochemical properties as well as SHE aspects. Further work can be conducted to improve the current CAMD framework. The environmental characteristic of a solvent recovery process is found to be heavily dependent on the physicochemical properties of the solvent applied in the process. Thus, the current methodology can be improved by considering the effect of environmental impact of solvent recovery process on solvent design. The revised approach which integrated the quantification of environmental impact of solvent recovery process into CAMD framework will be discussed in the next chapter.

CHAPTER 6

OPTIMAL MOLECULAR DESIGN TOWARDS AN ENVIRONMENTAL FRIENDLY SOLVENT RECOVERY PROCESS

6.1 Introduction

This chapter presents the third research scope, which aimed at developing a novel CAMD methodology for the design of solvents by considering environmental impact during the extraction and recovery processes. Throughout the years, CAMD techniques have been widely applied to design novel molecules for various applications, especially solvents. Most of the works in this area only focused on designing solvents that can achieve their functionality. There is no work reported on considering safety, health and environmental impacts of the recovery process in which the solvent was applied. In this work, a quantitative assessment of the total environmental burden for solvent recovery process was incorporated into a single stage CAMD framework. The CAMD formulation included molecular properties that affect the quantitative assessment of the environmental impact of a process. A multi-objective solvent design framework was then developed using FAHP weighting approach to design solvents that satisfied various target properties. With this approach, the designed solvent can simultaneously improve the overall environmental characteristic of a process and give a better balance of performance for a set of predefined properties. To illustrate the proposed methodology, a case study on solvent design for residual oil extraction from palm pressed fibre was presented.

6.2 Problem Statement

Most of the solvents applied in the chemical industry are organic substances which can be harmful to both human and environment. In previous chapters, methodologies had been developed to design solvents with desirable product functionalities and SHE characteristics. These methodologies only considered SHE properties based on molecular structures of the solvents. However, in terms of process aspect, these designed solvents may still cause environmental issues during the operation. This was mainly because energy consumption of a process is one of the factors leading to adverse environmental impacts (Young et al., 2000). Solvent recovery usually accounts for more than 40% of energy needed in a process. The energy consumption of solvent recovery process usually varies with type of solvent used. Hence it means that there is interrelationship between physicochemical properties of solvent and the difficulty level of its recovery process. Solvent recovery process with greater level of difficulty often associated with negative SHE issues due to excessive energy consumption. To date, no work is found on employing CAMD techniques to generate solvents with targeted properties that can simultaneously enhance the environmental characteristics of their recovery processes. Thus, the previously developed CAMD framework must be extended to account for the effect of environmental impact of solvent recovery process on solvent design. The methodology must be able to quantify the environmental impact of the solvent recovery process at the instant the solvent is generated.

6.3 Methodology

The methodology developed in this chapter served as an extension for the work done in Chapter 5. This work aimed to establish a novel CAMD methodology for the systematic design of a molecule that achieves its predefined properties and reduces the environmental impact of its recovery process. The main contribution of this work was the incorporation of quantitative evaluation of environmental impact of a solvent recovery process into a single stage multi-objective CAMD framework. Through this framework, a safe, healthy and environmental friendly molecule that simultaneously possessed good functionalities and improved the overall environmental characteristic of the solvent recovery process was designed. The proposed framework was summarised in the following steps:

6.3.1 Identification of design objective

The first step involved the specification of design objective for CAMD problem. This chapter considered properties from both molecular and process perspective. In terms of molecular properties, physicochemical properties and SHE criteria were included to design a molecule that fulfilled favourable functionality and met SHE targets. Safety and health characteristic of molecules were characterized by suitable indices reported in Section 5.3.3. The assumption made is that when the designed molecule possesses low safety and health indices scores, the process in which the molecule is applied will be safe and does not bring any health hazards to workers. In addition, from a process perspective, it is important to ensure that the molecules used can reduce the negative impact on the environment. The quantification of the environmental impact of a solvent

recovery process can be done by following the steps stated in Section 6.3.2. To ascertain that the designed molecules achieve both molecular and process performance, the desired target properties were chosen as design objectives.

6.3.2 Quantification of the environmental performance of a process

As mentioned earlier, there are interrelations between various environmental impacts and the use of solvents in an industry. The energy requirement of a solvent recovery process is heavily dependent on the physicochemical characteristics of the solvent. This is because different solvents require different amount of energy during solvent recovery process. The higher the energy consumption, the more the negative impact on the environment. For example, if a solvent needs a higher amount of energy to be recovered, more steam is required to vaporise the solvent, which will then lead to a greater emission of greenhouse gases. Hence, it is important to integrate the quantification of the environmental performance of solvent recovery process into CAMD formulation to identify optimal solvent that that will require lesser amount of energy in order to reduce the environmental impact.

The environmental impact of a solvent recovery process can be quantified by using the subsequent steps. First, critical parameters needed for the calculation of energy balance were identified for a specific process. For example, the energy balance of a process can be calculated using specific heat capacity and/ or latent heat of vaporisation of chemical product or substance if there were an occurrence of phase change. Next, it is important to identify potential energy sources, such as electricity, steam or natural gas, based on unit operations of the process. This is because the energy needed for a process can be converted into

greenhouse gaseous emissions such as carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), nitrogen oxide (NO_x), sulphur oxide (SO_x), nitrous oxide (N₂O) and volatile organic compound (VOC) by using the conversion factors stated in Table 6.1. A full list of conversion factors for energy consumption into greenhouse gases emissions was extracted from LCA Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model 2016 database. GREET model is a full life cycle model developed by Argonne National Laboratory, which enables researchers to evaluate different fuel and vehicle combinations on a full fuel-cycle or vehicle cycle basis. There are more than 100 fuel routes including natural gas fuels, biofuels, petroleum fuels and electricity produced from different energy feedstock sources. According to Argonne National Laboratory (Cai et al., (2013) and Clark et al., (2011)), the emission factors are usually expressed in grams of GHG per a functional unit such as energy (MJ), mass (tonne) or electricity (kWh) to allow comparison on the same platform. For example, GHG such as CO₂ can be quantified in terms of grams of CO₂ emitted per 1kWh of electricity.

Table 6.1: Conversion factors for converting energy consumption into greenhouse gases (GHG) emissions

GHG (g)	Natural Gas (1 tonne)	Steam (1 MJ)	Electricity (1 kWh)
CO	540	0.0677	0.0696
CO ₂	219,570	78.360	120
CH ₄	4620	0.3400	0.46
NO _x	750	0.0965	0.0870
SO _x	510	0.0142	0.0216
N ₂ O	1.54	0.0021	0.0017
VOC	290	0.0153	0.0164
References	(Clark et al., 2011)	(Clark et al., 2011)	(Cai et al., 2013)

Next, IChemE Sustainability Metrics were applied to assess the total environmental performance of the process. IChemE Sustainability Metrics were developed by the Institution of Chemical Engineers (IChemE) to measure the sustainability within the process industries. In order to give a best-balanced measure of sustainability performance, there are three key indicators in IChemE Sustainability Metrics such as environmental, economic and social indicators. Since this work focused on measuring the environmental impact of the process, only environmental indicators will be considered. The total environmental performance of the process can be evaluated by calculating environmental burden (EB) for various environmental impacts such as global warming, acidification potential, photochemical smog potential, eutrophication potential and etc. The EB for each environmental impact was given by comparing the impact of a specific pollutant with that of a standard substance, which was dictated in Table 6.2. For instance, in the case of photochemical smog formation, EB is usually stated as kg of ethylene/h and denotes the impact of emission of 1kg/h of a certain pollutant is equivalent to that of the emission of x kg/h of ethylene.

Table 6.2: EB equivalent for various types of pollution (IChemE, 2002)

Impacts	Pollution	EB equivalent
Atmospheric	Atmospheric acidification (AA)	Sulphur dioxide
	Global warming potential (GWP)	CO ₂
	Human health (carcinogenic) effects	Benzene
	Stratospheric ozone depletion	CFC-11
	Photochemical ozone (smog) formation potential (PCOP)	Ethylene
Aquatic	Aquatic acidification	Released H ⁺ ions
	Aquatic oxygen demand	Oxygen
	Ecotoxicity to aquatic life	Copper (for metals) Formaldehyde (for others)
	Eutrophication (EU)	Phosphate

EB of a process was then calculated by the summation of mass flow rates of the pollutants with their respectively potency factors. This rule was expressed mathematically in Equation (6.1):

$$EB = \sum M_u \times PR_{b,u} \quad \forall b \in B \quad \forall u \in U \quad (6.1)$$

where EB is the total environmental burden; M_u is the mass of pollutant u emitted; $PR_{b,u}$ denotes the potency factor of pollutant u for the environmental impact, b . The full list of potency factor of specific pollutant u can be extracted from IChemE sustainability metrics (IChemE, 2002). Table 6.3 shows the potency factor of each pollutant considered in this work.

Table 6.3: Potency factor of each pollutant (IChemE, 2002)

Pollutant u	GWP	PCOP	EU	AA
CO ₂	1	-	-	-
VOC	11	-	-	-
CO	3	0.027	-	-
NO _x	40	0.028	0.13	0.7
SO _x	0	-	-	-
CH ₄	21	-	-	-
N ₂ O	310	-	-	-

6.3.3 Selection of safety and health indices

The safety characteristic of a molecule can be evaluated via two safety parameters, flammability index (I_{FL}) and explosiveness index (I_{EX}). I_{FL} can be evaluated based on flash point (F_p) and boiling point (T_b) whereas the lower explosion limit (LEL) and upper explosion limit (UEL) were used to assess I_{EX} . The penalty scores for these two safety indices had been reported in Section 5.3.3 (Table 5.1 and Table 5.2).

Meanwhile, acute health hazards (I_{AH}) and exposure limit index (I_{EL}) were the chosen indices used to evaluate health performance of the molecules. Both I_{AH} and I_{EL} can be assessed by oral rat LD₅₀ toxicity and permissible exposure limit (PEL) respectively. The penalty score for both health indices were reported in Section 5.3.3 (Table 5.3 and Table 5.4). Equation (6.2) was used to calculate the total weighted penalty score ($I_{SHI,w}$) for both safety and health aspects of molecules, which is the sum of all sub-index values allocated to it. FAHP approach was then applied to identify weighting factor for each sub index.

In usual practice, the safety performance of a process was usually indicated by the operating temperature and pressure of the unit operation. However, in this case, the operating temperature of a unit operation is dependent on the physical properties of solvent such as T_b . If both operating temperature of unit operation and T_b of solvent were considered, there will be overlapping of design objectives. On the other hand, fugitive emissions should be considered when assessing the health performance of a process as they are the primary sources of origin of continuous exposure to the workers (Hassim et al., 2010). Depending on which type of chemical substance the workers are exposed to, the continuous exposure may chronically influence their health in different ways. Nevertheless, the estimation of fugitive emissions is beyond the scope of study. This is because this work is at early design stage where only mass and energy balance can be performed. The technique of using mass balance to estimate fugitive emissions is not accurate since only a very little amount of mass losses were involved (Hassim et al., 2010). Hence, the assumption made in this work is that by having a safe and healthy molecule (which is quantified by low $I_{SHI,w}$)

in a process, the process will have lower safety and health hazards compared to process with hazardous molecules.

$$I_{SHI,w} = w_{FL}I_{FL} + w_{EX}I_{EX} + w_{EL}I_{EL} + w_{AH}I_{AH} \quad (6.2)$$

where w_{FL} represents weighting factor for sub-index I_{FL} ; w_{EX} represents weighting factor for sub-index I_{EX} ; w_{EL} represents weighting factor for sub-index I_{EL} ; w_{AH} represents weighting factor for sub-index I_{AH} .

6.3.4 Identification of property prediction model

The next step includes identification of property prediction model for the estimation of all target properties stated in Sections 6.3.1, 6.3.2 and 6.3.3. The target properties in Section 6.3.1 were dependent on the nature of design problem. The target properties that were involved in environmental impact quantification as well as safety and health indices were stated in Sections 6.3.2 and Section 6.3.3 respectively. Most of the targeted properties can be estimated by using GCM equation.

The step was then followed by determining the upper and lower limits of property constraints. This step is important to ensure that the physical characteristics of the designed molecules will be similar to that of the conventional solvent. Product specification, which is usually defined by customers' requirement or process need, was used to determine the target property ranges.

6.3.5 Application of disjunctive programming on index scoring

Disjunctive programming is a modelling algorithm that employs discontinuous functions to define the abrupt changes over a specified decision variable (El-Halwagi, 2011). As mentioned in Section 6.3.3, the index score assigned to a molecule relied on the property value. Thus, disjunctive programming can be used to decipher the molecular properties into index scores, indicating the degree of hazard of the molecules (Ten et al., 2016b). The concept of transforming discontinuous functions into mixed-integer formulation using a binary integer variable (I) had been discussed in detailed in Section 5.3.4.

6.3.6 Computation of weighting factor of each objective function

As described in Sections 6.3.1, 6.3.2 and 6.3.3, there were multiple target properties to be optimised simultaneously in CAMD problem to design molecules that achieved both molecular and process performance. The weighting factor for each objective function can be determined systematically through FAHP approach. The detailed steps in employing FAHP approach to determine weighting factors were presented in Section 5.3.5 – 5.3.6.

6.3.7 Molecular design stage

The step was then followed by choosing potential first order molecular building blocks based on the nature of design problem. Structural constraints expressed in Section 4.3.6 were imposed to eliminate infeasible structural solution.

6.3.8 Optimisation model

When there are more than two design objectives, CAMD problem has to be formulated as a multi-objective optimisation problem. Similarly, in this work, multi-objective optimisation model was solved by applying weighted sum method. Via this method, multiple objectives were converted into an aggregated scalar objective function. This was done by first assign each objective function with a weighting factor pre-determined from FAHP approach, and then totalled up all the contributors to attain the overall objective function. Since previous sections had mentioned that all the target properties and/or sub-indices come from different categories such as physicochemical, safety, health and environmental aspects, it was unavoidable that properties were denoted by various measurement units and scales. Therefore, to bring them to the same magnitude, normalisation step was performed using either Equation (6.3) or Equation (6.4).

Equation (6.3) and Equation (6.4) were employed to normalise target property or sub-indices that needs to be maximised and minimised respectively. The normalised target property or sub-indices which was then termed as normalised target property operator, λ_{pm} , had value fall between 0 and 1.

$$\lambda_{pm} = \frac{\Omega_p - \Omega_{p\min}}{\Omega_{p\max} - \Omega_{p\min}} \quad (6.3)$$

$$\lambda_{pm} = \frac{\Omega_{p\max} - \Omega_p}{\Omega_{p\max} - \Omega_{p\min}} \quad (6.4)$$

where $\Omega_{p\min}$ and $\Omega_{p\max}$ are the lowest and highest values of target property operator which were determined by performing single-objective optimisation.

The overall objective function as shown in Equation (6.5):

$$F^{weighted\ sum} = w_1\lambda_{p1} + w_2\lambda_{p2} + \dots + w_m\lambda_{pm} \quad (6.5)$$

where $F^{weighted\ sum}$ is the overall objective function and w_m is the weighting factor for each normalised target property operator λ_{pm} . In this work, the design objective of this work was to maximize $F^{weighted\ sum}$. By performing integer cut procedure, a ranked list of optimal and near-optimal molecules can be attained. The solution with the highest $F^{weighted\ sum}$ value will be the optimal molecule. The developed methodology was presented in Figure 6.1.

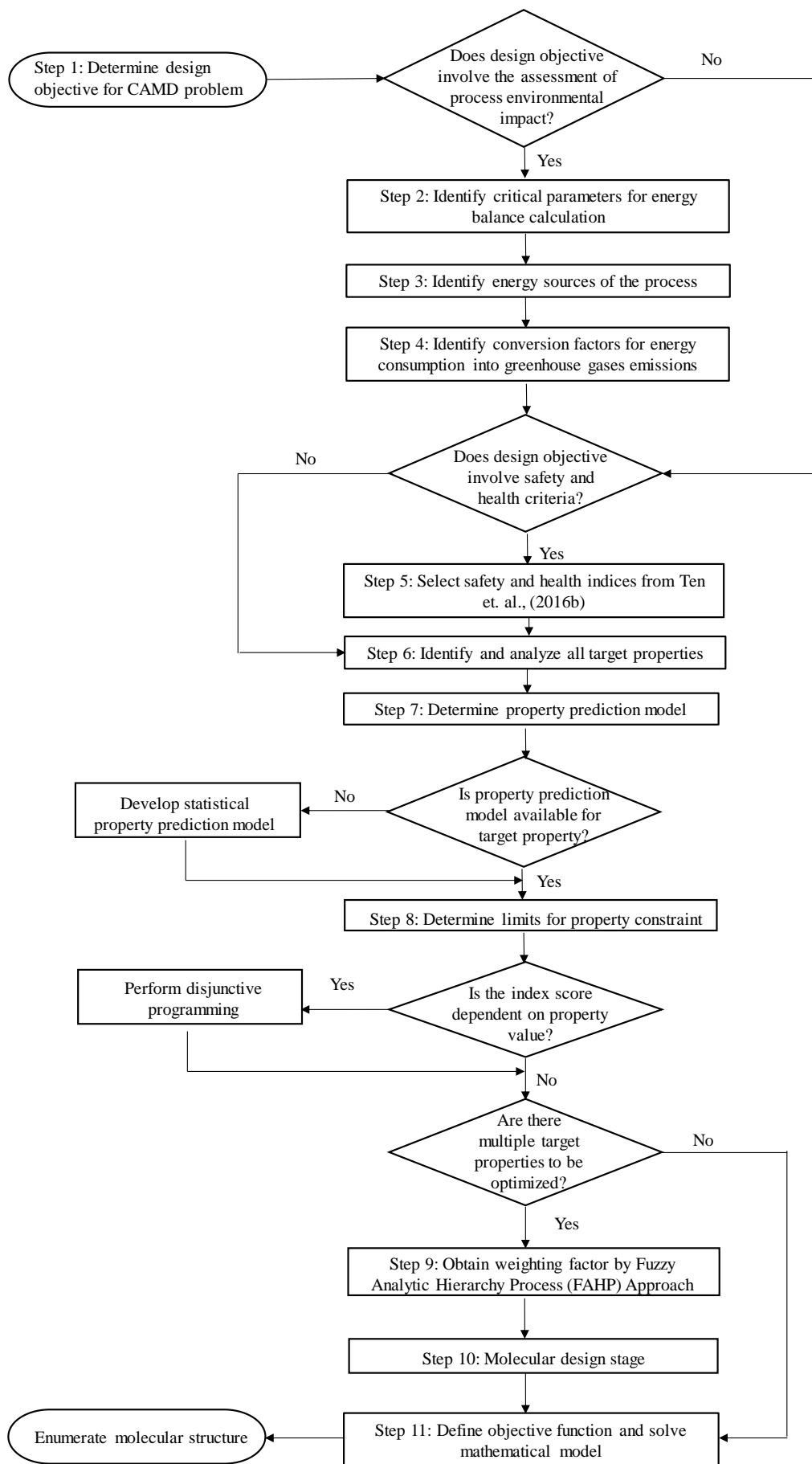


Figure 6.1: Methodology for research scope 3

6.4 Case study

6.4.1 Problem statement

The same case study presented in Section 4.4.1 was applied to illustrate the developed methodology. Palm pressed fibre (PPF) is the remaining by-product produced after extracting crude palm oil (CPO) from fresh fruit bunches (FFB). Nonetheless, Choo et al. (1996) revealed that the 5-7% of residual oil retained in the PPF is enriched with 4000 – 6000 ppm of carotenoids, 4500 – 8500 ppm of sterols and 2400 – 3500 ppm of vitamin E. Solvent extraction technique is one of the most established methods for extracting oil due to economic reasons (Kumar et al., 2017). Figure 6.2 showed the conventional process flow diagram of extracting residual oil from PPF using solvent extraction method. According to the current industrial practice, the flow of solvent into extractor (E1) is counterflow to the flow of PPF. The extraction takes place when the oil diffuses into the solvent. The solvent-saturated PPF (referred as meal) is then transferred to desolventiser toaster (E2) to further recover the solvent. On the other hand, the oil-rich solvent (which is known as miscella) then undergoes multistage evaporation (E3) by heat to separate oil from the solvent. The solvent vapours from both desolventising toaster and evaporators are then condensed using condenser (E4) before recycling back to the extractor. Hexane is always the top choice among all solvents for its high oil solubility and low cost (de Oliveira et al., 2013). However, hexane suffers from major drawbacks, which had been previously discussed in Section 4.4.1 and Section 5.4.1. Hence, this work employed multi-objective CAMD method to design solvents with improved physical characteristics that can reduce the adverse SHE impacts of their recovery processes.

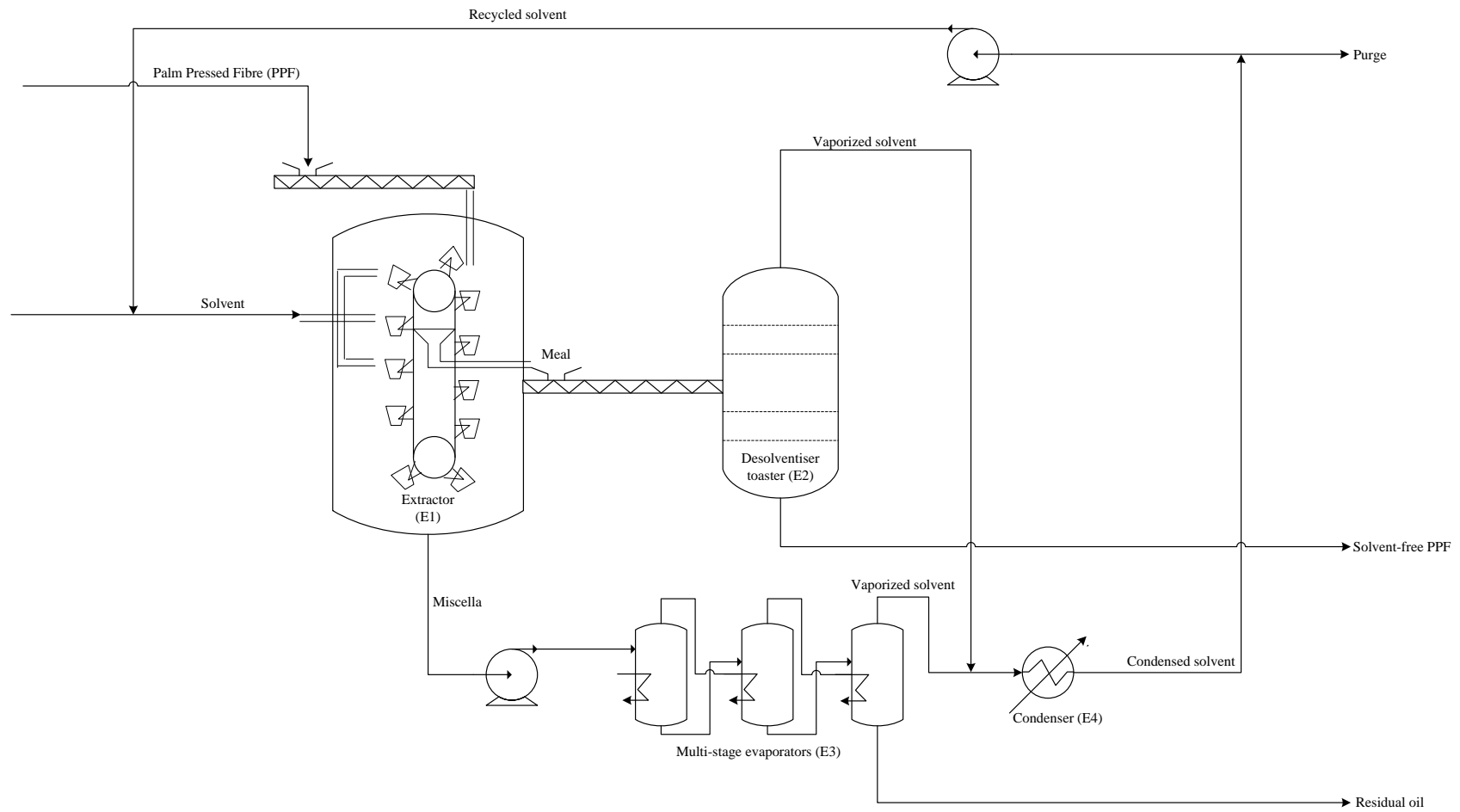


Figure 6.2: Process flow sheet of residual oil extraction from PPF using solvent extraction method

6.4.2 Determination of design objective

The main objective of this case study was to design alternate solvents to replace hexane for the process of extracting residual oil from PPF. The designed solvents must have desirable characteristics from both molecular and process aspects. For example, a solvent used in a process must achieve certain functionality in order to be used for an application. The solvent should also exert low potential in causing SHE issue if it were unintentionally leaked to the surrounding. Besides, the designed solvent should have features that can reduce the total environmental burden of a process when it is applied in an operation. The favourable qualitative attributes of the designed solvents were then translated into their respective measurable properties reported in Table 6.4.

Table 6.4: Translation of favourable qualitative attributes of designed solvent into their respective measurable properties

Categories		Favourable qualitative attributes	Measurable properties
Process	Environmental	Minimise environmental impact of the process	Low EB for the process
Molecular	Physical	Minimise the degradation rates of carotene	Low boiling point (T_b)
		Higher rates of oil extraction by having good percolation and surface wetting (Bockisch, 1998)	Low viscosity (μ) and surface tension (σ)
		Both carotene and triglycerides (TAGs) should be highly soluble in designed solvents	Small difference of Hildebrand solubility parameter (δ) between solvent and carotene (R_{carotene})
	Safety	Low flammability index I_{FL}	High flash point (F_p)
		Low explosiveness index I_{EX}	Small difference between lower explosion limit (LEL) and upper explosion limit (UEL)

Health	Low exposure limit index I_{EL}	High permissible exposure limit (PEL)
	Low acute health hazard index I_{AH}	High oral rat LD_{50}
Environmental	Low aquatic toxicity	High fathead minnow LC_{50}
	Reduce photochemical smog	Low photochemical oxidation potential (PCO)
	Minimise accumulation of solvent in one place	Low soil sorption coefficient ($\log K_{oc}$)
	Reduce the accumulation of solvent in aquatic organism	Low bioconcentration factor (BCF)

6.4.3 Quantification of the environmental performance of a process

Next, the environmental impact of residual oil extraction process from PPF using the designed solvent can be quantified using the steps mentioned in Section 6.3.2. First, critical parameters required for energy balance calculation were identified based on the information obtained from oil extraction process using hexane. The C_p of residual oil has the value of 1.902 kJ/kg K; PPF contains 10 % moisture and 5 % residual oil respectively; miscella has 25 weight % of oil in it and the final product contains 98 weight % of oil. The following steps integrated the energy balance of multistage evaporator into the CAMD formulation as it mainly affected the energy requirement of the process. Lastly, the operating temperature of multistage evaporator, T_{evp} was estimated based on the T_b of the solvent to ensure complete evaporation of the solvent.

The section below showed how environmental impact of the process (which mainly focusing on the evaporator) can be quantified and integrated into CAMD problem:

The energy balance around the evaporator can be calculated using Equation (6.6):

$$\Delta H^{feed, evap} + q_{H, evap} = \Delta H^{top, evap} + \Delta H^{bottom, evap} \quad (6.6)$$

where $\Delta H^{feed, evap}$ is enthalpy change for feed for the evaporator; $\Delta H^{top, evap}$ denotes enthalpy change for top product which is mainly solvent vapour; $\Delta H^{bottom, evap}$ depicts enthalpy change for bottom product which is the residual oil and $q_{H, evap}$ is the heat transferred from steam to the evaporator.

By having the temperature of feed as reference temperature, Equation (6.6) was further reduced to Equation (6.7), which can also be shown in the form as Equation (6.8).

$$q_{H, evap} = \Delta H^{top, evap} + \Delta H^{bottom, evap} \quad (6.7)$$

$$M_{steam} \lambda_{steam} = M_s C_{ps} (T_{evp} - T_{feed}) + M_{vs} H_v + M_{oil} C_{poil} (T_{evp} - T_{feed}) \quad (6.8)$$

where M_{steam} is the mass of steam needed (kg); λ_{steam} is the latent heat of steam (kJ/kg); M_s is the total mass of designed solvent fed (kg); M_{vs} is the mass of vaporised solvent (kg), C_{ps} is the average heat capacity of designed solvent (kJ/kg °C); T_{evp} is temperature of the evaporator (°C); T_{feed} is temperature of the feed (°C); H_v is the heat of vaporisation of the designed solvent (kJ/kg); M_{oil} is the mass of residual oil (kg); C_{poil} is the specific heat capacity of residual oil.

Thus, by using Equation (6.1) and Equation (6.8) together with the previous information from Table 6.1 and Table 6.3 shown in Section 6.3.2, the quantification of environmental impact of a solvent recovery process can be integrated into CAMD problem.

6.4.4 Identification of property prediction model

Once all the target properties were specified for the design problem, their respective property prediction models and/or empirical correlations must be identified. T_b , σ , μ , δ , F_p , PEL , M_w , LC_{50} , LD_{50} , PCO , $\log K_{oc}$, BCF , UEL and LEL were estimated through empirical correlations and/or GCM equations reported in Section 4.4.3 (Table 4.3) and Section 5.4.3. Additional properties such as heat of vaporisation (H_v) and heat capacity (C_p) were estimated through the equations depicted below. H_v was calculated using Equation (6.9) (Hukkerikar et al., 2012b):

$$H_v - H_{v0} = \sum_i N_i H_{vli} \quad (6.9)$$

where H_{vli} represents the heat of vaporization contribution of the first-order group of type- i that occurs N_i times while H_{v0} stands for the universal constant given by the value of 9.6127 kJ/mol. On the other hand, C_p can be estimated using Equation (6.10) to Equation (6.12) (Kolská et al., 2008):

$$C_p - C_{p0i} = \sum_i N_i C_{pli} \quad (6.10)$$

$$C_{p0i} = \sum_i a_{0i} + b_{0i} \left(\frac{T}{100} \right) + d_{0i} \left(\frac{T}{100} \right)^2 \quad (6.11)$$

$$C_{pli} = \sum_i a_{li} + b_{li} \left(\frac{T}{100} \right) + d_{li} \left(\frac{T}{100} \right)^2 \quad (6.12)$$

where C_{pli} is the heat capacity contribution of the first-order group of type- i that occurs N_i times whereas C_{p0i} is an additional adjustable parameter. a_{0i} , a_{li} , b_{0i} , b_{li} , d_{0i} and d_{li} are adjustable parameters for the temperature dependence of C_{p0i} and C_{pli} respectively. Next, upper and lower limits of property constraints

for solvent design were determined. The same property constraints ranges shown in Section 4.4.3 (Table 4.4) were applied.

6.4.5 Application of disjunctive programming on index scoring

The illustration for the application of disjunctive programming on the index scoring was performed using exposure limit index (I_{EL}). Consider the following criteria:

$$I_{EL} = \begin{cases} 1 & PEL \leq 1000 \\ 2 & PEL \leq 100 \\ 3 & PEL \leq 10 \\ 4 & PEL \leq 1 \end{cases} \quad (6.13)$$

I_{EL} may have the score of one, two, three or four relying on the PEL value of designed molecule. These functions were modelled using binary integer variables. By using four integer variables (I_{EL1} , I_{EL2} , I_{EL3} and I_{EL4}), I_{EL} functions can be transformed to the following mixed-integer formulation:

$$I_{EL} = I_{EL1} + I_{EL2} + I_{EL3} + I_{EL4} \quad (6.14)$$

Subjected to the following conditions:

$$I_{EL1} = \begin{cases} 0 & PEL > 1000 \\ 1 & PEL \leq 1000 \end{cases} \quad (6.15)$$

$$I_{EL2} = \begin{cases} 0 & PEL > 100 \\ 1 & PEL \leq 100 \end{cases} \quad (6.16)$$

$$I_{EL3} = \begin{cases} 0 & PEL > 10 \\ 1 & PEL \leq 10 \end{cases} \quad (6.17)$$

$$I_{EL4} = \begin{cases} 0 & PEL > 1 \\ 1 & PEL \leq 1 \end{cases} \quad (6.18)$$

In order to model conditions stated in Equation (6.15), (6.16), (6.17) and (6.18) which allocate the values of I_{EL1} , I_{EL2} , I_{EL3} and I_{EL4} to be either 0 or 1 based on PEL value of molecule, the following constraints are considered:

$$(0.01-1000) \times I_{EL1} < PEL - 1000 \leq (10000-1000) \times (1-I_{EL1}) \quad I_{EL1} \in \{0,1\} \quad (6.19)$$

$$(0.01-100) \times I_{EL2} < PEL - 100 \leq (10000-100) \times (1-I_{EL2}) \quad I_{EL2} \in \{0,1\} \quad (6.20)$$

$$(0.01-10) \times I_{EL3} < PEL - 10 \leq (10000-10) \times (1-I_{EL3}) \quad I_{EL3} \in \{0,1\} \quad (6.21)$$

$$(0.01-1) \times I_{EL4} < PEL - 1 \leq (10000-1) \times (1-I_{EL4}) \quad I_{EL4} \in \{0,1\} \quad (6.22)$$

6.4.6 Construction of hierarchical decision model

A four-level hierarchical decision model was developed for this case study and depicted in Figure 6.3. Besides having desirable SHE properties and achieve their functionalities, the designed solvents should simultaneously improve environmental characteristics of the process. As shown in Figure 6.3, molecular and process aspects were the two main criteria to achieve the design objective. From molecular aspects, there were four important sub-properties known as physical, safety, health and environmental properties whereas environmental performance was the main sub-property under process aspect. Each of these properties were further divided into quantitative sub-properties which had been stated in Section 6.4.2 (Table 6.4).

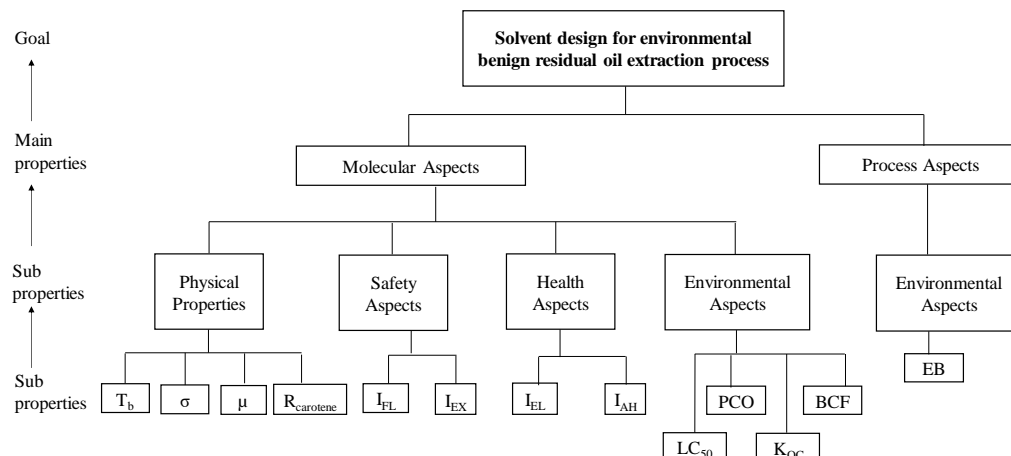


Figure 6.3: Hierarchical decision structure for this case study

6.4.7 Computation of weighting factor of each objective function

This section depicted the process in evaluating the relative importance of each property or criterion based on supporting theory or literature. The pairwise comparative judgements among the properties were elicited using FAHP approach presented in Chapter 5.

In this case study, both molecular and process aspects were assumed to be more or less equally important with a moderate level of confidence. This was to ensure that the designed solvent achieved its expected functionalities as well as being environmental friendly and harmless to surrounding community. In addition, it aimed in improving the overall environmental characteristic of the process when the designed solvent being used for operation. This was because the resulting environmental impact from the process was also an important aspect to evaluate the process. Table 6.5 showed the fuzzy pairwise comparison matrix of main properties with respect to the main goal. It reflected the relative importance of molecular aspects over process aspects together with the lower and upper bound of the comparison, which was dictated based on the degree of

confidence. Note that the judgement was perfectly consistent in this pairwise comparison matrix as the λ value is equal to one.

Table 6.5: Fuzzy pairwise comparison matrix of main properties for solvent design in residual oil extraction process

	Molecular Aspects	Process Aspects	Priority Vector
Molecular Aspects	1	(1/3, 1, 3)	0.5
Process Aspects		1	0.5
$\lambda = 1$			

The comparative judgements for all the molecular sub-properties had been elicited in the Chapter 5 under Section 5.4.6. The final weighting factors of each target property in the overall molecular design problem for this case study were obtained by the multiplication between the weighting factors of sub-properties and their respective main properties, as shown in Table 6.6.

Table 6.6: Final weighting factors of target properties in the overall molecular design problem

Target Property	Final weighting factor
EB	0.5
T_b	0.0809
R_{carotene}	0.0156
σ	0.0294
μ	0.0294
LC_{50}	0.0077
PCO	0.0278
$\log K_{oc}$	0.0034
BCF	0.0034
I_{FL}	0.1302
I_{EX}	0.1302
I_{EL}	0.0211
I_{AH}	0.0211

6.4.8 Molecular design stage

At this stage, first-order molecular building blocks were selected based on molecular structure of the traditionally used solvents in oil extraction process. There were fourteen molecular groups chosen for this case study which included C, CH, CH₂, CH₃, OH, COOH, CHO, CH-O, CH₃CO, CH₃O, CH₂O, CH₃COO, NH₂ and CH₂=CH. Structural constraints mentioned in Section 4.3.6 were imposed in this model to ensure the synthesis of feasible molecule.

6.4.9 Optimisation model

The step was then followed by transforming all targeted properties into their respective target property operators (Ω_p) as presented in Table 6.7. This step was important in reducing non-linearity equations in the optimisation model. Ω_p was usually signified by the linear summation of number of appearance for a molecular group of type-*i* and its respective contribution. After that, normalisation of Ω_p was performed using either Equation (6.3) or Equation (6.4) depending on whether minimisation or maximisation of a target property was desired.

Equation (6.23) reported the overall objective function for this case study:

$$F^{weighted\ sum} = w_1\lambda_{T_b} + w_2\lambda_{\sigma} + w_3\lambda_{\mu} + w_4\lambda_{R_{carotene}} + w_5\lambda_{LC_{50}} + w_6\lambda_{PCO} + w_7\lambda_{\log K_{oc}} + w_8\lambda_{BCF} + w_9\lambda_{I_{FL}} + w_{10}\lambda_{I_{EX}} + w_{11}\lambda_{I_{EL}} + w_{12}\lambda_{I_{AH}} + w_{13}\lambda_{EB} \quad (6.23)$$

where w_1, w_2, \dots, w_{13} are the weighting factors obtained from FAHP approach.

The design objective of this model was to maximise $F^{weighted\ sum}$ subjected to the determined structural and property constraints. The optimisation model was a

MINLP model. The integer cuts procedure was then applied to produce alternate molecular structures.

Table 6.7: Property and property operator

Property, p	Property operator, Ω_p
T_b	$\exp(T_b/T_{b0})$
σ	σ
M_w	M_w
μ	$\ln \mu$
δ	$\delta - \delta_0$
C_p	C_p
H_v	H_v
F_p	$F_p - F_{p0}$
LC_{50}	$-\log LC_{50}(FM) + FM_0$
LD_{50}	$-\log LD_{50} - A_{LD50} - B_{LD50} M_w$
PCO	$-\log PCO$
BCF	$\log BCF$
$\log K_{oc}$	$\log K_{ow} - K_{ow0}$
PEL	$-\log PEL$
I_{FL}	I_{FL}
I_{EX}	I_{EX}
I_{EL}	I_{EL}
I_{AH}	I_{AH}
EB	$GWP + PCOP + EU + AA$

6.4.10 Results and discussions

In this work, both acyclic and monocyclic solvents had been generated using the proposed optimisation model. The best ten acyclic solvents were represented by solvents A1 – A10 whereas the top ten monocyclic solvents were listed as solvents M1 – M10. Figure 6.4 depicts the molecular structures of the generated acyclic and monocyclic solvents. The MINLP optimisation model was solved using LINGO 14.0 with global solver by a laptop with Intel® Core™

i7-6500U CPU @ 2.50GHz. Negligible computational time (17 second) was needed for the first generated solution.

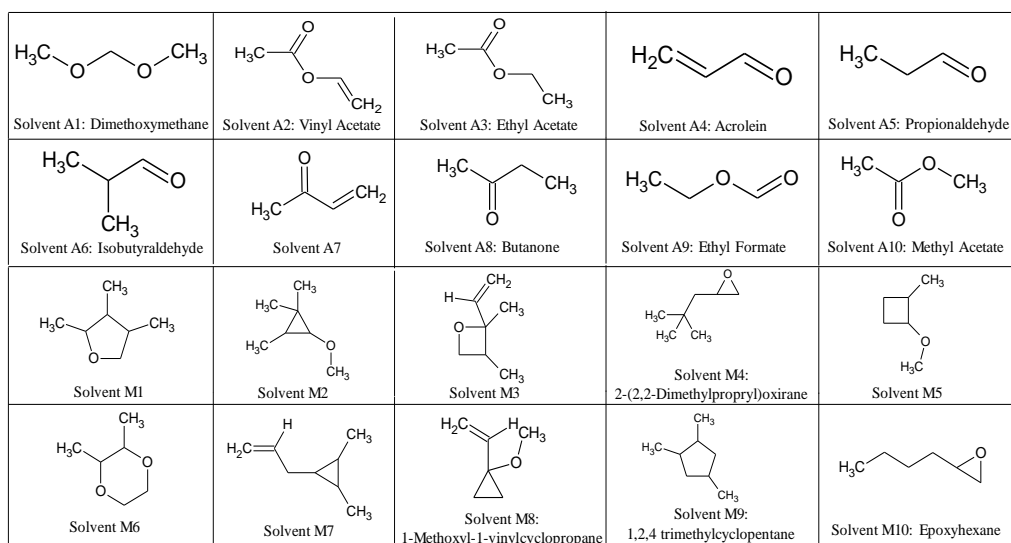


Figure 6.4: Generated acyclic and monocyclic solvents with their respective molecular structures

The properties of the top ten generated acyclic solvents were reported in Table 6.8 and Table 6.9 whereas the properties of the best ten monocyclic solvent were shown in Table 6.10 and Table 6.11. Besides, the designed acyclic and monocyclic solvents with their respective safety and health indices scores were depicted in Table 6.12 and Table 6.13 respectively. In this case, $F^{weighted\ sum}$ was used to represent the ranking of each molecule. The higher the value of $F^{weighted\ sum}$, the higher the ranking of the molecule. The ranking of each molecule solely represented the potentiality of a molecule to be useful for a specific application. The designed molecules were chosen based on their rankings; the higher the ranking, the better the potential a molecule had for a respective application. However, this generated ranking was not absolute due to the uncertainties in prediction model, and hence the value of target properties. Therefore, the potential molecules will be selected for further verification through experiments in a later stage.

Table 6.8: The generated acyclic solvents with their respective properties

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	C _p (kJ/ kg °C)	H _v (kJ/kg)
A1	0.92	48.49	20.18	0.31	0.31	0.91	2.01	2.01	1.91	76.10	2.19	393.97
A2	0.68	66.96	24.58	0.36	0.49	1.09	2.19	2.19	2.09	86.09	1.94	408.60
A3	0.66	68.70	23.47	0.43	0.92	1.52	2.62	2.62	2.52	88.11	2.04	416.96
A4	0.62	40.36	24.34	0.34	2.15	2.75	3.85	3.85	3.75	56.06	2.03	505.27
A5	0.60	42.30	23.23	0.41	2.57	3.17	4.27	4.27	4.17	58.08	2.16	514.59
A6	0.59	61.69	22.86	0.44	1.74	2.34	3.44	3.44	3.34	72.11	2.24	449.67
A7	0.56	69.62	25.09	0.31	1.02	1.62	2.72	2.72	2.62	70.09	2.20	430.98
A8	0.54	71.34	23.98	0.37	1.45	2.05	3.15	3.15	3.05	72.11	2.32	440.57
A9	0.47	68.95	25.00	0.61	2.70	3.30	4.40	4.40	4.30	74.08	2.13	455.19
A10	0.46	77.57	25.10	0.42	2.01	2.61	3.71	3.71	3.61	74.08	2.17	439.34

Table 6.9: The generated acyclic solvents with their respective properties (continued)

Solvent	F _p (°C)	S (vol%)	PEL (ppm)	Solubility (mPA)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}	Energy Requirement (kJ)	EB
A1	-7.00	14.74	1.16	18.11	-2.95	711.06	0.45	3.99	-0.28	66.48	6.02
A2	3.36	13.40	7.41	18.29	-0.72	840.82	0.74	14.79	-0.06	74.99	6.78
A3	4.52	12.28	194.48	18.72	-1.37	1236.33	0.28	14.43	0.17	77.43	7.01
A4	-8.01	16.37	0.57	19.95	-0.56	558.31	2.77	2.60	-0.40	79.42	7.19
A5	-6.85	14.74	15.03	20.37	-1.21	831.00	1.04	2.54	-0.16	81.81	7.40
A6	-1.74	11.34	13.59	19.54	-1.16	899.72	1.04	3.83	0.10	80.45	7.28
A7	0.60	12.28	5.28	18.82	-1.08	506.77	1.30	27.33	0.02	80.76	7.31
A8	1.76	11.34	138.57	19.25	-1.73	749.04	0.49	26.66	0.26	83.58	7.56
A9	14.54	16.37	2.10	20.50	-1.71	840.56	1.53	1.60	-0.76	83.85	7.59
A10	10.46	16.37	7.27	19.81	-2.63	719.56	0.51	8.29	-0.81	85.14	7.70

Table 6.10: The generated monocyclic solvents with their respective properties

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	C _p (kJ/kg °C)	H _v (kJ/kg)
M1	0.94	43.04	3.14	4.41	0.87	1.47	2.57	2.57	51.00	114.19	2.29	351.17
M2	0.92	48.21	1.92	5.35	0.04	0.64	1.74	1.74	1.64	114.19	2.25	345.22
M3	0.91	47.17	4.05	5.44	0.02	0.62	1.72	1.72	1.62	112.17	2.21	342.13
M4	0.89	49.05	2.94	6.52	0.44	1.04	2.14	2.14	2.04	114.19	2.28	349.75
M5	0.84	40.93	3.49	3.83	1.98	2.58	3.68	3.68	3.58	100.16	2.24	392.05
M6	0.82	50.86	5.28	6.09	1.83	2.43	3.53	3.53	3.43	116.16	2.26	356.36
M7	0.82	51.89	3.10	3.05	0.17	0.77	1.87	1.87	1.77	110.20	2.31	358.14
M8	0.82	45.10	4.40	4.72	1.13	1.73	2.83	2.83	2.73	98.14	2.14	382.56
M9	0.81	53.74	1.99	3.65	0.59	1.19	2.29	2.29	2.19	112.22	2.38	365.61
M10	0.80	41.81	4.50	4.67	2.39	2.99	4.09	4.09	3.99	100.16	2.28	397.22

Table 6.11: The generated monocyclic solvents with their respective properties (continued)

Solvent	F _P (°C)	S (vol%)	PEL (ppm)	Solubility (mPA)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}	Energy Requirement (kJ)	EB
M1	-19.65	6.69	1290.86	18.67	-1.39	459.64	0.98	5.19	1.86	58.01	5.25
M2	-25.24	6.69	396.35	17.84	-2.32	451.98	0.48	3.57	1.95	59.23	5.36
M3	-18.80	7.01	44.50	17.82	-1.32	300.54	1.81	4.91	1.93	58.24	5.27
M4	-17.65	6.69	1167.29	18.24	-1.97	439.56	0.68	4.79	2.17	60.36	5.46
M5	-25.94	7.75	453.82	19.78	-1.55	491.75	0.62	2.11	1.58	63.10	5.71
M6	-3.37	8.18	199.47	19.63	-1.94	425.21	1.44	2.16	1.00	62.07	5.62
M7	-30.69	5.89	298.04	17.97	0.05	351.20	1.59	10.50	2.67	62.89	5.69
M8	-25.09	8.18	15.65	18.93	-1.49	320.73	1.14	2.00	1.65	63.24	5.72
M9	-29.53	5.66	7817.70	18.39	-0.59	513.82	0.60	10.24	2.90	65.05	5.89
M10	-18.35	7.75	1336.53	20.19	-1.20	478.23	0.87	2.83	1.79	64.31	5.82

Table 6.12: The generated acyclic solvents with their safety and health indices scores

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI _w
A1	3	1	3	1	0.605
A2	3	1	3	1	0.605
A3	3	1	1	1	0.563
A4	3	1	4	1	0.626
A5	3	1	2	1	0.584
A6	3	1	2	1	0.584
A7	3	1	3	1	0.605
A8	3	1	1	1	0.563
A9	3	1	3	1	0.605
A10	3	1	3	1	0.605

Table 6.13: The generated monocyclic solvents with their safety and health indices scores

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI _w
M1	3	1	0	2	0.563
M2	3	1	1	2	0.584
M3	3	1	2	2	0.605
M4	3	1	0	2	0.563
M5	3	1	1	2	0.584
M6	3	1	1	2	0.584
M7	3	1	1	2	0.584
M8	3	1	2	2	0.605
M9	3	1	0	1	0.542
M10	3	1	0	2	0.563

From the results, solvents A1 and M1 were positioned at the first ranking among the other generated solvents as they have the highest $F^{weighted\ sum}$ values. The comparison between properties of the designed molecules with that of hexane was made. Table 6.14 shows the properties of hexane. From the process perspective, solvents A1 and A2 as well as solvents M1 – M10 exerted lower total EB compared to that of hexane. This was because the mentioned molecules required lower energy during solvent recovery process. In terms of molecular environmental aspects, all the generated solvents had a lower tendency in causing aquatic toxicity as their $-\log LC_{50}$ values were lower than that of hexane.

By referring to BCF and $\log K_{oc}$ values, all the designed solvents possessed improved bioconcentration factor and soil sorption properties.

Table 6.14: Properties of hexane

Property	Property value
T_b (°C)	68.7
σ (mN/m)	17.91
μ (cp)	0.297
R_{carotene} (unit)	2.9
R_{TAG} (unit)	2.3
R_{LA} (unit)	1.2
R_{PA} (unit)	1.2
R_{OA} (unit)	1.3
F_p (°C)	-30.9
H_v (kJ/kg)	33.18
C_p (kJ/kg °C)	219.97
$-\log LC_{50}$	4.54
LD_{50} (mg/kg)	28000
PCO	0.43
$\log k_{oc}$	3.62
BCF	51.36
PEL (ppm)	50
S (%)	7.013
I_{FL}	3
I_{EX}	1
I_{EL}	2
I_{AH}	0
I_{SHI}	0.563
Energy requirement (kJ)	76.61
EB	6.93

Although the generated solvents had similar I_{FL} and I_{EX} scores, F_p of designed solvents, especially acyclic compounds were significantly higher than that of hexane. Owing to higher F_p of the designed solvents, the processes in which the designed solvents were applied will be safer compared to that of hexane. By comparing their health aspects, Solvent A3 and A8 as well as solvent M1 – M10 (except solvent M3 and solvent M8) had better I_{EL} score due to high PEL values. When comparing the overall $I_{SHI,w}$ scores, solvent M9 exhibited better safety and health performance compared to all solvents. This implied that

when solvent M9 was used in a process, the process will have the lowest safety and health impact compared to other designed solvents and hexane even if there were an unintentional leak of solvent M9 to the atmosphere. Besides, solvent A1, A4 and A5 as well as the other generated monocyclic solvents had significantly lower T_b than that of hexane. In addition, the solubility of carotenoids in all generated solvents was better than hexane as the generated solvents had smaller R_{carotene} . Solvent M2 and M3 exert the lowest values of R_{carotene} among other generated solvents. When the generated solutions were compared with the existing solvents in literature, solvent A3 (Ethyl acetate) was found out to give a better carotenoid yield (42.61 mg/kg) as compared to that of hexane (34.45 mg/kg) (Strati and Oreopoulou, 2011). Moreover, based, solvent A10 (methyl acetate) demonstrated its capability in extracting oil from the oilseeds (Su et al., 2007). Hence, the other generated solvents should have better or at least comparable extraction yield as compared to hexane.

A graphical representation of the trade-off between the process and molecular performance of the top solvents (Solvent A1 and M1) and hexane was shown in Figure 6.5. The radar chart was bounded by value zero to one, which was obtained by normalizing the target property. The closer the property to the value of one, the better the property. Based on the chart, it was observed that both solvent A1 and M1 possessed a well-balanced distribution between all the target property values. As compared to hexane, the generated solvents had more favourable molecular functionalities and able to achieve good process environmental performance.

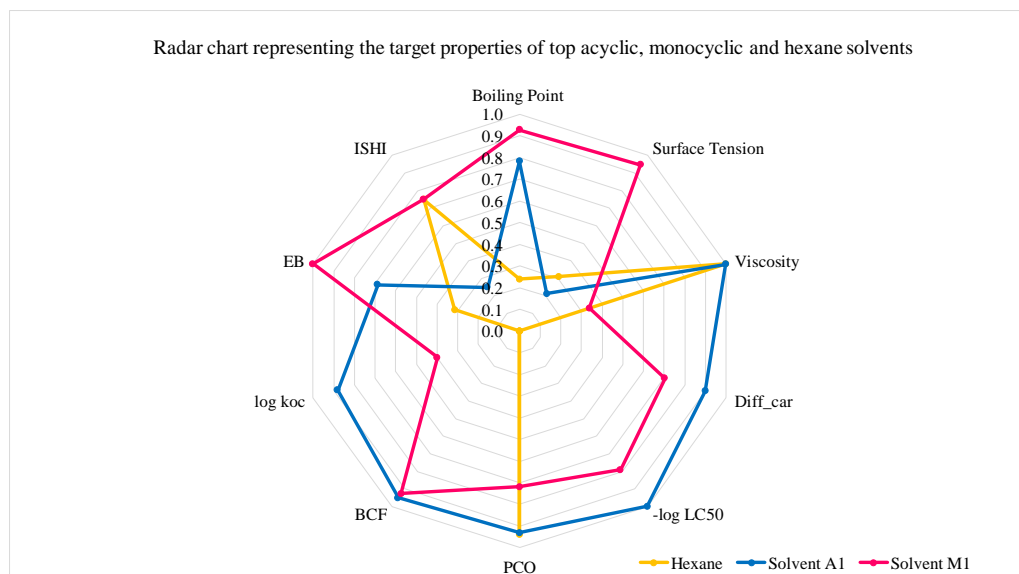


Figure 6.5: Radar chart representing the target properties of top acyclic, monocyclic solvents and hexane

Sensitivity analysis was also carried out by assuming molecular aspect is slightly more important than process aspect. The process aspect was now carrying weighting factor of 0.25 instead of 0.5. The results were displayed from Table 6.15 to Table 6.20. Based on the obtained results, it can be seen that the rankings for both acyclic and monocyclic solvents had been abruptly changed. For acyclic solvents, ethyl acetate and methyl acetate which previously ranked at the 3rd and 10th positions had become the 2nd and 9th best solutions respectively. On the other hand, for monocyclic solvents, solvent M6 and solvent M10 which were ranked at the 6th and 10th positions were now located at 10th and 7th places respectively. However, solvents A1 and M1 remained their positions at the top among the other solvents. Thus, it can be concluded that no matter whether the process and molecular aspects were treated equally importance or molecular aspect was slightly more important than process aspect, solvent A1 and M1 will still carry the highest potential to be useful for extracting residual oil from PPF.

Table 6.15: The generated acyclic solvents with their respective properties [sensitivity analysis results]

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	C _p (kJ/ kg °C)	H _v (kJ/kg)
B1	0.91	48.49	20.18	0.31	0.31	0.91	2.01	2.01	1.91	76.10	2.19	393.97
B2	0.72	68.70	23.47	0.43	0.92	1.52	2.62	2.62	2.52	88.11	2.04	416.96
B3	0.72	42.30	23.23	0.41	2.57	3.17	4.27	4.27	4.17	58.08	2.16	514.59
B4	0.71	66.96	24.58	0.36	0.49	1.09	2.19	2.19	2.09	86.09	1.94	408.60
B5	0.70	40.36	24.34	0.34	2.15	2.75	3.85	3.85	3.75	56.06	2.03	505.27
B6	0.68	61.69	22.86	0.44	1.74	2.34	3.44	3.44	3.34	72.11	2.24	449.67
B7	0.65	71.34	23.98	0.37	1.45	2.05	3.15	3.15	3.05	72.11	2.32	440.57
B8	0.63	69.62	25.09	0.31	1.02	1.62	2.72	2.72	2.62	70.09	2.20	430.98
B9	0.57	77.57	25.10	0.42	2.01	2.61	3.71	3.71	3.61	74.08	2.17	439.34
B10	0.56	68.95	25.00	0.61	2.70	3.30	4.40	4.40	4.30	74.08	2.13	455.19

Table 6.16: The generated acyclic solvents with their respective properties [sensitivity analysis results] (continued)

Solvent	F _p (°C)	S (vol%)	PEL (ppm)	Solubility (mPA)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}	Energy Requirement (kJ)	EB
B1	-7.00	14.74	1.16	18.11	-2.95	711.06	0.45	3.99	-0.28	66.48	6.02
B2	4.52	12.28	194.48	18.72	-1.37	1236.33	0.28	14.43	0.17	77.43	7.01
B3	-6.85	14.74	15.03	20.37	-1.21	831.00	1.04	2.54	-0.16	81.81	7.40
B4	3.36	13.40	7.41	18.29	-0.72	840.82	0.74	14.79	-0.06	74.99	6.78
B5	-8.01	16.37	0.57	19.95	-0.56	558.31	2.77	2.60	-0.40	79.42	7.19
B6	-1.74	11.34	13.59	19.54	-1.16	899.72	1.04	3.83	0.10	80.45	7.28
B7	1.76	11.34	138.57	19.25	-1.73	749.04	0.49	26.66	0.26	83.58	7.56
B8	0.60	12.28	5.28	18.82	-1.08	506.77	1.30	27.33	0.02	80.76	7.31
B9	10.46	16.37	7.27	19.81	-2.63	719.56	0.51	8.29	-0.81	85.14	7.70
B10	14.54	16.37	2.10	20.50	-1.71	840.56	1.53	1.60	-0.76	83.85	7.59

Table 6.17: The generated monocyclic solvents with their respective properties [sensitivity analysis results]

Solvent	F _{weightedsum}	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	R _{LA} (unit)	R _{PA} (unit)	R _{OA} (unit)	M _w (g/mol)	C _p (kJ/ kg °C)	H _v (kJ/ kg)
N1	0.91	43.04	3.14	4.41	0.87	1.47	2.57	2.57	51.00	114.19	2.29	351.17
N2	0.90	48.21	1.92	5.35	0.04	0.64	1.74	1.74	1.64	114.19	2.25	345.22
N3	0.88	49.05	2.94	6.52	0.44	1.04	2.14	2.14	2.04	114.19	2.28	349.75
N4	0.87	47.17	4.05	5.44	0.02	0.62	1.72	1.72	1.62	112.17	2.21	342.13
N5	0.86	40.93	3.49	3.83	1.98	2.58	3.68	3.68	3.58	100.16	2.24	392.05
N6	0.86	53.74	1.99	3.65	0.59	1.19	2.29	2.29	2.19	112.22	2.38	365.61
N7	0.83	41.81	4.50	4.67	2.39	2.99	4.09	4.09	3.99	100.16	2.28	397.22
N8	0.83	51.89	3.10	3.05	0.17	0.77	1.87	1.87	1.77	110.20	2.31	358.14
N9	0.82	47.00	3.29	5.66	1.56	2.16	3.26	3.26	3.16	100.16	2.22	390.44
N10	0.81	50.86	5.28	6.09	1.83	2.43	3.53	3.53	3.43	116.16	2.26	356.36

Table 6.18: The generated monocyclic solvents with their respective properties [sensitivity analysis results] (continued)

Solvent	F _p (°C)	S (vol%)	PEL (ppm)	Solubility (mPA)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log K _{oc}	Energy Requirement (kJ)	EB
N1	-19.65	6.69	1290.86	18.67	-1.39	459.64	0.98	5.19	1.86	58.01	5.25
N2	-25.24	6.69	396.35	17.84	-2.32	451.98	0.48	3.57	1.95	59.23	5.36
N3	-17.65	6.69	1167.29	18.24	-1.97	439.56	0.68	4.79	2.17	60.36	5.46
N4	-18.80	7.01	44.50	17.82	-1.32	300.54	1.81	4.91	1.93	58.24	5.27
N5	-25.94	7.75	453.82	19.78	-1.55	491.75	0.62	2.11	1.58	63.10	5.71
N6	-29.53	5.66	7817.70	18.39	-0.59	513.82	0.60	10.24	2.90	65.05	5.89
N7	-18.35	7.75	1336.53	20.19	-1.20	478.23	0.87	2.83	1.79	64.31	5.82
N8	-30.69	5.89	298.04	17.97	0.05	351.20	1.59	10.50	2.67	62.89	5.69
N9	-23.93	7.75	410.37	19.36	-2.14	470.26	0.43	1.95	1.89	65.39	5.92
N10	-3.37	8.18	199.47	19.63	-1.94	425.21	1.44	2.16	1.00	62.07	459.64

Table 6.19: The generated acyclic solvents with their safety and health indices scores [sensitivity analysis results]

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI _w
B1	3	1	3	1	0.908
B2	3	1	1	1	0.844
B3	3	1	2	1	0.876
B4	3	1	3	1	0.908
B5	3	1	4	1	0.939
B6	3	1	2	1	0.876
B7	3	1	1	1	0.844
B8	3	1	3	1	0.908
B9	3	1	3	1	0.908
B10	3	1	3	1	0.908

Table 6.20: The generated monocyclic solvents with their safety and health indices scores [sensitivity analysis results]

Solvent	I _{FL}	I _{EX}	I _{EL}	I _{AH}	ISHI _w
N1	3	1	0	2	0.844
N2	3	1	1	2	0.876
N3	3	1	0	2	0.844
N4	3	1	2	2	0.908
N5	3	1	1	2	0.876
N6	3	1	0	1	0.813
N7	3	1	0	2	0.844
N8	3	1	1	2	0.876
N9	3	1	1	2	0.876
N10	3	1	1	2	0.876

6.5 Summary

In this work, a novel CAMD framework was developed to simultaneously optimise the predefined properties of solvent and environmental performance of its recovery process. Through this method, the quantification of environmental impact of solvent recovery process was incorporated into a single stage CAMD framework. The main highlight of this contribution was that the total environmental burden and energy requirement of a process was available when a molecule was generated. The total environmental burden of a solvent recovery process was calculated using IChemE Sustainability Metrics. A case study on the solvent design for extracting residual oil from PPF was solved to demonstrate the proposed methodology. The results showed that the designed solvents exerted a well-balanced of molecular and process properties. The solvents had the ability to reduce energy consumption of the recovery process as well as the total environmental burden of the process. Besides, the sensitivity analysis results also reported that both top acyclic and monocyclic solvents remained at their rankings despite of the changes in weighting factors of molecular and process properties. This current CAMD framework can be further extended to include the effect of various solvent recovery processes on molecular design. The improved CAMD methodology will be presented in the following chapter.

CHAPTER 7

A SYSTEMATIC MOLECULAR DESIGN FRAMEWORK WITH THE

CONSIDERATION OF COMPETING SOLVENT RECOVERY

PROCESSES

7.1 Introduction

This chapter presents the fourth research scope, which is an extension of the third research scope, aimed to develop a novel CAMD framework that considers the entire solvent application steps. Through this framework, both the solute extraction and solvent recovery steps were considered simultaneously during the solvent design step. To date, none of the CAMD problem compares the effect on solvent selection if the designed solvent were to be recovered through different technologies. The existing works only focused on designing solvents for specific applications, neglecting the importance of its recovery process. However, in addition to the type of solvents used, energy required to recover the solvents are also heavily dependent on the chosen recovery techniques. From Chapter 6, it showed that large energy consumption will result in detrimental environmental impacts. Hence, besides the generation of solvents with desirable attributes, this newly developed methodology ensured that the designed solvents were recovered through less energy intensive separation process. Other than physicochemical and SHE properties, the utilities cost was considered along with the energy required to recover the solvent. FAHP approach was then applied to assign consistent weights to the multiple objective

functions. Via this approach, the designed solvents with favourable functionalities can be recovered through an economically efficient and environment friendly process.

7.2 Problem Statement

Solvent often acts as a medium for chemical reactions and purification processes. Most of the chemical solvents applied in industries are usually toxic and expensive. Additionally, solvent disposal costs and increasing environmental legislation against emissions have been the primary concerns in chemical industries. Hence, chemical industries actively look for numerous methods to reduce the usage of solvent. Among the existing separation techniques in literature, evaporation is commonly utilised by chemical industries to recover solvents. Excessive amount of thermal energy is supplied when components are separated from a mixture by evaporation. Nonetheless, large energy requirements usually impose negative impacts on the environment and economic feasibility. To counter this issue, separation techniques that require less energy and more economically viable should be identified to recover solvent. Thus far, no work has been done on comparing the effect of separation techniques on solvent design. The appropriate selection of solvent that considers its recovery process is important to enhance the economic feasibility and sustainability of a chemical process. This is because optimal solvent for an application will also change with the selected separation technique. For example, if a solvent with high boiling point were to extract a heat sensitive material, distillation may destruct the material as temperature has to be raised to vaporise the solvent. However, if a non-thermal separation technique were chosen, the solvent with high boiling point will become an optimal solvent as heat sensitive

material will not undergo degradation. For this reason, the previously developed CAMD framework is further extended to account for both the solvent application and its recovery step.

7.3 Methodology

The main purpose of this work was to develop a systematic CAMD framework that considered the complete cycle of solvent from its application to its recovery process. Solvent recovery using different separation techniques were integrated into CAMD framework to evaluate its effect on solvent selections. The total utilities cost and energy required for solvent recovery were integrated into CAMD formulation. Through this method, designed solvents with optimal functionalities can be regenerated by the cheapest, safest and environmentally favourable process. The developed methodology was summarised in the following steps:

7.3.1 Identification of design objective

The methodology started with the determination of design objective for CAMD problem. Since the entire cycle of solvent from its application to recovery were integrated into molecular design, criteria belonged to both molecular and process perspectives were considered. Under molecular properties, physicochemical and SHE properties were included to design a safe and environmentally favourable solvent for a certain application. Safety and health performance of the designed solvents were assessed by suitable indices presented in Section 5.3.3. In terms of process perspective, yield and economic potential were the chosen criteria. It is important to ensure that the designed solvent can achieve the targeted performance such as process yield during its

application. Besides, this chapter compared the effect on solvent design if the designed solvent were to be recovered through different separation techniques. Hence, the suitability of a separation technique can be dictated by estimating the total utilities cost required for recovering the designed solvents. The steps in integrating different solvent recovery processes into CAMD framework will be further illustrated in Section 7.3.2. The desired criteria and/or properties were then selected as design objectives.

7.3.2 Assessment of separation techniques for solvent recovery

As previously mentioned, solvent selection affects the sustainability of a chemical process. In Chapter 6, the generated solutions had shown that environmental burden of a process can be drastically reduced by minimizing the energy needed to recover the solvent. The methodology developed in Chapter 6 only focused on reducing the energy required to regenerate solvent through a specific separation technique. However, there are numerous separation techniques available in literature that can be used to recover solvent from a mixture. Operating condition of a separation technique often affects performance and energy consumption of a chemical process. For example, heat sensitive material can only be recovered through low temperature operating condition. If heat sensitive material were to be separated through high temperature process, process yield will be reduced due to degradation. Hence, it is important to incorporate the effect of various separation techniques on solvent design into CAMD framework.

To begin with, preliminary screening on existing methods for solvent recovery was performed to select suitable separation techniques based on the

design problem. After that, important parameters were identified for estimating energy balance for each chosen separation technique. For example, information such as specific heat capacity and/or latent heat of vaporization of a chemical substance was usually needed to calculate energy balance of evaporation process under standard condition. Energy balance around the evaporator (either normal or vacuum condition) can be calculated using Equation (7.1):

$$\Delta H^{feed, evap} + q_{H, evap} = \Delta H^{top, evap} + \Delta H^{bottom, evap} \quad (7.1)$$

where $\Delta H^{feed, evap}$ is enthalpy change for feed for the evaporator; $\Delta H^{top, evap}$ denotes enthalpy change for top product which is mainly solvent vapour; $\Delta H^{bottom, evap}$ depicts enthalpy change for bottom product which is the residual oil and $q_{H, evap}$ is the heat transferred from steam to the evaporator.

Besides, if a process were to be performed under vacuum condition, energy needed to create vacuum had to be calculated. Steam ejector has been widely chosen to create vacuum for evaporator owing to its low capital cost and virtually maintenance free characteristic. Steam ejector creates vacuum using expansion of motive steam. A single stage steam ejector can normally create a vacuum up to 75 mmHg. Motive steam consumption in a single stage steam ejector can be estimated using the following equations depicted below. Equations (7.2) to Equation (7.4) can be used for the estimation of temperature entrainment ratios, TC_a and molecular weight entrainment ratio of solvent vapour, MW_c respectively (Reddy et al., 2013).

$$TC_a = -4 \times 10^{-10} T_{sg}^3 + 3 \times 10^{-7} T_{sg}^2 - 0.0005 T_{sg} + 1.0131 \quad (7.2)$$

$$\begin{aligned} & \text{For } 0 < M_w < 60; \\ & MW_c = 1 \times 10^{-5} M_w^3 - 0.0013 M_w^2 + 0.0642 M_w + 0.0161 \end{aligned} \quad (7.3)$$

$$\begin{aligned} & \text{For } 60 < M_w < 150; \\ & MW_c = -2 \times 10^{-5} M_w^3 + 0.0077 M_w + 0.9464 \end{aligned} \quad (7.4)$$

where T_{sg} is the suction gas temperature in °C, M_w is the molecular weight of designed solvent. Later, suction gas stream was converted into dry air equivalent (DAE) using Equation (7.5).

$$DAE \text{ of suction gas} = \frac{M_{vs}}{TC_a \times MW_c} \quad (7.5)$$

R_a can be defined as the consumption of motive steam for compressing a unit DAE mass of suction gas in a steam ejector, which can be estimated through Equation (7.6) (Trambouze, 1999).

$$R_a = \left[\frac{P_d}{P_a} \left(0.434 - \frac{1.338}{P_a} + 0.475 \times 10^{-3} P_a \right) - 0.187 \right] \left(1.2 - \frac{P_v - 10.2}{20} \right) \quad (7.6)$$

where P_a and P_d are the suction and discharge pressures measured in torr respectively, P_v is the motive steam pressure in barg. Equation (7.7) can then be used to estimate the amount of motive steam, $M_{steam,motive}$ needed for a steam ejector.

$$M_{steam,motive} = DAE \times R_a \quad (7.7)$$

The following step was to identify the utilities required for each separation process. Typical utilities include steam, electricity, natural gas, cooling water, refrigeration etc. The price for each utility was then identified based on current market rate. Table 7.1 showed the costs of each utility based on

the latest tariff given by Malaysia. The production costs of cooling water, refrigeration and steam were estimated using the steps given by Turton et al., (2008). The cost stated in Ringgit was then converted into USD for standardisation.

Table 7.1: Cost of each utility

Utility	Cost \$/ Unit
Natural Gas	\$ 8.025/ MMBTU
Electricity:	
8am – 10pm	\$ 0.0843/ kWh
10pm – 8 am	\$ 0.0505/ kWh
Water	\$ 0.825 / tonne
Cooling water	\$ 0.3598 / GJ
Refrigerant	\$ 5.1136 / GJ
Medium Pressure steam	\$ 17.55 / tonne

The total utilities cost for a normal evaporation process, $Cost_{evap,n}$, can be calculated using Equation (7.8). For evaporation process operated under vacuum condition, steam ejector utility cost had to be considered in the calculation. The estimation of total operating cost for vacuum evaporation, $Cost_{evap,v}$, was shown in Equation (7.9). By performing all these steps, the total energy consumption along with utilities cost can be integrated into CAMD formulation.

$$Cost_{evap,n} = \text{heating utility cost} + \text{cooling utility cost} \quad (7.8)$$

$$Cost_{evap,v} = \text{heating utility cost} + \text{cooling utility cost} + \text{steam ejector utility cost} \quad (7.9)$$

7.3.3 Selection of safety and health indices

Next, flammability index (I_{FL}) and explosiveness index (I_{EX}) were utilised to assess safety performance of a molecule. On the other hand, health

characteristic of a molecule can be evaluated through exposure limit index (I_{EL}) and acute health hazards (I_{AH}). The penalty scores for the abovementioned safety and health indices had been dictated in Section 5.3.3. The safety and health aspects of all generated molecules can later be compared by calculating their total weighted penalty score ($I_{SHI,w}$), which was expressed in Equation (7.10). The lower the $I_{SHI,w}$ value, the better the safety and health performance of a molecule.

$$I_{SHI,w} = w_{FL}I_{FL} + w_{EX}I_{EX} + w_{EL}I_{EL} + w_{AH}I_{AH} \quad (7.10)$$

where w_{FL} denotes weighting factor for sub-index I_{FL} ; w_{EX} indicates weighting factor for sub-index I_{EX} ; w_{EL} represents weighting factor for sub-index I_{EL} ; w_{AH} indicates weighting factor for sub-index I_{AH} . Since safety and health penalty scores were dependent on property value, disjunctive programming was employed to translate molecular properties into index scores. The detailed steps on how to perform disjunctive programming had been discussed in Section 5.3.4.

7.3.4 Identification of property prediction model

The following step involved the estimation of all targeted properties through property prediction models. Most of the targeted properties can be predicted by GCM equations. The upper and lower bounds of property constraints were then defined based on process requirement or customers' need.

7.3.5 Computation of weighting factor of each objective function

Since this was a multi-objective CAMD problem, FAHP approach, which was presented in Section 5.3.5 – Section 5.3.6, can be implemented to determine weighting factor for each chosen objective function.

7.3.6 Molecular design phase

In molecular design phase, appropriate first order molecular building blocks were selected based on the nature of CAMD problem. To generate structurally feasible acyclic and monocyclic compounds, structural constraints presented in Section 4.36 were applied.

7.3.7 Optimisation model

Since there were more than two design objectives, CAMD problem was formulated as a multi-objective optimisation problem. Firstly, the selected targeted properties were transformed into linear membership functions, indicated by their respective target property operators, Ω_p . The step was then followed by the normalisation of Ω_p using Equation (7.11) or Equation (7.12). This step was necessary to ensure that all properties exerted the same magnitudes. Equation (7.11) and Equation (7.12) were applied to normalise Ω_p that needed to be maximised and minimised respectively.

$$\lambda_{pm} = \frac{\Omega_p - \Omega_{p \min}}{\Omega_{p \max} - \Omega_{p \min}} \quad (7.11)$$

$$\lambda_{pm} = \frac{\Omega_{p \max} - \Omega_p}{\Omega_{p \max} - \Omega_{p \min}} \quad (7.12)$$

where $\Omega_{p_{\min}}$ and $\Omega_{p_{\max}}$ are the lowest and highest values of target property operator which were determined by performing single-objective optimisation. The normalised target property operator, λ_{p_m} , now had the value between 0 and 1. After that, weighted sum method was employed to solve this multi-objective optimisation model. By multiplying weighting factor (which was predetermined by FAHP approach) to each objective, multiple objectives can be aggregated into a scalar objective function. Equation (7.13) showed the overall objective function.

$$F^{\text{weighted sum}} = w_1\lambda_{p_1} + w_2\lambda_{p_2} + \dots + w_m\lambda_{p_m} \quad (7.13)$$

where $F^{\text{weighted sum}}$ is the overall objective function and w_m is the weighting factor for each normalised target property operator λ_{p_m} . The design objective of this work was to maximize $F^{\text{weighted sum}}$. Thus, optimal molecule will be the solution with the highest $F^{\text{weighted sum}}$ value. Besides, a list of optimal and near-optimal molecules with proper rankings can be obtained by applying integer cuts. The developed methodology was presented in Figure 7.1.

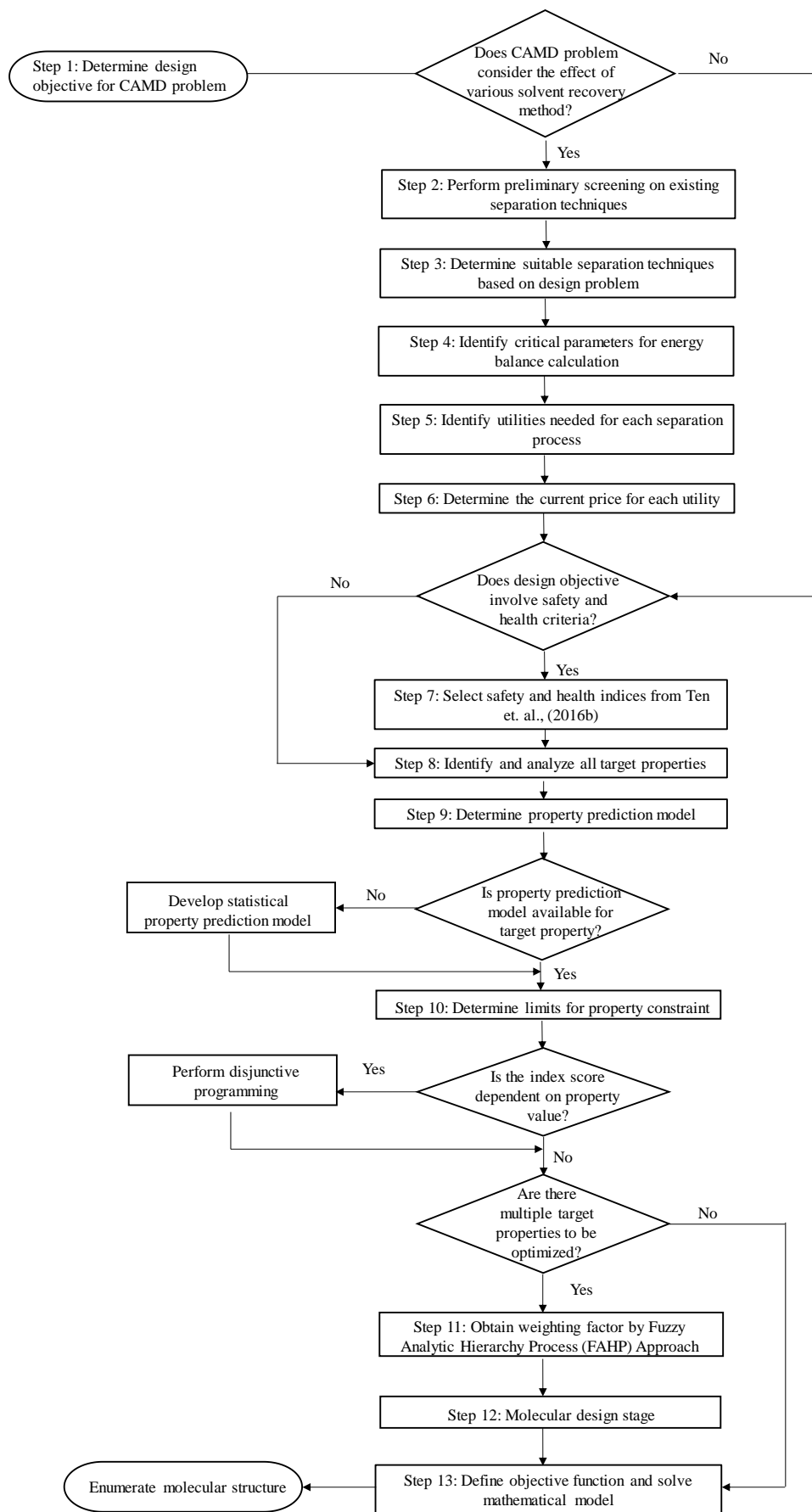


Figure 7.1: Methodology for research scope 4

7.4 Case study

7.4.1 Problem statement

The same case study presented in Section 4.4.1 was used to demonstrate the proposed methodology. The objective of this case study was to identify a suitable solvent to replace hexane for extracting carotenes from the residual oil retained in Palm Pressed Fibre (PPF). Among all the existing solvents, hexane has been the popular choice in industries for its low cost and high oil solubility (de Oliveira et al., 2013). In conventional practice, normal evaporation is used to recover hexane from residual oil after the solvent extraction process.

The conventional process flow diagram of extracting residual oil from PPF using solvent extraction method was shown in Figure 7.2. To ensure efficient oil removal, counter current extractor (E1) was usually employed by industries. Extraction took place when there was a diffusion of oil into the solvent. The solvent-saturated PPF (referred as meal) was then transferred to desolventiser toaster (E2) for further solvent recovery. On the other hand, multistage evaporation recovered residual oil from the oil-rich solvent (which was known as miscella). Solvent vapours from both desolventising toaster and evaporators were then condensed using condenser (E4) before recycling back to the extractor. Nonetheless, there are a few drawbacks for using hexane to extract residual oil from PPF, which had been previously discussed in Section 4.4.1 and Section 5.4.1. Besides, carotene starts to degrade when the operating temperature is higher than 70°C. Since hexane has a boiling point of 69°C, the higher temperature in the evaporation process will inevitably lead to carotene degradation. Thus, besides design solvents with improved physicochemical and

SHE properties, this work aimed in exploring the potential of various separation processes for solvent recovery through multi-objective CAMD method.

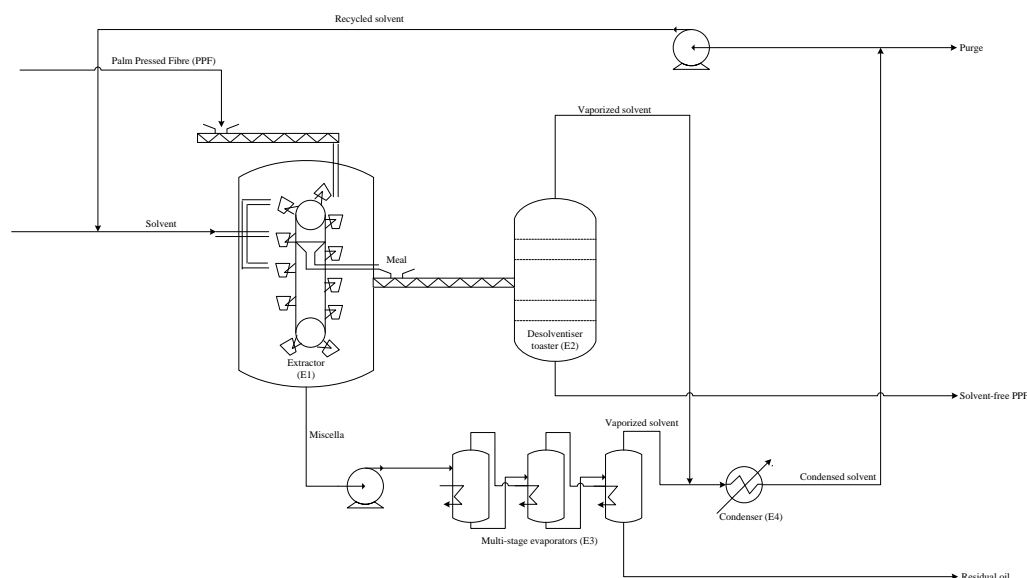


Figure 7.2: Process flow sheet of residual oil extraction from PPF using solvent extraction method

7.4.2 Identification of design objective

This case study aimed to design alternate solvents for replacing hexane in residual oil extraction from PPF. The designed solvents must exert desirable properties from both molecular and process perspective. For instance, solvent must attain expected functionalities for it to be utilised in an application. Moreover, solvent should be less hazardous environmental friendly. From process perspective, the process should be able to achieve high carotene yield with minimal utilities cost when the designed solvents were recovered through the selected separation technique. Since the major energy requirement of a process usually comes from solvent recovery, process economic can be dictated by the utilities cost needed to recover the solvent. Table 7.2 shows the translation

of all favourable qualitative attributes of the designed solvents into their respective measurable properties.

Table 7.2: Translation of favourable qualitative attributes of designed solvent into their respective measurable properties

Categories		Favourable qualitative attributes	Measurable properties
Process	Performance	Maximum carotene yield	Low degradation kinetics of carotene
	Economic	Maximum process economic	Low utilities cost during solvent recovery
Molecular	Physical	Higher rates of oil extraction by having good percolation and surface wetting (Bockisch, 1998)	Low viscosity (μ) and surface tension (σ)
		Both carotene and triglycerides (TAGs) should be highly soluble in designed solvents	Small difference of Hildebrand solubility parameter (δ) between solvent and carotene (R_{carotene})
	Safety	Low flammability index I_{FL}	High flash point (F_p)
		Low explosiveness index I_{EX}	Small difference between lower explosion limit (LEL) and upper explosion limit (UEL)
Health	Low exposure limit index I_{EL}	High permissible exposure limit (PEL)	
	Low acute health hazard index I_{AH}	High oral rat LD_{50}	
Environmental	Low aquatic toxicity	High fathead minnow LC_{50}	
	Reduce photochemical smog	Low photochemical oxidation potential (PCO)	
	Minimise accumulation of solvent in one place	Low soil sorption coefficient ($\log K_{\text{oc}}$)	
	Reduce the accumulation of solvent in aquatic organism	Low bioconcentration factor (BCF)	

7.4.3 Assessment of separation techniques for solvent recovery

Preliminary screening had been performed on all the existing separation processes used for recovering solvent from miscella. As mentioned before, carotene degradation usually occurs when solvent was recovered from miscella through normal multistage evaporation. This was because the operating temperature of the evaporator must be equal to or higher than the boiling point of the designed solvent to vaporise solvent from the oil. Thus, there was a need to identify other separation techniques that can recover solvent from oil at a lower temperature to minimise degradation of carotene.

Based on literature review, vacuum evaporation, cooling crystallisation and membrane technology can be used for recovering solvent from miscella at a lower temperature. Vacuum evaporation enables a solvent to be recovered at a temperature lower than its boiling point by reducing the operating pressure of evaporator using vacuum. The relationship between boiling point of a liquid solvent and its vapor pressure can be estimated using Clausius-Clapeyron Equation, expressed by Equation (7.14).

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{H_v}{R} \left(\frac{1}{T_{b1}} - \frac{1}{T_{b2}} \right) \quad (7.14)$$

where T_{b1} and P_1 represent the initial operating temperature and pressure of the evaporator respectively. T_{b2} is the estimated boiling point of the solvent at operating pressure, P_2 , H_v is the heat of vaporisation of designed solvent and R is the universal gas constant. On the other hand, cooling crystallisation involves cooling of miscella at a controlled temperature to allow crystallisation of solid portion followed by the filtration of two phases. Figure 7.3 and Figure 7.4

showed the process flow diagram of residual oil extraction from PPF using solvent extraction method followed by vacuum evaporation and cooling crystallisation process respectively.

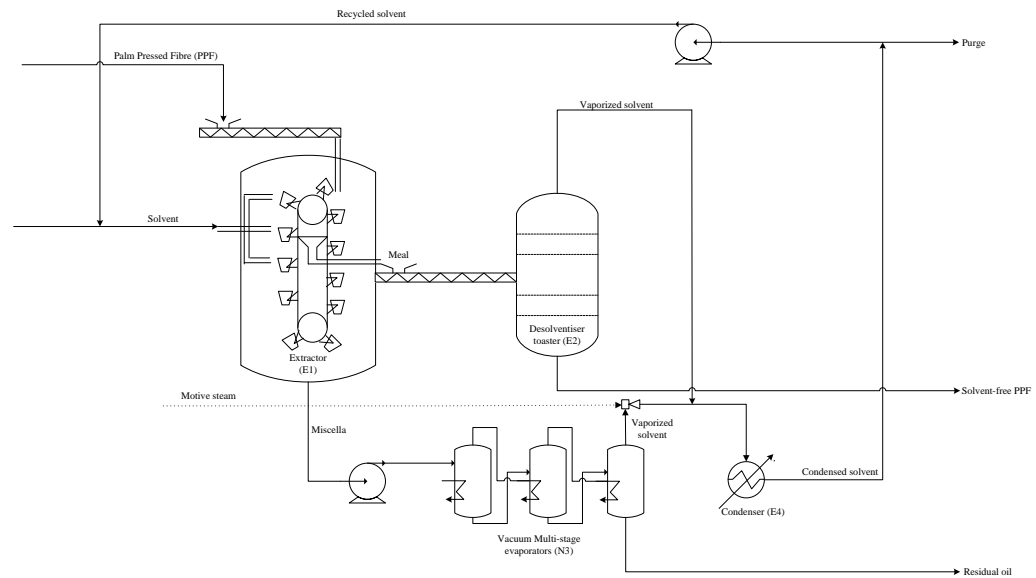


Figure 7.3: Process flow diagram of residual oil extraction from PPF using solvent extraction followed by vacuum evaporation process

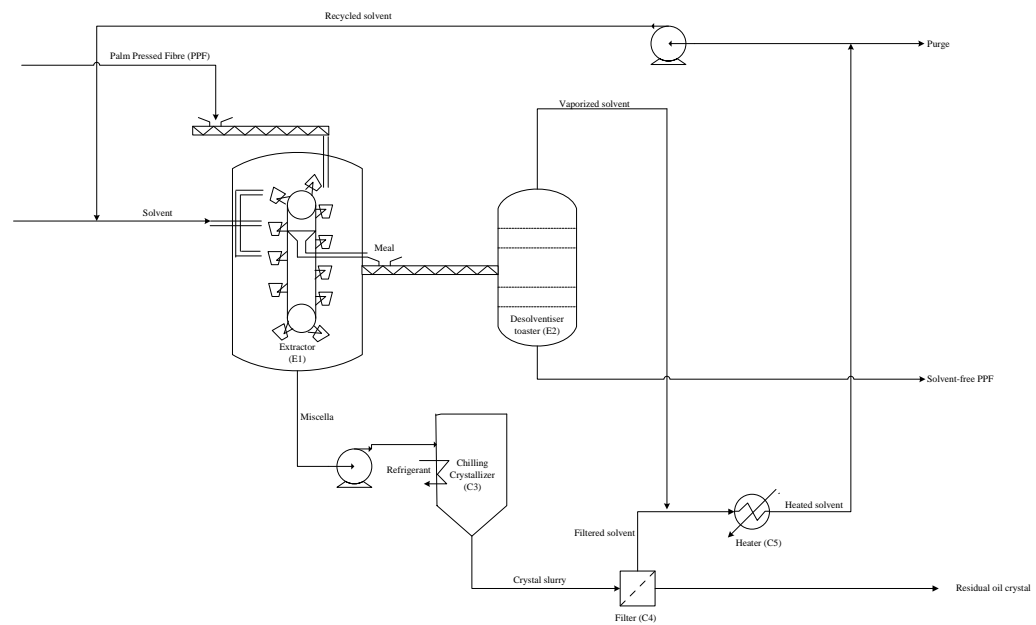


Figure 7.4: Process flow diagram of residual oil extraction from PPF using solvent extraction followed by cooling crystallisation process

However, this work only focused on comparing the effect of vacuum evaporation and cooling crystallisation on solvent design to that by normal evaporation. Membrane technology was excluded from this work due to its limitation in industrial use. Some examples of conventional membrane separation processes are microfiltration, ultrafiltration, nanofiltration, electrodialysis, reverse osmosis etc. The factors hindering the use of membrane technology in industries included its poor stability in relation to organic solvents and low membrane flux which affects the process economic (Ladhe and Krishna Kumar, 2010). Furthermore, membrane is prone to fouling which results in a deterioration in process performance. This means that membrane process can initially achieve a very good performance, characterised by high flux but decreases drastically when materials accumulate on the surface. The fouling phenomenon also causes an increase in operating cost since chemical cleaning must be done to remove the foulant. Besides, when fouling occurs, there will be an increase in mass transfer resistance which leads to an increase in energy consumption. Larger amount of energy is needed to increase the pressure of membrane for maintaining constant flux (Wenten et al., 2016).

7.4.3.1 Energy balance calculation for each solvent recovery process

Next, parameters required for energy balance calculation were determined based on the data obtained from oil extraction process using hexane. The C_p of residual oil has the value of 1.902 kJ/kg K whereas the heat of fusion of oil, ΔH_{fus} has the value of -91.3 kJ/kg; PPF contains 10 % moisture and 5 % residual oil respectively; miscella has 25 weight % of oil in it. The final product contains 98 weight % of oil if miscella were recovered through normal

evaporation and vacuum evaporation. Nonetheless, if miscella were recovered through cooling crystallisation, the final product was assumed to contain 100 weight % of oil. The basis chosen for this work was to produce 250 kg of oil with the use of 750 kg of solvent. The extractor was assumed to operate at 35°C isothermally. Operating temperature of normal multistage evaporator, T_{evp} was estimated based on the T_b of the solvent to ensure complete evaporation of the solvent. For vacuum multistage evaporator, its operating temperature was fixed at 65°C to avoid degradation of carotene. The total amount of vacuum needed to ensure the designed solvent has boiling point of 65°C at the suppressed operating pressure can then be estimated using Clausius-Clapeyron equation.

By having the temperature of feed as reference temperature, Equation (7.1) that used to calculate energy balance around the evaporator can be reduced to Equation (7.15), which can also be shown in the form as Equation (7.16).

$$q_{H, evap} = \Delta H^{top, evap} + \Delta H^{bottom, evap} \quad (7.15)$$

$$M_{steam} \lambda_{steam} = M_s C_{ps} (T_{evp} - T_{feed}) + M_{vs} H_v + M_{oil} C_{poil} (T_{evp} - T_{feed}) \quad (7.16)$$

where M_{steam} is the mass of steam needed (kg); λ_{steam} is the latent heat of steam (kJ/kg); M_s is the total mass of designed solvent fed (kg); M_{vs} is the mass of vaporised solvent (kg), C_{ps} is the average heat capacity of designed solvent (kJ/kg °C); T_{evp} is temperature of the evaporator (°C); T_{feed} is temperature of the feed (°C); H_v is the heat of vaporisation of the designed solvent (kJ/kg); M_{oil} is the mass of residual oil (kg); C_{poil} is the specific heat capacity of residual oil.

The vaporised solvent was then condensed to 35°C for it to be recycled back to

the extractor. The energy balance around the condenser can be calculated using Equation (7.17):

$$q_{c, evap} = M_{vs} C_{ps} (T_{out, condenser} - T_{evp}) - M_s H_v \quad (7.17)$$

where $q_{c, evap}$ represents the duty of condenser located after evaporator (kJ), $T_{out, condenser}$ is the condenser outlet temperature which was fixed at 35°C.

In this work, steam ejector has been chosen to create vacuum for evaporator. Discharge pressure of steam ejector was assumed to be 1.5 bar to account for the pressure drop in equipment. Besides, motive steam at 8 barg was supplied to steam ejector. Note that suction gas temperature was equal to operating temperature of vacuum evaporator (65°C). Equation (7.2) to Equation (7.7) were then applied to calculate the amount of motive steam needed for creating vacuum using steam ejector.

Palm oil comprises 93 % - 95% triacylglycerols (TAG). Crystallisation of palm oil can be classified into two distinct categories of TAG which crystallise at different temperature (Omar et al., 2015). Crystallisation of higher melting TAG usually starts at temperature around 28.5 °C whereas lower melting TAG crystallise around 12.4 °C (Omar et al., 2015). Hence, in this work, the operating temperature of cooling crystalliser was set at 10°C to ensure complete crystallisation of residual oil. Energy balance around the cooling crystalliser can be estimated using Equation (7.18).

$$q_{c, crys} = M_s C_{ps} (T_{crys} - T_{feed}) + M_{oil} H_{foil} + M_{oil} C_{poil} (T_{crys} - T_{feed}) \quad (7.18)$$

where $q_{c,crys}$ is cooling duty needed for crystallisation (kJ), T_{crys} is operating temperature of crystalliser (°C). For heater, energy balance can be estimated using Equation (7.19).

$$q_{H,crys} = M_s C_{ps} (T_{out,heater} - T_{crys}) \quad (7.19)$$

where $q_{H,crys}$ is the heating duty needed for heater located after crystalliser (kJ), $T_{out,heater}$ is heater outlet temperature at 35°C.

7.4.3.2 Utilities cost calculation for each solvent recovery process

For this case study, the cost of each utility was extracted from Table 7.1 under section 7.3.2. Equation (7.8) which was previously presented to calculate the utilities cost needed for normal evaporation, $Cost_{evap,n}$ can also be expressed in the form of Equation (7.20). On the other hand, Equation (7.9) can be rewritten in the form of Equation (7.21) to calculate the total operating cost for vacuum evaporation, $Cost_{evap,v}$.

$$Cost_{evap,n} = M_{steam} \times \text{Price of steam /kg} + q_{c,evap} \times \text{Cost of cooling water/kJ} \quad (7.20)$$

$$Cost_{evap,v} = M_{steam} \times \text{Cost of steam /kg} + q_{c,evap} \times \text{Cost of cooling water/kJ} \\ + M_{steam,motive} \times \text{Cost of steam /kg} \quad (7.21)$$

For cooling crystallisation, the utilities cost was calculated by the same equation expressed by Equation (7.8). However, refrigerant cost was accounted for the cooling utilities cost since cooling water was not able to bring down the temperature to 10°C. Hence, Equation (7.20) was rewritten in the form of Equation (7.22) for calculating total operating cost needed for cooling crystallisation, $Cost_{crys}$.

$$Cost_{crys} = M_{steam} \times \text{Cost of steam /kg} + q_{c,crys} \times \text{Cost of refrigerant/kJ} \quad (7.22)$$

7.4.4 Quantification of the yield of extracted carotene

Yield of extracted carotene can be deduced from its degradation kinetics. The degradation kinetics of carotene was represented by first order kinetic model (Dutta et al., 2006), which was given by Equation (7.23).

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (7.23)$$

where C is the concentration of carotene (mg/kg) at time t , C_0 is the initial concentration of carotene (mg/kg), k is the temperature dependent rate constant (min^{-1}), t is the heating time (min). In this work, C_0 was assumed to be 5000 ppm as 4000 – 6000 ppm of carotene can be found in residual oil (Choo et al., 1996). Since the degradation rate constant, k was dependent on the temperature, Arrhenius equation was used to represent the relationship. Arrhenius equation was expressed by Equation (7.24):

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (7.24)$$

where k is the rate constant at temperature T (K), k_0 is the pre-exponential factor, E_a is the activation energy (J/mol) and R is the gas constant (8.314 J/mol K). Based on Arrhenius equation, a straight line can be obtained from the plot of $\ln k$ versus $\frac{1}{T}$ and the gradient represents $\frac{-E_a}{R}$.

In this work, k_0 and E_a were estimated from the real experiment carried out by Dutta et al., (2006). In their work, the degradation kinetics of carotene of

pumpkin puree were determined at a temperature range of 70 – 100°C for 2 hours. Their results showed that at temperature range from 70 - 100°C, the degradation of carotene followed first order reaction kinetics. Based on their experimental data, Equation (7.24) can be re-written as:

$$k = 47.98 \exp\left(\frac{-3231.7}{T}\right) \quad (7.25)$$

It was evident that degradation kinetics of carotene was dependent on unit operation with the highest operating temperature. For this case study, separation unit such as multistage evaporator under standard condition usually operated at a temperature higher than boiling point of solvent to vaporise the solvent from miscella. Hence, boiling point of a designed solvent will indirectly affect the yield of extracted carotene. Besides, degradation of carotene followed first order kinetics at temperature range from 70 - 100°C and there was no degradation of carotene at temperature below 70°C. For these reasons, disjunctive programming can be applied to simultaneously calculate the yield of carotene when a solvent was designed. The yield of carotene can be calculated using Equation (7.26).

$$\text{Yield of carotene} = \frac{\text{Final concentration of carotene, } C_f}{\text{Initial concentration of carotene, } C_0} \times 100\% \quad (7.26)$$

The value of C_f can either be the same as C_0 or can be found from degradation kinetics expressed in Equation (7.23), depending on the operating temperature of separation unit. Table 7.3 depicted the relationship between concentration of carotene and operating temperature of separation unit.

Table 7.3: The relationship between concentration of carotene and temperature

Temperature, T (K)	Concentration of carotene after time t, C (mg/kg)
$T < 343.15$	$C_0 = 5000$
$343.15 \leq T \leq 373.15$	$C = C_0 \exp(-kt);$ $k = 47.98 \exp\left(\frac{-3231.7}{T}\right)$

Binary integer variable was used to model these functions. By introducing integer variable, I_{conc} , C_f can be then calculated based on T.

$$C_f = C_0 \times I_{conc} + C \times (1 - I_{conc}) \quad (7.27)$$

Subject to the condition:

$$I_{conc} = \begin{cases} 0 & T \geq 343.15K \\ 1 & T < 343.15K \end{cases} \quad (7.28)$$

In order to model condition (7.28) which allocated the value of I_{conc} to be either 0 and 1 based on value of T, the following constraint was considered:

$$(0 - 343.15) \times (I_{conc}) \leq T - 343.15 < (1000 - 343.15) \times (1 - I_{conc}) \quad I_{conc} \in \{0,1\} \quad (7.29)$$

7.4.5 Identification of property prediction model

After determining all the target properties for the design problem, their respective property prediction models and/or empirical correlations were identified. T_b , σ , μ , δ , F_p , PEL , M_w , LC_{50} , LD_{50} , PCO , $\log K_{oc}$, BCF , UEL , LEL , H_v and C_p were estimated through empirical correlations and/or GCM equations reported previously in Section 4.4.3, Section 5.4.3 as well as Section 6.4.4. Additional property such as normal melting point, T_m was estimated through Equation (7.30) (Hukkerikar et al., 2012b).

$$\exp\left[\frac{T_m}{T_{m0}}\right] = \sum_i N_i T_{mli} \quad (7.30)$$

where T_{mli} represents the normal melting point contribution of the first-order group of type- i that occurs N_i times while T_{m0} stands for the universal constant given by the value of 143.5706 K.

The subsequent step included the determination of upper and lower bounds of property constraint for solvent design. For this case study, lower bound was introduced to F_p as solvent with higher F_p will have lower potential in causing fire and explosion. Besides, to ensure that the designed solvent had a better properties than hexane, upper and lower limits were also introduced to target properties such as R_{carotene} as well as $\log K_{oc}$ and BCF . Note that the constraints set for T_b were different if the solvent were to be recovered through different separation techniques. Table 7.4 reported the summary of property constraints ranges of the solvent.

Table 7.4: Upper and lower limit of properties for solvent design

Property		Lower Bound	Upper Bound
T_b (°C)	Normal evaporation process	40	100
	Vacuum evaporation process	65	-
	Cooling crystallisation	40	-
F_p (K)		242	-
R_{carotene} (unit)		-	3.4
$\log K_{oc}$		-	4.5
$\log BCF$		-	3.3

7.4.6 Development of hierarchical decision structure

Figure 7.3 showed the four-level hierarchical decision model constructed for this case study. The main goal of this case study was to design solvents with desirable physical and SHE properties for its application in extracting residual oil from PPF. Besides, the designed solvents should simultaneously improve the yield of carotene as well as being recovered through a cheaper separation technique. From Figure 7.5, two main properties such as molecular and process aspects had been selected to achieve the design objective. There were four sub-properties including physical, safety, health and environmental properties classified under molecular aspects. On the other hand, economic and performance were the sub-properties considered under process aspect. Each of these mentioned properties were then further sorted into quantitative sub-properties which were stated in Section 7.4.2 (Table 7.1).

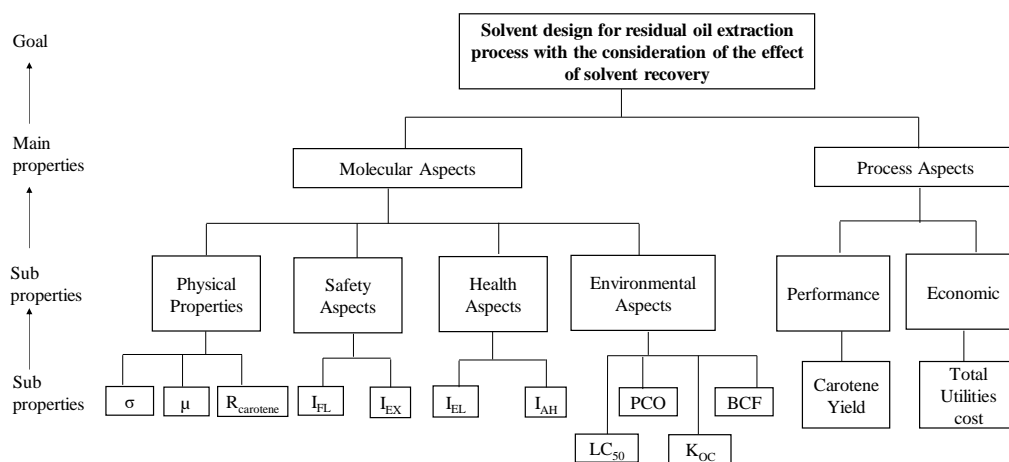


Figure 7.5: Hierarchical decision model for this case study

7.4.7 Computation of weights for each objective function

At this stage, FAHP approach were applied to elicit the pairwise comparative judgements. The relative importance of each criterion was

evaluated based on supporting theory or literature. The detailed steps on how to perform FAHP approach were discussed in Chapter 5.

In this work, both molecular and process aspects were assumed to be more or less equally important with a moderate level of confidence. This was to ensure that the designed solvents exert desirable physicochemical properties and fulfil SHE regulations. Moreover, it was important to ensure that maximum amount of carotene and good economic potential can be attained when the designed solvents were applied in the process. The fuzzy pairwise comparison matrix of main properties with respect to the goal were reported in Table 7.5. Based on confidence level, relative importance of molecular aspect over process aspect was reflected together with lower and upper bound of the comparison. This judgement was perfectly consistent in this pairwise comparison matrix as the λ value is equal to one.

Table 7.5: Fuzzy pairwise comparison matrix of main properties for solvent design in residual oil extraction process

	Molecular Aspects	Process Aspects	Priority Vector
Molecular Aspects	1	(1/3, 1, 3)	0.5
Process Aspects		1	0.5
$\lambda = 1$			

Table 7.6 showed the pairwise comparison matrix of process sub-properties using fuzzy scale. Process performance and economic were assumed to be more or less equally importance with moderate degree of confidence. It was of vital importance to ensure that the process can reach the targeted performance with minimum energy cost required for solvent regeneration. Other than achieving maximum carotene yield, process with low utilities cost was an additional merit to business investors.

Table 7.6: Fuzzy pairwise comparison matrix of process sub-properties for solvent design in residual oil extraction process

	Performance	Economic	Priority Vector
Performance	1	(1/3, 1, 3)	0.5
Economic		1	0.5
$\lambda = 1$			

On the other hand, comparative judgements for all the molecular sub-properties were previously performed in Chapter 5 under Section 5.4.6. The step was then followed by the calculation of final weighting factors of each sub property in the overall system. It can be obtained by the multiplication between weighting factors of sub-properties and their respective main properties, as reported in Table 7.7.

Table 7.7: Final weighting factors of target properties in the overall system

Target Property	Final weighting factor
Carotene yield	0.25
Total utilities cost	0.25
R_{carotene}	0.0311
σ	0.0621
μ	0.0621
LC_{50}	0.0077
PCO	0.0278
$\log K_{oc}$	0.0034
BCF	0.0034
I_{FL}	0.1302
I_{EX}	0.1302
I_{EL}	0.0211
I_{AH}	0.0211

Note that if the solvents were to be recovered through vacuum evaporation or crystallisation, process economic carried the weighting factor of 0.5 since process performance was omitted as an objective. This was because the operating temperature of vacuum evaporator and crystalliser were less than the

degradation temperature of carotene. Hence, there will be no carotene loss if solvents were to be recovered through vacuum evaporator or crystalliser.

7.4.8 Molecular design stage

Based on the molecular structure of conventional solvents applied in oil extraction process, fourteen first order molecular groups were selected for this case study. The chosen molecular groups comprised C, CH, CH₂, CH₃, OH, COOH, CHO, CH-O, CH₃CO, CH₃O, CH₂O, CH₃COO, NH₂ and CH₂=CH. Feasible acyclic and monocyclic compounds can be synthesised by the implementation of structural constraints stated in Section 4.3.6.

7.4.9 Optimisation model

In the final stage, the chosen design objectives were then converted into their respective property operator, Ω_p , to reduce the non-linearity equations in the model. Subsequently, Ω_p was normalised using the steps stated in Section 7.3.7. Equation (7.31) showed the overall objective function for the case where the designed solvent was assumed to be recovered through normal evaporation. On the other hand, when the designed solvent was assumed to be recovered through vacuum evaporation or cooling crystallisation, the overall objective function expressed by Equation (7.32) was used.

$$F^{weighted\ sum} = w_1\lambda_\sigma + w_2\lambda_\mu + w_3\lambda_{R_{carotene}} + w_4\lambda_{LC_{50}} + w_5\lambda_{PCO} + w_6\lambda_{\log K_{oc}} + w_7\lambda_{BCF} + w_8\lambda_{I_{FL}} + w_9\lambda_{I_{EX}} + w_{10}\lambda_{I_{EL}} + w_{11}\lambda_{I_{AH}} + w_{12}\lambda_{yield} + w_{13}\lambda_{cost} \quad (7.31)$$

$$F^{weighted\ sum} = w_1\lambda_\sigma + w_2\lambda_\mu + w_3\lambda_{R_{carotene}} + w_4\lambda_{LC_{50}} + w_5\lambda_{PCO} + w_6\lambda_{\log K_{oc}} + w_7\lambda_{BCF} + w_8\lambda_{I_{FL}} + w_9\lambda_{I_{EX}} + w_{10}\lambda_{I_{EL}} + w_{11}\lambda_{I_{AH}} + w_{12}\lambda_{cost} \quad (7.32)$$

where w_1, w_2, \dots, w_{13} were the weighting factors obtained from FAHP approach. The design objective of this model was to maximise $F^{weighted\ sum}$ along with structural and property constraints. The optimisation model had become a MINLP model. To produce alternate molecular structures, integer cuts procedure was employed.

7.4.10 Results and discussions

In this work, both acyclic and monocyclic solvents had been designed for all the three cases, where the solvents were recovered through normal evaporation, vacuum evaporation and cooling crystallisation. Figure 7.6 showed molecular structures of the generated acyclic and monocyclic solvents when the designed solvents were to be recovered through normal evaporation. For designed solvents which were recovered through vacuum evaporation, their molecular structures were reported in Figure 7.7. Lastly, the molecular structures for acyclic and monocyclic solvents that recovered through cooling crystallisation were depicted in Figure 7.8.

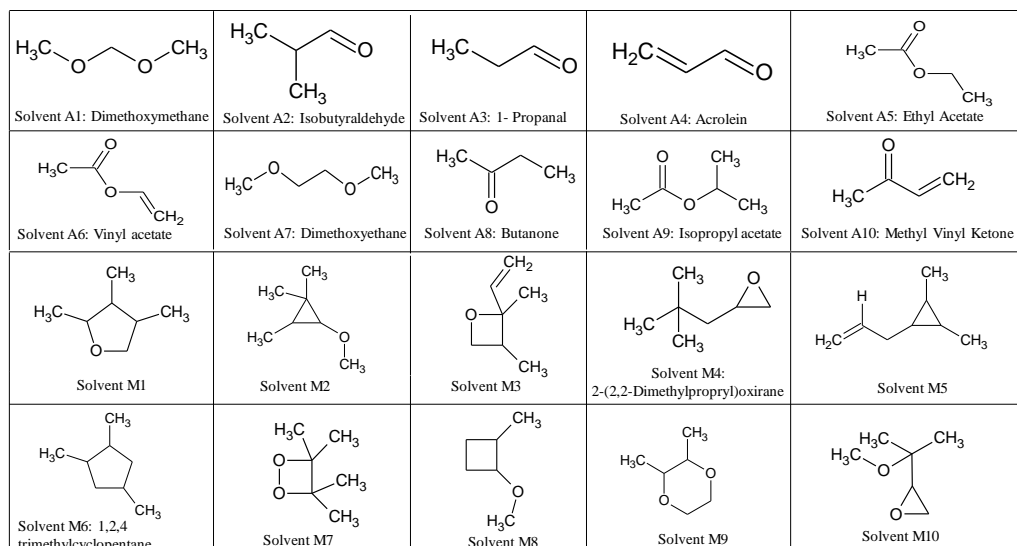


Figure 7.6: Generated acyclic and monocyclic solvents with their respective molecular structures if solvents were to be recovered through normal evaporation

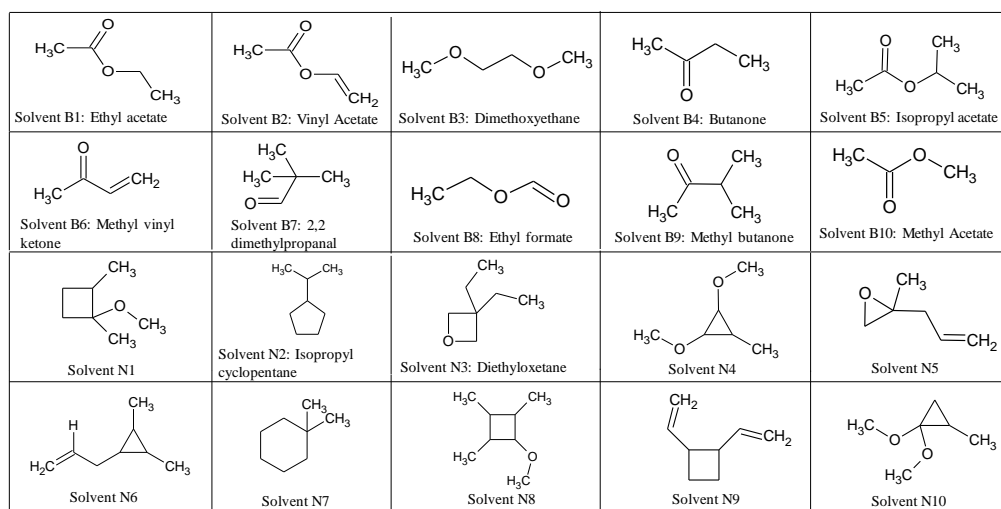


Figure 7.7: Generated acyclic and monocyclic solvents with their respective molecular structures if solvents were to be recovered through vacuum evaporation

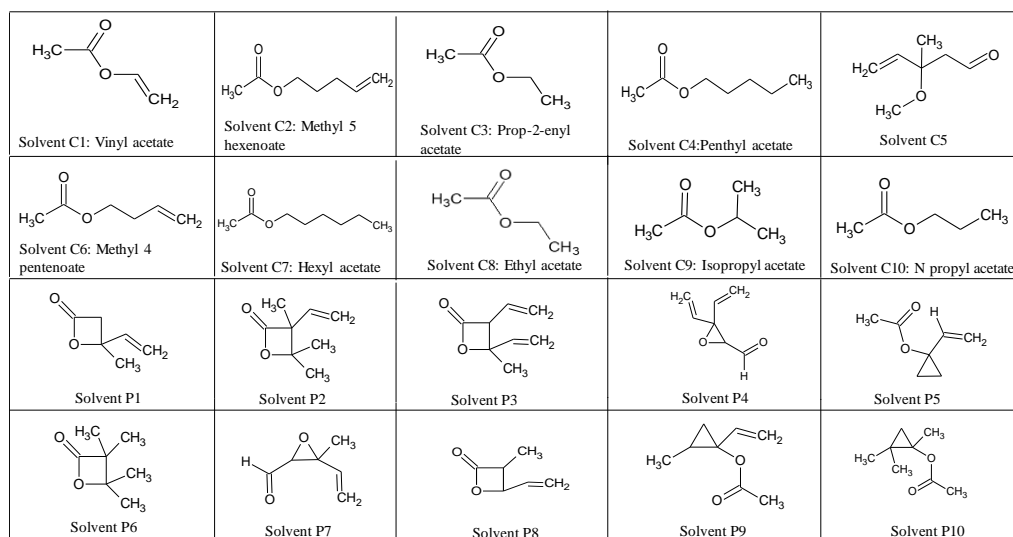


Figure 7.8: Generated acyclic and monocyclic solvents with their respective molecular structures if solvents were to be recovered through cooling crystallisation

The MINLP optimisation model was solved using LINGO 14.0 with global solver by a laptop with Intel® Core™ i7-6500U CPU @ 2.50GHz. Negligible computational time (18 second) was needed for the first generated solution. The properties of top ten generated acyclic and monocyclic solvents for all three cases were reported from Table 7.9 to Table 7.20. Similar to all the previous chapters, the ranking of each molecule was indicated by $F^{weighted\ sum}$. Molecule with the highest $F^{weighted\ sum}$ will have the highest potential for a respective application. Since this ranking was not absolute, the potential molecules will still have to be verified through experiments in a later stage.

From the results, it showed that there will be no carotene degradation if the applied solvents were recovered by cooling crystallisation or vacuum evaporation process. For solvents recovered through normal evaporation process, it was discovered that solvent A5 to solvent A10 were not able to achieve 100%

carotene yield due to their high boiling point. However, solvent A5 to solvent A10 turned out to be the top 6 solvents when designed solvents were assumed to be regenerated through vacuum evaporation. This was because their higher boiling points resulted in carotene degradation when they were recovered through normal evaporation process. Through vacuum evaporation, their boiling points can be suppressed by lower their vapor pressures. In addition to good abilities in extracting carotene (which were indicated by low R_{carotene} values), their better SHE features such as having higher F_p value and lower tendency in causing aquatic toxicity, led to their higher rankings when recovered through vacuum evaporation. Nonetheless, operating cost for vacuum evaporation was at least three times higher compared to normal evaporation process despite no carotene loss. On the other hand, when solvent design was performed by assuming that the solvent will be subjected to cooling crystallisation for recovery, all the designed solvents were able to achieve 100% carotene yield with minimum utilities cost. The reason behind was that energy needed for crystallise small amount of residual oil was remarkably lower compared to the energy required to vaporise large amount of solvents. Besides, the generated acyclic and monocyclic solvents had significantly higher F_p compared to cases where solvents were recovered through normal and vacuum evaporation.

Properties of all designed solvents were then compared with that of hexane. Table 7.8 depicted the properties of hexane. It can be seen that all monocyclic solvents of all three cases have smaller σ compared to that of hexane. This indicated that these solvents will have good surface wetting, which aided their diffusion into PPF for residual oil extraction. When total utilities costs were compared for all cases, it was figured out that cooling crystallisation process was

nearly 6 to 7 times cheaper compared to that of hexane which was recovered using normal evaporation process. The solubility of carotene in all generated solvents was better than hexane as the generated solvents had smaller R_{carotene} . Besides having lower toxicity, all the designed solvents were less likely to accumulate in soil and aquatic organism.

Table 7.8: Properties of Hexane

Property	Property value
T_b (°C)	68.7
σ (mN/m)	17.91
μ (cp)	0.297
R_{carotene} (unit)	2.9
R_{TAG} (unit)	2.3
F_p (°C)	-30.9
$-\log LC_{50}$	4.54
LD_{50} (mg/kg)	28000
PCO	0.43
$\log k_{oc}$	3.62
BCF	51.36
PEL (ppm)	50
S (%)	7.013
I_{FL}	3
I_{EX}	1
Carotene Yield (%)	57.1
Utility cost (\$)	4.6

All generated solutions were then compared with existing solvents in literature. Based on the results obtained by Strati and Oreopoulou, (2011), a higher carotene extraction yield of 42.61 mg/kg can be achieved by using Ethyl acetate (solvent B1) compared to hexane which can only extract 34.45 mg/kg carotene. Moreover, in a recent study, Ethyl acetate was shown to be a better solvent in extracting oil from echium seed at low temperature compared to hexane (Castejón et al., 2018). Despite being the best solvent for the case where it was recovered through vacuum evaporation, Ethyl acetate was also one of the top 10 solvents for the other two cases. 1,2-Dimethoxyethane (Solvent B3) was found to be able to extract the highest yield of algal oil (80.2%) from wet algal biomass compared to other tested solvents such as hexane, chloroform and ethyl

acetate (Liu et al., 2013). In another contribution, 1,2-dimethoxyethane was applied to extract carotene (Treszczanowicz et al., 2003). The solubility of carotene in 1,2-dimethoxyethane was better than that of 2-propanone but lower than that of hexane. Additionally, methyl acetate (Solvent B10) also has the ability in recovering oil from oilseeds (Su et al., 2007). Thus, it can be concluded that all the other generated solvents should have at least or better extraction yield compared to hexane.

Table 7.9: The generated acyclic solvents with their respective properties (normal evaporation process)

Solvent	F _{weightedsum}	Carotene Yield (%)	Utilities Cost (\$)	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	M _w (g/mol)
A1	0.97	100.00	4.02	48.49	20.18	0.31	0.31	0.91	76.10
A2	0.86	100.00	4.84	61.69	22.86	0.44	1.74	2.34	72.11
A3	0.84	100.00	4.96	42.30	23.23	0.41	2.57	3.17	58.08
A4	0.82	100.00	4.82	40.36	24.34	0.34	2.15	2.75	56.06
A5	0.73	59.61	4.65	68.70	23.47	0.43	0.92	1.52	88.11
A6	0.72	61.04	4.50	66.96	24.58	0.36	0.49	1.09	86.09
A7	0.69	46.49	4.81	83.95	20.80	0.38	0.16	0.76	90.12
A8	0.68	57.40	5.02	71.34	23.98	0.37	1.45	2.05	72.11
A9	0.68	44.54	4.78	86.17	23.10	0.46	0.08	0.68	102.13
A10	0.67	58.84	4.85	69.62	25.09	0.31	1.02	1.62	70.09

Table 7.10: The generated acyclic solvents with their respective properties (normal evaporation process) (continued')

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log K _{oc}	I _{FL}	I _{EX}	I _{EL}	I _{AH}
A1	-7.00	14.74	1.16	-2.95	711.06	0.45	3.99	-0.28	3	1	3	1
A2	-1.74	11.34	13.59	-1.16	899.72	1.04	3.83	0.10	3	1	2	1
A3	-6.85	14.74	15.03	-1.21	831.00	1.04	2.54	-0.16	3	1	2	1
A4	-8.01	16.37	0.57	-0.56	558.31	2.77	2.60	-0.40	3	1	4	1
A5	4.52	12.28	194.48	-1.37	1236.33	0.28	14.43	0.17	3	1	1	1
A6	3.36	13.40	7.41	-0.72	840.82	0.74	14.79	-0.06	3	1	3	1
A7	4.52	11.34	0.98	-2.66	759.69	0.41	4.96	0.16	3	1	4	1
A8	1.76	11.34	138.57	-1.73	749.04	0.49	26.66	0.26	3	1	1	1
A9	9.63	9.82	175.78	-1.32	1249.84	0.28	21.78	0.43	3	1	1	1
A10	0.60	12.28	5.28	-1.08	506.77	1.30	27.33	0.02	3	1	3	1

Table 7.11: The generated monocyclic solvents with their respective properties (normal evaporation process)

Solvent	F _{weightedsum}	Carotene Yield (%)	Utilities Cost (\$)	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	M _w (g/mol)
M1	0.93	100	3.51	43.04	3.14	4.41	0.87	1.47	114.19
M2	0.93	100	3.57	48.21	1.92	5.35	0.04	0.64	114.19
M3	0.91	100	3.52	47.17	4.05	5.44	0.02	0.62	112.17
M4	0.89	100	3.64	49.05	2.94	6.52	0.44	1.04	114.19
M5	0.84	100	3.79	51.89	3.10	3.05	0.17	0.77	110.20
M6	0.84	100	3.92	53.74	1.99	3.65	0.59	1.19	112.22
M7	0.82	100	3.85	60.78	2.84	8.97	0.17	0.77	116.16
M8	0.82	100	3.82	40.93	3.49	3.83	1.98	2.58	100.16
M9	0.81	100	3.74	50.86	5.28	6.09	1.83	2.43	116.16
M10	0.81	100	3.80	55.87	4.06	7.39	1.00	1.60	116.16

Table 7.12: The generated monocyclic solvents with their respective properties (normal evaporation process) (continued')

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}	I _{FL}	I _{EX}	I _{EL}	I _{AH}
M1	-19.65	6.69	1290.86	-1.39	459.64	0.98	5.19	1.86	3	1	0	2
M2	-25.24	6.69	396.35	-2.32	451.98	0.48	3.57	1.95	3	1	1	2
M3	-18.80	7.01	44.50	-1.32	300.54	1.81	4.91	1.93	3	1	2	2
M4	-17.65	6.69	1167.29	-1.97	439.56	0.68	4.79	2.17	3	1	0	2
M5	-30.69	5.89	298.04	0.05	351.20	1.59	10.50	2.67	3	1	1	2
M6	-29.53	5.66	7817.70	-0.59	513.82	0.60	10.24	2.90	3	1	0	1
M7	-14.53	8.18	18.80	-3.81	411.15	0.35	1.00	1.19	3	1	2	2
M8	-25.94	7.75	453.82	-1.55	491.75	0.62	2.11	1.58	3	1	1	2
M9	-3.37	8.18	199.47	-1.94	425.21	1.44	2.16	1.00	3	1	1	2
M10	-8.95	8.18	61.25	-2.88	418.12	0.71	1.49	1.10	3	1	2	2

Table 7.13: The generated acyclic solvents with their respective properties (vacuum evaporation process)

Solvent	F _{weightedsum}	Carotene Yield (%)	Utilities Cost (\$)	P ₂ (bar)	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	M _w (g/mol)
B1	0.94	100	10.28	0.71	68.70	23.47	0.43	0.92	1.52	88.11
B2	0.92	100	13.26	0.77	66.96	24.58	0.36	0.49	1.09	86.09
B3	0.90	100	16.48	0.43	83.95	20.80	0.38	0.16	0.76	90.12
B4	0.90	100	15.12	0.69	71.34	23.98	0.37	1.45	2.05	72.11
B5	0.89	100	17.06	0.36	86.17	23.10	0.46	0.08	0.68	102.13
B6	0.88	100	14.79	0.74	69.62	25.09	0.31	1.02	1.62	70.09
B7	0.87	100	17.20	0.42	84.85	22.28	0.71	0.48	1.08	86.13
B8	0.86	100	14.72	0.73	68.95	25.00	0.61	2.70	3.30	74.08
B9	0.85	100	18.14	0.38	88.64	23.60	0.40	0.61	1.21	86.13
B10	0.85	100	16.27	0.56	77.57	25.10	0.42	2.01	2.61	74.08

Table 7.14: The generated acyclic solvents with their respective properties (vacuum evaporation process) (continued')

Solvent	F _p (°C)	S (vol%)	PEL(ppm)	-log LC50	LD50 (mg/kg)	PCO	BCF	log koc	I _{FL}	I _{EX}	I _{EL}	I _{AH}
B1	4.52	12.28	194.48	-1.37	1236.33	0.28	14.43	0.17	3	1	4	1
B2	3.36	13.40	7.41	-0.72	840.82	0.74	14.79	-0.06	3	1	1	1
B3	4.52	11.34	0.98	-2.66	759.69	0.41	4.96	0.16	3	1	1	1
B4	1.76	11.34	138.57	-1.73	749.04	0.49	26.66	0.26	3	1	3	1
B5	9.63	9.82	175.78	-1.32	1249.84	0.28	21.78	0.43	3	1	2	1
B6	0.60	12.28	5.28	-1.08	506.77	1.30	27.33	0.02	3	1	3	1
B7	5.37	9.21	11.11	-1.68	896.31	0.73	5.34	0.66	3	1	2	1
B8	14.54	16.37	2.10	-1.71	840.56	1.53	1.60	-0.76	3	1	3	1
B9	6.87	9.21	125.25	-1.67	780.30	0.49	40.24	0.52	3	1	1	1
B10	10.46	16.37	7.27	-2.63	719.56	0.51	8.29	-0.81	3	1	3	1

Table 7.15: The generated monocyclic solvents with their respective properties (vacuum evaporation process)

Solvent	F _{weightedsum}	Carotene Yield (%)	Utilities Cost (\$)	P ₂ (bar)	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	M _w (g/mol)
N1	0.93	100	11.48	0.77	66.04	2.91	6.12	0.72	1.32	114.19
N2	0.92	100	12.82	0.60	71.19	2.98	4.18	1.27	1.87	112.22
N3	0.92	100	11.67	0.74	66.83	3.93	7.46	1.12	1.72	114.19
N4	0.91	100	11.57	0.73	66.94	4.24	4.69	1.71	2.31	116.16
N5	0.90	100	11.37	0.80	65.07	5.04	6.22	0.70	1.30	112.17
N6	0.90	100	12.43	0.66	69.47	4.09	3.49	0.85	1.45	110.20
N7	0.90	100	14.11	0.48	76.56	2.78	6.18	0.85	1.45	112.22
N8	0.89	100	13.52	0.43	78.49	2.74	4.47	0.31	0.91	128.22
N9	0.89	100	12.08	0.72	67.73	5.21	2.91	0.42	1.02	108.18
N10	0.89	100	12.64	0.58	72.41	4.04	6.94	1.28	1.88	116.16

Table 7.16: The generated monocyclic solvents with their respective properties (vacuum evaporation process) (continued')

Solvent	F _P (°C)	S (vol%)	PEL(ppm)	-log LC50	LD50 (mg/kg)	PCO	BCF	log koc	I _{FL}	I _{EX}	I _{EL}	I _{AH}
N1	-18.82	6.69	370.92	-2.08	467.54	0.43	2.94	2.14	3	1	1	2
N2	-23.12	5.66	7316.09	-0.36	531.51	0.53	8.44	3.10	3	1	0	1
N3	-11.23	6.69	1092.39	-1.73	454.69	0.60	3.95	2.36	3	1	0	2
N4	-12.13	8.18	21.52	-2.41	465.05	0.65	0.99	0.76	3	1	2	2
N5	-12.39	7.01	41.65	-1.08	310.89	1.61	4.04	2.12	3	1	2	2
N6	-24.27	5.89	278.92	0.29	363.29	1.42	8.65	2.86	3	1	1	2
N7	-21.11	5.66	6615.75	-0.94	508.29	0.37	7.79	3.40	3	1	0	1
N8	-15.73	5.89	370.75	-1.45	478.73	0.63	4.81	2.09	3	1	1	2
N9	-25.43	6.13	10.63	0.94	248.24	3.80	8.87	2.62	3	1	2	2
N10	-10.13	8.18	19.46	-2.99	444.73	0.45	0.91	1.07	3	1	2	2

Table 7.17: The generated acyclic solvents with their respective properties (cooling crystallisation process)

Solvent	F _{weightedsum}	Carotene Yield (%)	Utilities Cost (\$)	T _m (°C)	T _b (°C)	σ (mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	M _w (g/mol)
C1	0.813	100	0.66	-94.4	66.9	24.5	0.36	0.49	1.09	86.09
C2	0.807	100	0.67	-61.4	155.1	26.4	0.67	0.03	0.63	128.17
C3	0.784	100	0.66	-82.5	100	25.2	0.44	0.34	0.94	100.12
C4	0.777	100	0.69	-64.1	156.3	25.3	0.81	0.45	1.05	130.19
C5	0.762	100	0.68	-4.45	170.8	26.3	1.27	0.15	0.75	128.17
C6	0.761	100	0.67	-71.6	129.1	25.8	0.54	0.18	0.78	114.14
C7	0.759	100	0.69	-54.4	179.7	25.9	1.00	0.30	0.90	144.21
C8	0.759	100	0.68	-97.8	68.7	23.4	0.43	0.92	1.52	88.11
C9	0.746	100	0.68	-94.6	86.1	23.1	0.46	0.08	0.68	102.13
C10	0.740	100	0.68	-85.6	101.5	24.1	0.53	0.76	1.36	102.13

Table 7.18: The generated acyclic solvents with their respective properties (cooling crystallisation process) (continued')

Solvent	F _P (°C)	S (vol%)	PEL (ppm)	-log LC ₅₀	LD ₅₀ (mg/kg)	PCO	BCF	log k _{oc}	I _{FL}	I _{EX}	I _{EL}	I _{AH}
C1	3.36	13.40	7.41	-0.72	840.82	0.74	14.8	-0.06	3	1	3	1
C2	37.92	7.36	4.49	0.14	919.00	0.54	28.5	1.28	2	1	3	1
C3	14.88	10.53	6.27	-0.43	882.10	0.67	18.4	0.39	3	1	3	1
C4	39.08	7.01	117.70	-0.50	1341.12	0.20	27.8	1.52	2	1	1	1
C5	47.47	7.36	0.01	-1.08	637.26	1.47	3.27	0.70	2	1	4	1
C6	26.40	8.67	5.30	-0.14	907.24	0.60	22.9	0.83	3	1	3	1
C7	50.60	6.13	99.56	-0.22	1340.19	0.18	34.6	1.97	2	1	2	1
C8	4.52	12.28	194.48	-1.37	1236.33	0.28	14.4	0.17	3	1	1	1
C9	9.63	9.82	175.78	-1.32	1249.84	0.28	21.8	0.43	3	1	1	1
C10	16.04	9.82	164.50	-1.08	1292.87	0.25	17.9	0.62	3	1	1	1

Table 7.19: The generated monocyclic solvents with their respective properties (cooling crystallisation process)

Solvent	F _{weightedsum}	Carotene Yield (%)	Utilities Cost (\$)	T _m (°C)	T _b (°C)	σ(mN/m)	μ (cp)	R _{carotene} (unit)	R _{TAG} (unit)	M _w (g/mol)
P1	0.72	100	0.66	-84.15	71.95	8.81	7.35	2.29	2.89	112.13
P2	0.70	100	0.66	-50.12	110.00	7.86	12.69	0.20	0.80	140.18
P3	0.70	100	0.66	-67.54	118.14	10.17	8.19	0.88	1.48	138.16
P4	0.70	100	0.65	-35.64	121.18	10.64	79.77	1.94	2.54	124.14
P5	0.69	100	0.66	-73.07	104.37	9.43	9.09	2.14	2.74	126.15
P6	0.69	100	0.67	-62.19	80.03	6.13	12.31	0.78	1.38	128.17
P7	0.68	100	0.66	-46.51	92.64	8.90	77.35	2.52	3.12	112.13
P8	0.68	100	0.67	-121.02	66.48	9.01	4.97	2.72	3.32	112.13
P9	0.68	100	0.67	-70.38	119.55	9.06	9.82	1.31	1.91	140.18
P10	0.67	100	0.68	-52.64	111.46	6.75	15.22	0.62	1.22	142.20

Table 7.20: The generated monocyclic solvents with their respective properties (cooling crystallisation process) (continued')

Solvent	F _P (°C)	S (vol%)	PEL(ppm)	-log LC50	LD50 (mg/kg)	PCO	BCF	log koc	I _{FL}	I _{EX}	I _{EL}	I _{AH}
P1	-4.87	9.21	137.33	-0.82	514.53	0.74	2.24	1.04	3	1	1	1
P2	7.35	6.69	101.46	-1.29	467.84	0.52	4.72	1.86	3	1	1	2
P3	10.60	7.01	4.00	0.17	347.16	1.78	4.32	1.51	3	1	3	2
P4	-4.58	8.18	0.38	-0.73	129.32	8.91	0.91	0.95	3	1	4	2
P5	6.65	7.75	116.17	-0.53	522.22	0.66	2.79	1.49	3	1	1	1
P6	-3.01	7.36	3146.15	-2.23	681.27	0.22	3.70	1.65	3	1	0	1
P7	-14.95	9.21	11.82	-1.66	186.04	3.71	0.72	0.74	3	1	2	2
P8	-6.88	9.21	151.87	-0.23	538.03	1.07	2.43	0.73	3	1	1	1
P9	11.75	6.69	105.00	-0.47	506.06	0.67	4.21	1.74	3	1	1	1
P10	8.51	6.40	2661.21	-1.94	681.83	0.19	4.61	2.10	3	1	0	1

7.5 Summary

In this chapter, the effect of various separation techniques on solvent selection was integrated into multi-objective CAMD framework. The main contribution of this improved methods was that the entire solvent application steps were considered during solvent design. This CAMD framework considered the whole cycle of solvent from its application to its recovery process. Despite having expected functionalities, the designed solvents can be recovered through a more economically viable separation technique. Normal evaporation, vacuum evaporation and cooling crystallisation were the separation techniques selected to evaluate its effect on solvent design in this work. Other than targeted properties, utilities cost consumption together with process performance were incorporated into CAMD framework. A case study on the solvent design for extracting residual oil from PPF was solved to demonstrate the proposed methodology. The results showed that most of the generated solvents offered better performance in terms of functionalities and SHE properties than that of hexane. Besides, it showed that solvent recovery through cooling crystallisation was the cheapest pathway since the utilities cost was significantly lower than that of normal and vacuum evaporation. Hence, it can be concluded that by considering both solvent application and its recovery process simultaneously, it can maximise process performance and enhance the overall cost saving.

CHAPTER 8

CONCLUSION

This chapter concludes all the research works that had been presented in this thesis. The research gaps presented in Section 3.1 were successfully filled in through the completion of research scopes proposed in Section 3.2. This thesis provides several important contributions which aided in integrating environmental aspects into Computer Aided Molecular Design (CAMD). Nevertheless, there still exists several opportunities to extend and enhance the developed approaches in this area of interest.

8.1 Achievements

The overall achievements of this research include the development of mathematical models to quantify the subjectivity involved in eliciting value judgements for various multi-objective molecular design problems. The following developed methodology emphasized on the effect of molecular design on environmental aspects of its recovery process. Later, the methodology was further extended to integrate different separation techniques into CAMD framework for evaluating their effects on molecular design in terms of process performance and economic. A case study on solvent design for residual oil extraction from palm pressed fibre (PPF) had been applied to demonstrate all the proposed methodologies. The detailed explanation of each achievement is given below:

8.1.1 Integration of physical and environmental properties into CAMD framework through AHP

First of all, environmental aspect along with physicochemical properties were successfully incorporated into multi-objective CAMD framework through the newly developed approach. The integration of Analytic Hierarchy Process (AHP) into CAMD framework was able to treat rigorously the inherent subjectivity in assessing the relative importance of each property involved in CAMD problem. AHP approach provides a systematic procedure to obtain ratio-scale priority weights from the value judgement of decision maker. Thus, this AHP-CAMD framework addressed the limitation in multi-objective CAMD problem by enabling consistent weighting factors to be allocated to each objective. Through this approach, a molecule with optimum product functionality and environmental properties can be generated.

8.1.2 Incorporation of SHE aspects into CAMD framework via FAHP

Another achievement was the development of a CAMD framework embedded with Fuzzy Analytic Hierarchy Process (FAHP) approach to manage the highly subjectivity nature of multi-objective molecular design problem. It was aware that in some situations, safety, health and environmental (SHE) aspects together with physicochemical properties were considered in molecular design problems. In such cases, nature of the problem became more fuzzy and complex because the information needed for evaluating their relative importance is more uncertain compared to the situation that considered only physicochemical and environmental properties. Because of this, confidence level

of decision maker is often affected when performing pairwise comparison. It becomes harder for a decision maker to allocate exact numerical values when elicit the judgement. Via FAHP approach, confidence level of decision makers can be captured through fuzzy scale when performing pairwise comparison. Based on the results obtained from case study, solvent that provided a better balance of performance and SHE aspects can be generated.

8.1.3 Development of a systematic CAMD framework that considers quantitative assessment of environmental impact of solvent recovery process

The subsequent developed CAMD methodology successfully quantified environmental impact of solvent recovery process instantaneously when a solvent was generated. LCA GREET model 2016 database was accessed to identify a list of factors for converting energy consumption into greenhouse gases emissions. After estimating greenhouse gases emissions based on energy consumption, IChemE Sustainability Metrics had been utilized for evaluating the environmental performance of solvent recovery process. Besides being able to fulfil all the predefined properties, solvents generated through this framework managed to minimise the energy requirement and environmental burden of their recovery processes.

8.1.4 Development of a systematic CAMD framework that considers the effect of various solvent recovery processes on solvent selection

The fourth contribution was the development of a systematic CAMD methodology that took entire solvent application steps into consideration. Both application and regeneration of solvents were considered when performing solvent design step. In addition to targeted properties, process performance and operating cost were also integrated into CAMD framework. Hence, solvents that were designed through this method can simultaneously achieve optimal performance for its application and being recovered using a cheaper separation technique. As a whole, this thesis presented various novel approaches with the purpose of designing solvents with improved environmental characteristic that can simultaneously maximise its process economic.

8.2 Future Works

When developing the presented methodologies, there were some aspects not being taken into consideration. There exist several opportunities to improve and enhance these methodologies for this area of research. The potential future works are categorised into short-term and long-term plans. The short-term plans can be referred to Section 8.2.1 to Section 8.2.3 whereas Section 8.2.4 refers to the work that needs a longer period of time to complete.

8.2.1 Develop a systematic CAMD methodology to optimise the minimum deviation from the best profit that leads to huge improvement in SHE aspects

Apart from process operating cost, capital cost and product cost should also be considered along with other target properties to determine the optimal process-product combination for the design of chemical solvent. Separation techniques not only affect the selection of separation equipment but also equipment such as compressor, pump, rotary filter etc. Each of these equipment is associated with different capital cost. In addition, although both process operating cost and SHE aspects had been selected as design objective in CAMD framework, the generated results may not be 'ideal' for business stakeholders. This was mainly because there might be a huge sacrifice in process profit for having a trade-off solution with good SHE features. For this reason, a systematic methodology should be developed to optimise the minimum deviation allowed from the best profit that will lead to a huge improvement in SHE characteristics. Business stakeholders can then identify their optimal results since a trend that showed real significance between the results can be obtained through this proposed methodology.

8.2.2 Consideration of social aspect in product-process design framework

Since there is a growing awareness on sustainability development, integrated product-process design framework should also move towards a sustainable future. Other than economic and SHE aspects that were previously considered, there is a need to incorporate social aspect in CAMD design. Social

concerns usually include employment opportunities, process safety and health risk, societal income etc. Even though some safety and health properties had been chosen as criteria during solvent design, social metrics that involve the quantification of equipment process safety, process reliability as well as health risks associated with a product-process design were not included. The integrated product-process design framework can be extended to take all of these social concerns into considerations to assist in designing a sustainable framework.

8.2.3 Develop a sustainable integrated product-process framework through Analytic Network Process

The main concepts in driving sustainable development was the interdependence of economy, environment and society. When integrated product-process design framework considered all the sustainability elements, a better mathematical model should be developed for capturing their interrelationships. For example, a safe product-process system will usually result in a lower process profit due to the instalment of extra safety layer. Thus, it shows that economic aspect is indirectly dependent on SHE characteristics of the product-process system. In such cases, AHP and/ or FAHP is no longer suitable for evaluating the relative importance of each criterion. The assumption made for AHP and/or FAHP is that each criterion is independent of each other. To solve this issue, Analytic Network Process (ANP) can be applied. ANP is a useful tool for addressing more complex decision structure when there are network dependencies and interrelations among the criteria. Instead of decomposing the decision problem into hierarchy structure, ANP uses a network

which is made up of clusters of elements to model the problem. In ANP, all the elements of network can interact with each other and can be classified into inner dependency and outer dependency. Inner dependency occurs when some elements of one cluster influence each other whereas outer dependency happens when elements of a cluster affect elements in another cluster.

8.2.4 Validation of CAMD solutions through experimental works

Furthermore, experimental works should be carried out after molecular design stage to verify the performance of designed solvents. Since the solvents were designed solely based on theoretical knowledge, these solvents may not necessarily reach the expected performance when they are applied in the real process. This is because there will be uncertainties in property prediction models used for predicting the properties of designed solvents. Besides, some information and/or parameters were assumed when the experimental data was not available. Hence, to validate the performance of designed solvents based on assumed parameters, experimental works should be performed. Instead of testing the performance of all available solvents through trial and error approach, CAMD techniques are powerful tools that can shortlist the potential solvents from a huge database. After obtaining a ranked list of optimal solvents using CAMD framework, these shortlisted solvents should be tested for their performances in laboratory. The actual performance of these solvents can then be compared with the theoretical performance using CAMD framework. If theoretical performance of solvent were on par with its actual result, this means that the designed solvent can be utilised for real application.

In conclusion, these proposed plans are important in bringing a huge breakthrough in this area of research. A CAMD methodology that optimises the deviation from the best revenue that brings great improvement in SHE aspects is important for business stakeholders. This methodology can aid stakeholders in identifying whether a project is worth for investment. In addition, by developing a mathematical model for incorporating all sustainability elements into integrated product-process design framework, their actual interdependencies can be captured. This sustainable integrated product-process framework can then be applied in various chemical industries. Last but not least, experimental works should be performed to further validate the performance of shortlisted solvents from CAMD techniques. The combination of both CAMD techniques and experimental works can certainly further enhance research output and quality.

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APPENDICES

This chapter presents the coding used to develop the CAMD programming model with LINGO software (version 14.0).

Appendix A: Lingo Coding (Chapter 4)

```
model:

!objective function;

max = obj_function; @free(obj_function);

obj_function = 0.4433*Tb + 0.081*sol + 0.1545*st + 0.1545*vis +
0.0311*LC50 + 0.0159*LD50 + 0.0991*PCO + 0.0103*BCF + 0.0103*KOW;

!For acyclic compound;
Tb = (4.2146 - tb_total)/(4.2146 - 3.6044); @free(Tb);

sol = (2.697 - Diff_car)/(2.697 - 0.3102);@free(sol);

st = (25.1026 - st_total)/(25.1026 - 20.1833);@free(st);

vis = (-0.4904 - vis_total)/(-0.4904 + 1.1851);@free(vis);

LC50 = (1.9233 - LC50_total)/(1.9233 + 1.2578);@free(LC50);

LD50 = (0.0915 - LD50_total)/(0.0915 + 0.1857);@free(LD50);

PCO = (PCO_total + 0.4427)/(0.3461 + 0.4427);@free(PCO);

BCF = (1.4366 - BCF_total)/(1.4366 - 0.2037);@free(BCF);

KOW = (0.3862 - logkow_total)/(0.3862 + 0.7509);@free(KOW);

!For monocyclic compound;
!Tb = (4.2389 - tb_total)/(4.2389 - 3.6129); !@free(Tb);

!sol = (2.7909 -Diff_car)/(2.7909 - 0.0181);!@free(sol);

!st = (7.489 - st_total)/(7.489 - 1.7853);!@free(st);

!vis = (4.171 - vis_total)/(4.171 - 1.067);!@free(vis);

!LC50 = (3.1332 - LC50_total)/(3.1332 + 2.1457);!@free(LC50);

!LD50 = (0.8022 - LD50_total)/(0.8022 - 0.1561);!@free(LD50);

!PCO = (PCO_total + 0.795)/(0.4584 + 0.795);!@free(PCO);

!BCF = (1.0211 - BCF_total)/(1.0211 + 0.5468);!@free(BCF);

!KOW = (3.4101 - logkow_total)/(3.4101 + 0.4278);!@free(KOW);

!Defining the chemical building blocks
```

```

n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13;
H_number = n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13;
O_number = n5+n6*2+n7+n8+n9+n12+n13;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
n5+n6+n7+n8+n10 <3;

!Free bonds for each group;
val1 = 1;
val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;
val8 = 1;
val9 = 1;
val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;

!Structural constraint, the molecule generated must not contain
free bonds;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13) + 2 =
0; !monocyclic compound;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13) =
0; !acyclic compound;

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);

```

```

!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);
LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);
LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);
LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);
LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);
PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);

```

```

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);
BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);
BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);
BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);
BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;
mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;

!Group contribution for flash point;
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);
sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);
sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);

```

```

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);
vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);
st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);
st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);

!Property Constraints;
!Equation for normal boiling point;
tb_total =
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13; @free(tb_total);

!Equation for viscosity (vis);
vis_total =
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13;
@free(vis_total);

!Equation for surface tension (st);
st_total =
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13; @free(st_total);

!Equation for solubility (sol);
sol_total =
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13;
@free(sol_total);

!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacglycerol = 17.1822MPa;
!sol0= 21.6654 MPa (sol0 = solubility constant);

```



```

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

sol_final < 20.6;
sol_final > 14.4;

tb_total < 4.239;
tb_total > 3.599;

!Equation for molecular weight (mw);
mw_total =
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13;

!Equation for flash point (fp);
fp_total =
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13; @free(fp_total);

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

fp > 242;

!Equation for aquatic toxicity (LC50);
LC50_total =
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013;
@free(LC50_total);

!Equation for terrestrial toxicity (LD50);
LD50_total =
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013;
@free(LD50_total);

!Equation for photochemical oxidation potential (PCO);
PCO_total =
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13;
@free(PCO_total);

```

```

!Equation for bioconcentration factor (BCF);
BCF_total =
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13;
@free(BCF_total);

BCF_total < 3.3;

!Equation for octanol-water partition coefficient (logKow);
logkow_total =
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

End

```

Appendix B: Lingo Coding (Chapter 5)

Part A: Weighting factor obtained by FAHP approach

```

model:

!objective function;

max = obj_function; !@free(obj_function);

obj_function = 0.1618*Tb + 0.0312*sol + 0.0587*st + 0.0587*vis +
0.0154*LC50 + 0.0556*PCO + 0.0067*BCF + 0.0067*KOW +
0.2603*Iflfinal + 0.2603*Iex + 0.0507*Ielfinal + 0.0507*IAHfinal;

ISHI_total = 0.2603*Iflfinal + 0.2603*Iex + 0.0507*Ielfinal +
0.0507*IAHfinal; @free(ISHI_total);

!For acyclic compound;
!Tb = (4.2146 - tb_total)/(4.2146 - 3.6044); !@free(Tb);

!sol = (2.697 - Diff_car)/(2.697 - 0.3102); !@free(sol);

!st = (25.1026 - st_total)/(25.1026 - 20.1833); !@free(st);

!vis = (-0.4904 - vis_total)/(-0.4904 + 1.1851); !@free(vis);

!LC50 = (1.9233 - LC50_total)/(1.9233 + 1.2578); !@free(LC50);

!LD50 = (0.0915 - LD50_total)/(0.0915 + 0.1857); !@free(LD50);

!PCO = (PCO_total + 0.4427)/(0.3461 + 0.4427); !@free(PCO);

!BCF = (1.4366 - BCF_total)/(1.4366 - 0.2037); !@free(BCF);

```

```

!KOW = (0.3862 - logkow_total)/(0.3862 + 0.7509);!@free(KOW);

!Iflfinal = Ifl/3; !@free(Iflfinal);

!Ielfinal = (4-Iel)/(4-1); !@free(Ielfinal);

!IAHfinal = IAH/1; !@free(IAHfinal);

!For monocyclic compound;
Tb = (4.2389 - tb_total)/(4.2389 - 3.6129); @free(Tb);

sol = (2.7909 - Diff_car)/(2.7909 - 0.0181);@free(sol);

st = (7.489 - st_total)/(7.489 - 1.7853);@free(st);

vis = (4.171 - vis_total)/(4.171 - 1.067);@free(vis);

LC50 = (3.1332 - LC50_total)/(3.1332 + 2.1457);@free(LC50);

LD50 = (0.8022 - LD50_total)/(0.8022 - 0.1561);@free(LD50);

PCO = (PCO_total + 0.795)/(0.4584 + 0.795);@free(PCO);

BCF = (1.0211 - BCF_total)/(1.0211 + 0.5468);@free(BCF);

KOW = (3.4101 - logkow_total)/(3.4101 + 0.4278);@free(KOW);

Iflfinal = Ifl/3; @free(Iflfinal);

Ielfinal = (4-Iel)/(4-0); @free(Ielfinal);

IAHfinal = (2-IAH)/(2-1); @free(IAHfinal);

!Defining the chemical building blocks
n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13;
H_number = n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13;
O_number = n5+n6*2+n7+n8+n9+n12+n13;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
n5+n6+n7+n8+n10 <3;

!Free bonds for each group;
val1 = 1;
val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;

```

```

val8 = 1;
val9 = 1;
val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;

!Structural constraint, the molecule generated must not contain
free bonds;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13-1))          -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13)          +    2    =
0; !monocyclic compound;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13-1))          -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13)          =
0; !acyclic compound;

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);

!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);
LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);

```

```

LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);
LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);
LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);

!constant for LD50;
A= 1.9372;
B= 0.0016;

!calculate for LD50 in mol/kg;
LD50_mol = 10^(-(LD50_total + A + B*mw_total)); @free(LD50_mol);

!Calculate for LD50 in mg/kg;
LD50_mg = LD50_mol*mw_total*1000; @free(LD50_mg);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);
PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);
BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);
BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);
BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);
BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;

```

```

mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;

!Group contribution for flash point;
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);
sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);
sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);
vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);

```

```

st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);
st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);

!Group contribution for permissible exposure limit (PEL);
PEL1 = 0.7723; @free(PEL1);
PEL2 = 0.0727; @free(PEL2);
PEL3 = -0.6557; @free(PEL3);
PEL4 = -1.3404; @free(PEL4);
PEL5 = 1.3612; @free(PEL5);
PEL6 = 2.3281; @free(PEL6);
PEL7 = 1.4016; @free(PEL7);
PEL8 = 2.3662; @free(PEL8);
PEL9 = 2.1251; @free(PEL9);
PEL10 = 2.0449; @free(PEL10);
PEL11 = 2.2638; @free(PEL11);
PEL12 = 0.9276; @free(PEL12);
PEL13 = -0.7462; @free(PEL13);

!Property Constraints;
!Equation for normal boiling point;
tb_total =
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13; @free(tb_total);

!Equation for viscosity (vis);
vis_total =
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13;
@free(vis_total);

!Equation for surface tension (st);
st_total =
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13; @free(st_total);

!Equation for solubility (sol);
sol_total =
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13;
@free(sol_total);

!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacglycerol = 17.1822MPa;
!sol0= 21.6654 MPa (sol0 = solubility constant);

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

```

```

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

sol_final < 20.6;
sol_final > 14.4;

tb_total < 4.239;
tb_total > 3.599;

!Equation for molecular weight (mw);
mw_total =
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13;

!Equation for flash point (fp);
fp_total =
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13; @free(fp_total);

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

fp > 242;

fpcelcius = fp - 273.15; @free(fpcelcius);

!Equation for aquatic toxicity (LC50);
LC50_total =
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013;
@free(LC50_total);

!Equation for terrestrial toxicity (LD50);
LD50_total =
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013;
@free(LD50_total);

!Equation for photochemical oxidation potential (PCO);
PCO_total =
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13;
@free(PCO_total);

```



```

!Equation for bioconcentration factor (BCF);
BCF_total =
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13;
@free(BCF_total);

BCF_total < 3.3;

!Equation for octanol-water partition coefficient (logKow);
logkow_total =
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

!Equation for permissible exposure limit (PEL);
PEL_total =
n1*PEL1+n2*PEL2+n3*PEL3+n4*PEL4+n5*PEL5+n6*PEL6+n7*PEL7+n8*PEL8
+n9*PEL9+n10*PEL10+n11*PEL11+n12*PEL12+n13*PEL13;
@free(PEL_total);

!Calculate PEL in ppm;
!molar volume of gas, Vgas, in dm3/mol, Note that 1L=1dm3;
Vgas = 24.45;
PEL = Vgas*1000*10^(-PEL_total);

!Calculate for oxygen stoichiometric coefficient, Co;
Co = C_number + (H_number/4) - (O_number/2);

!Calculate for Lower explosion limit, LEL;
LEL = (100/(1+9.045*Co));

!Calculate for Upper explosion limit, UEL;
UEL = (100/(1+1.1843*Co));

!Calculate explosiveness, Iex using S= (UEL - LEL)vol%;
S = UEL - LEL;

!Disjunctive equation for explosiveness, Iex;
Iex = Iex1 + Iex2 + Iex3 +1; @bin(Iex1); @bin(Iex2); @bin(Iex3);
(0-20)*(1-Iex1) < S - 20;
S - 20 <= (100 - 20)*(Iex1);
(0-45)*(1-Iex2) < S - 45;
S - 45 <= (100 - 45)*(Iex2);
(0-70)*(1-Iex3) < S - 70;
S - 70 <= (100 - 70)*(Iex3);

!!Disjunctive equation for acute health hazard;
IAH = IAH1 + IAH2 + IAH3 + IAH4; @bin(IAH1); @bin(IAH2);
@bin(IAH3); @bin(IAH4);
(0.00001-2000)*(IAH1) < LD50_mg- 2000;
LD50_mg- 2000 <= (10000 - 2000)*(1-IAH1);
(0.00001-500)*(IAH2) < LD50_mg - 500;
LD50_mg- 500 <= (10000 - 500)*(1-IAH2);
(0.00001-50)*(IAH3) < LD50_mg - 50;
LD50_mg - 50 <= (10000 - 50)*(1-IAH3);

```

```

(0.00001-5)*(IAH4) < LD50_mg- 5;
LD50_mg - 5 <= (10000 - 5)*(1-IAH4);

!Calculate for Tb in C;
!Tb constant,tb0 in K;
tb0 = 244.5165;
Tbcelcius = @log(tb_total)*tb0 -273.15; @free(Tbcelcius);

!Disjunctive equation for volatility;
!Iv = Iv1 + Iv2 + Iv3; @bin(Iv1); @bin(Iv2); @bin(Iv3);
!(-10000-150)*Iv1 < Tbcelcius - 150;
!Tbcelcius - 150 <= (10000 - 150)*(1-Iv1);
!(-10000-50)*Iv2 < Tbcelcius - 50;
!Tbcelcius - 50 <= (10000 - 50)*(1-Iv2);
!(-10000-0)*Iv3 < Tbcelcius - 0;
!Tbcelcius - 0 <= (10000 - 0)*(1-Iv3);

!Disjunctive equation for material phase;
! To ensure solvent boiling pt in between (40-80C) and it should
be a liquid;
!Ims = Ims1 + 1; @bin (Ims1);
!(39.99-80)*Ims1 < Tbcelcius - 80;
!Tbcelcius - 80 <= (10000 - 80)* (1-Ims1);

!Disjunctive equation for flammability. Ifl;
Ifl = Ifl1 + Ifl2 + Ifl5 + 1; @bin(Ifl1); @bin(Ifl2); @bin(Ifl3);
@bin(Ifl4); @bin(Ifl5);
(-1000-93.4)*(Ifl1) < Fpcelcius - 93.4;
Fpcelcius - 93.4 <= (10000-93.4)*(1-Ifl1);
(-1000-37.8)*(Ifl2) < Fpcelcius - 37.8;
Fpcelcius - 37.8 <= (10000-37.8)*(1-Ifl2);
(-1000-22.8)*(Ifl3) < Fpcelcius - 22.8;
Fpcelcius - 22.8 <= (10000-22.8)*(1-Ifl3);
(-1000-37.8)*(Ifl4) < Tbcelcius - 37.8;
Tbcelcius - 37.8 <= (10000-37.8)*(1-Ifl4);
Ifl3 + Ifl4 = g;
(0-2)*(1-Ifl5) < g- 2;
g - 2 <= (5-2)*Ifl5;

!Disjunctive equation for exposure limit, Iel;
Iel = Iel1 + Iel2 + Iel3 + Iel4; @bin(Iel1); @bin(Iel2);
@bin(Iel3); @bin(Iel4);
(0.0001-1000)*(Iel1) < PEL -1000;
PEL - 1000 <= (10000 - 1000)*(1-Iel1);
(0.0001-100)*(Iel2) < PEL -100;
PEL - 100 <= (10000 - 100)*(1-Iel2);
(0.0001-10)*(Iel3) < PEL -10;
PEL - 10 <= (10000 - 10)*(1-Iel3);
(0.0001-1)*(Iel4) < PEL -1;
PEL - 1 <= (10000 - 1)*(1-Iel4);

End

```

Part B: Assume equal weighting factor

model:

!objective function;

```

max = obj_function; !@free(obj_function);

obj_function = 0.0833*Tb + 0.0833*sol + 0.0833*st + 0.0833*vis +
0.0833*LC50 + 0.0833*PCO + 0.0833*BCF + 0.0833*KOW +
0.0833*Iflfinal + 0.0833*Iex + 0.0833*Ielfinal + 0.0833*IAHfinal;

ISHI_total = 0.25*Ifl + 0.25*Iex + 0.25*Iel + 0.25*IAH;
@free(ISHI_total);

!For acyclic compound;
!Tb = (4.2146 - tb_total)/(4.2146 - 3.6044); !@free(Tb);

!sol = (2.697 - Diff_car)/(2.697 - 0.3102);!@free(sol);

!st = (25.1026 - st_total)/(25.1026 - 20.1833);!@free(st);

!vis = (-0.4904 - vis_total)/(-0.4904 + 1.1851);!@free(vis);

!LC50 = (1.9233 - LC50_total)/(1.9233 + 1.2578);!@free(LC50);

!LD50 = (0.0915 - LD50_total)/(0.0915 + 0.1857);!@free(LD50);

!PCO = (PCO_total + 0.4427)/(0.3461 + 0.4427);!@free(PCO);

!BCF = (1.4366 - BCF_total)/(1.4366 - 0.2037);!@free(BCF);

!KOW = (0.3862 - logkow_total)/(0.3862 + 0.7509);!@free(KOW);

!Iflfinal = Ifl/3; !@free(Iflfinal);

!Ielfinal = (4-Iel)/(4-1); !@free(Ielfinal);

!IAHfinal = IAH/1; !@free(IAHfinal);

!For monocyclic compound;
Tb = (4.2389 - tb_total)/(4.2389 - 3.6129); @free(Tb);

sol = (2.7909 - Diff_car)/(2.7909 - 0.0181);@free(sol);

st = (7.489 - st_total)/(7.489 - 1.7853);@free(st);

vis = (4.171 - vis_total)/(4.171 - 1.067);@free(vis);

LC50 = (3.1332 - LC50_total)/(3.1332 + 2.1457);@free(LC50);

LD50 = (0.8022 - LD50_total)/(0.8022 - 0.1561);@free(LD50);

PCO = (PCO_total + 0.795)/(0.4584 + 0.795);@free(PCO);

BCF = (1.0211 - BCF_total)/(1.0211 + 0.5468);@free(BCF);

KOW = (3.4101 - logkow_total)/(3.4101 + 0.4278);@free(KOW);

Iflfinal = Ifl/3; @free(Iflfinal);

Ielfinal = (4-Iel)/(4-0); @free(Ielfinal);

IAHfinal = (2-IAH)/(2-1); @free(IAHfinal);

!Defining the chemical building blocks

```

```

n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13;
H_number = n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13;
O_number = n5+n6*2+n7+n8+n9+n12+n13;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
n5+n6+n7+n8+n10 <3;

!Free bonds for each group;
val1 = 1;
val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;
val8 = 1;
val9 = 1;
val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;

!Structural constraint, the molecule generated must not contain
free bonds;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13) + 2 =
0; !monocyclic compound;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13) =
0; !acyclic compound;

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);

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!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);
LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);
LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);
LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);
LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);

!constant for LD50;
A= 1.9372;
B= 0.0016;

!calculate for LD50 in mol/kg;
LD50_mol = 10^(-(LD50_total + A + B*mw_total)); @free(LD50_mol);

!Calculate for LD50 in mg/kg;
LD50_mg = LD50_mol*mw_total*1000; @free(LD50_mg);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);

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PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);
BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);
BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);
BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);
BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;
mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;

!Group contribution for flash point;
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);

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sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);
sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);
vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);
st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);
st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);

!Group contribution for permissible exposure limit (PEL);
PEL1 = 0.7723; @free(PEL1);
PEL2 = 0.0727; @free(PEL2);
PEL3 = -0.6557; @free(PEL3);
PEL4 = -1.3404; @free(PEL4);
PEL5 = 1.3612; @free(PEL5);
PEL6 = 2.3281; @free(PEL6);
PEL7 = 1.4016; @free(PEL7);
PEL8 = 2.3662; @free(PEL8);
PEL9 = 2.1251; @free(PEL9);
PEL10 = 2.0449; @free(PEL10);
PEL11 = 2.2638; @free(PEL11);
PEL12 = 0.9276; @free(PEL12);
PEL13 = -0.7462; @free(PEL13);

!Property Constraints;
!Equation for normal boiling point;
tb_total
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13; @free(tb_total);
=

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!Equation for viscosity (vis);
vis_total =
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13;
@free(vis_total);

!Equation for surface tension (st);
st_total =
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13; @free(st_total);

!Equation for solubility (sol);
sol_total =
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13;
@free(sol_total);

!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacglycerol = 17.1822MPa;
!sol0= 21.6654 MPa (sol0 = solubility constant);

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

sol_final < 20.6;
sol_final > 14.4;

tb_total < 4.239;
tb_total > 3.599;

!Equation for molecular weight (mw);
mw_total =
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13;

!Equation for flash point (fp);

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```

fp_total
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13; @free(fp_total);

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

fp > 242;

fpcelcius = fp - 273.15; @free(fpcelcius);

!Equation for aquatic toxicity (LC50);
LC50_total
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013;
@free(LC50_total);

!Equation for terrestrial toxicity (LD50);
LD50_total
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013;
@free(LD50_total);

!Equation for photochemical oxidation potential (PCO);
PCO_total
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13;
@free(PCO_total);

!Equation for bioconcentration factor (BCF);
BCF_total
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13;
@free(BCF_total);

BCF_total < 3.3;

!Equation for octanol-water partition coefficient (logKow);
logkow_total
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

!Equation for permissible exposure limit (PEL);
PEL_total
n1*PEL1+n2*PEL2+n3*PEL3+n4*PEL4+n5*PEL5+n6*PEL6+n7*PEL7+n8*PEL8
+n9*PEL9+n10*PEL10+n11*PEL11+n12*PEL12+n13*PEL13;
@free(PEL_total);

!Calculate PEL in ppm;
!molar volume of gas, Vgas, in dm3/mol, Note that 1L=1dm3;
Vgas = 24.45;
PEL = Vgas*1000*10^(-PEL_total);

```

```

!Calculate for oxygen stoichiometric coefficient, Co;
Co = C_number + (H_number/4) - (O_number/2);

!Calculate for Lower explosion limit, LEL;
LEL = (100/(1+9.045*Co));

!Calculate for Upper explosion limit, UEL;
UEL = (100/(1+1.1843*Co));

!Calculate explosiveness, Iex using S= (UEL - LEL)vol%;
S = UEL - LEL;

!Disjunctive equation for explosiveness, Iex;
Iex = Iex1 + Iex2 + Iex3 + 1; @bin(Iex1); @bin(Iex2); @bin(Iex3);
(0-20)*(1-Iex1) < S - 20;
S - 20 <= (100 - 20)*(Iex1);
(0-45)*(1-Iex2) < S - 45;
S - 45 <= (100 - 45)*(Iex2);
(0-70)*(1-Iex3) < S - 70;
S - 70 <= (100 - 70)*(Iex3);

!!Disjunctive equation for acute health hazard;
IAH = IAH1 + IAH2 + IAH3 + IAH4; @bin(IAH1); @bin(IAH2);
@bin(IAH3); @bin(IAH4);
(0.00001-2000)*(IAH1) < LD50_mg- 2000;
LD50_mg- 2000 <= (10000 - 2000)*(1-IAH1);
(0.00001-500)*(IAH2) < LD50_mg - 500;
LD50_mg- 500 <= (10000 - 500)*(1-IAH2);
(0.00001-50)*(IAH3) < LD50_mg - 50;
LD50_mg - 50 <= (10000 - 50)*(1-IAH3);
(0.00001-5)*(IAH4) < LD50_mg- 5;
LD50_mg - 5 <= (10000 - 5)*(1-IAH4);

!Calculate for Tb in C;
!Tb constant,tb0 in K;
tb0 = 244.5165;
Tbcelcius = @log(tb_total)*tb0 -273.15; @free(Tbcelcius);

!Disjunctive equation for volatility;
!Iv = Iv1 + Iv2 + Iv3; @bin(Iv1); @bin(Iv2); @bin(Iv3);
!(-10000-150)*Iv1 < Tbcelcius - 150;
!Tbcelcius - 150 <= (10000 - 150)*(1-Iv1);
!(-10000-50)*Iv2 < Tbcelcius - 50;
!Tbcelcius - 50 <= (10000 - 50)*(1-Iv2);
!(-10000-0)*Iv3 < Tbcelcius - 0;
!Tbcelcius - 0 <= (10000 - 0)*(1-Iv3);

!Disjunctive equation for material phase;
! To ensure solvent boiling pt in between (40-80C) and it should
be a liquid;
!Ims = Ims1 + 1; @bin (Ims1);
!(39.99-80)*Ims1 < Tbcelcius - 80;
!Tbcelcius - 80 <= (10000 - 80)* (1-Ims1);

!Disjunctive equation for flammability. Ifl;
Ifl = Ifl1 + Ifl2 + Ifl5 + 1; @bin(If11); @bin(If12); @bin(If13);
@bin(If14); @bin(If15);
(-1000-93.4)*(If11) < Fpcelcius - 93.4;
Fpcelcius - 93.4 <= (10000-93.4)*(1-If11);
(-1000-37.8)*(If12) < Fpcelcius - 37.8;
Fpcelcius - 37.8 <= (10000-37.8)*(1-If12);

```

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(-1000-22.8)*(If13) < Fpcelcius - 22.8;
Fpcelcius - 22.8 <= (10000-22.8)*(1-If13);
(-1000-37.8)*(If14) < Tbcelsius - 37.8;
Tbcelsius - 37.8 <= (10000-37.8)*(1-If14);
If13 + If14 = g;
(0-2)*(1-If15) < g- 2;
g - 2 <= (5-2)*If15;

!Disjunctive equation for exposure limit, Iel;
Iel = Iel1 + Iel2 + Iel3 + Iel4; @bin(Iel1); @bin(Iel2);
@bin(Iel3); @bin(Iel4);
(0.0001-1000)*(Iel1) < PEL -1000;
PEL - 1000 <= (10000 - 1000)*(1-Iel1);
(0.0001-100)*(Iel2) < PEL -100;
PEL - 100 <= (10000 - 100)*(1-Iel2);
(0.0001-10)*(Iel3) < PEL -10;
PEL - 10 <= (10000 - 10)*(1-Iel3);
(0.0001-1)*(Iel4) < PEL -1;
PEL - 1 <= (10000 - 1)*(1-Iel4);

End

```

Appendix C: Lingo Coding (Chapter 6)

```

model:

!objective function;

max = obj_function; @free(obj_function);

!obj_function = 0.0809*Tb + 0.0156*sol + 0.02935*st + 0.02935*vis
+ 0.0077*LC50 + 0.0278*PCO + 0.0034*BCF + 0.0034*KOW +
0.13015*If1final + 0.13015*Iex + 0.0211*Iel1final +
0.0211*IAHfinal + 0.5*EB;
obj_function = 0.1214*Tb + 0.0234*sol + 0.044*st + 0.044*vis +
0.0116*LC50 + 0.0417*PCO + 0.005*BCF + 0.005*KOW +
0.1952*If1final + 0.1952*Iex + 0.0317*Iel1final + 0.0317*IAHfinal
+ 0.25*EB;

ISHI_total = 0.1952*If1 + 0.1952*Iex + 0.0317*Iel + 0.0317*IAH;
@free(ISHI_total);
!ISHI_total = 0.13015*If1 + 0.13015*Iex + 0.0211*Iel +
0.0211*IAH; !@free(ISHI_total);

!For acyclic compound;
!Tb = (4.2146 - tb_total)/(4.2146 - 3.6044); @free(Tb);

!sol = (2.697 - Diff_car)/(2.697 - 0.3102);@free(sol);

!st = (25.1026 - st_total)/(25.1026 - 20.1833);@free(st);

!vis = (-0.4904 - vis_total)/(-0.4904 + 1.1851);@free(vis);

!LC50 = (1.9233 - LC50_total)/(1.9233 + 0.7533);@free(LC50);

!LD50 = (0.0915 - LD50_total)/(0.0915 + 0.2253);@free(LD50);

!PCO = (PCO_total + 0.4427)/(0.5548 + 0.4427);@free(PCO);

!BCF = (1.4259 - BCF_total)/(1.4259 - 0.2037);@free(BCF);

```

```

!KOW = (0.3862 - logkow_total)/(0.3862 + 0.6804);@free(KOW);

!Iflfinal = Ifl/3; @free(Iflfinal);

!Ielfinal = (3-Iel)/(3-1); @free(Ielfinal);

!IAHfinal = IAH/1; @free(IAHfinal);

!EB = (8.34298 - EB_total)/(8.527895 - 6.01503);@free(EB);

!For monocyclic compound;
Tb = (4.2256 - tb_total)/(4.2256 - 3.6129); !@free(Tb);

sol = (2.7874 - Diff_car)/(2.7874 - 0.0181);!@free(sol);

st = (9.014 - st_total)/(9.014- 1.7853);!@free(st);

vis = (3.8575 - vis_total)/(3.8575 - 1.067);!@free(vis);

LC50 = (3.1332 - LC50_total)/(3.1332+ 0.7942);!@free(LC50);

LD50 = (0.7494 - LD50_total)/(0.7494 + 0.0611);!@free(LD50);

PCO = (PCO_total + 0.795)/(0.5577 + 0.795);!@free(PCO);

BCF = (1.0211 - BCF_total)/(1.0211 + 0.2181);!@free(BCF);

KOW = (3.4101 - logkow_total)/(3.4101 - 0.5966);!@free(KOW);

Iflfinal = Ifl/3; !@free(Iflfinal);

Ielfinal = (4-Iel)/(4-0); !@free(Ielfinal);

IAHfinal = (2-IAH)/(2-1); !@free(IAHfinal);

EB = (7.514133- EB_total)/(7.514133- 5.24847);!@free(EB);

!Defining the chemical building blocks
n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O, n14 = CH3COO;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13); @GIN (n14);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13+n14*2;
H_number =
n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13+n14*3;
O_number = n5+n6*2+n7+n8+n9+n12+n13+n14*2;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
O_number <2;

!Free bonds for each group;
vall = 1;

```

```

val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;
val8 = 1;
val9 = 1;
val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;
val14 = 1;

!Structural constraint, the molecule generated must not contain
free bonds;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14) + 2
= 0; !monocyclic compound;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14) =
0; !acyclic compound;

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);
tb14 = 2.5805; @free(tb14);

!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);
logkow14 = -0.4615; @free(logkow14);

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);

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LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);
LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);
LC5014 = 0.4393; @free(LC5014);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);
LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);
LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);
LD5014 = -0.1734; @free(LD5014);

!constant for LD50;
A= 1.9372;
B= 0.0016;

!calculate for LD50 in mol/kg;
LD50_mol = 10^(-(LD50_total + A + B*mw_total)); @free(LD50_mol);

!Calculate for LD50 in mg/kg;
LD50_mg = LD50_mol*mw_total*1000; @free(LD50_mg);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);
PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);
PCO14 = 0.3858; @free(PCO14);

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);
BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);

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```

BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);
BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);
BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);
BCF14 = 0.3988; @free(BCF14);

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;
mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;
mw14 = 59.044;

!Group contribution for flash point;
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);
fp14 = 73.7; @free(fp14);

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);
sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);
sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);
sol14 = -0.6905; @free(sol14);

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);

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```

vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);
vis14 = -0.0358; @free(vis14);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);
st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);
st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);
st14 = 14.8168; @free(st14);

!Group contribution for permissible exposure limit (PEL);
PEL1 = 0.7723; @free(PEL1);
PEL2 = 0.0727; @free(PEL2);
PEL3 = -0.6557; @free(PEL3);
PEL4 = -1.3404; @free(PEL4);
PEL5 = 1.3612; @free(PEL5);
PEL6 = 2.3281; @free(PEL6);
PEL7 = 1.4016; @free(PEL7);
PEL8 = 2.3662; @free(PEL8);
PEL9 = 2.1251; @free(PEL9);
PEL10 = 2.0449; @free(PEL10);
PEL11 = 2.2638; @free(PEL11);
PEL12 = 0.9276; @free(PEL12);
PEL13 = -0.7462; @free(PEL13);
PEL14 = 1.2544; @free(PEL14);

!Property Constraints;
!Equation for normal boiling point;
tb_total =
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13+n14*tb14; @free(tb_total);

!Equation for viscosity (vis);
vis_total =
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13+n14*vis14;
@free(vis_total);

!Equation for surface tension (st);

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st_total =
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13+n14*st14; @free(st_total);

!Equation for solubility (sol);
sol_total =
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13+n14*sol14;
@free(sol_total);

!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacylglycerol = 17.1822MPa;
!sol0= 21.6654 MPa (sol0 = solubility constant);

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

sol_final < 20.6;
sol_final > 14.4;

tb_total < 4.239;
!tb_total < 3.986;
tb_total > 3.599;

!Group contribution for heat of vaporisation(Hv);
Hv1 = 2.2643; @free(Hv1);
Hv2 = 4.7607; @free(Hv2);
Hv3 = 5.0336; @free(Hv3);
Hv4 = 5.1448; @free(Hv4);
Hv5 = 24.1639; @free(Hv5);
Hv6 = 20.4196; @free(Hv6);
Hv7 = 15.1303; @free(Hv7);
Hv8 = 13.2496; @free(Hv8);
Hv9 = 7.8029; @free(Hv9);
Hv10 = 17.5679; @free(Hv10);
Hv11 = 5.4644; @free(Hv11);
Hv12 = 8.5931; @free(Hv12);
Hv13 = 9.1274; @free(Hv13);

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Hv14 =20.0986; @free(Hv14);

!Group contribution for heat capacity (CP);
Cp0a= 89.53; Cp0b = -40.13; Cp0d= 5.19; @free(Cp0a); @free(Cp0b);
@free(Cp0d);
Cp1a= 1.04; Cp1b = 8.29; Cp1d= 0.76; @free(Cp1a); @free(Cp1b);
@free(Cp1d);
Cp2a= 19.64; Cp2b = 0.78; Cp2d= 0.80; @free(Cp2a); @free(Cp2b);
@free(Cp2d);
Cp3a= 12.20; Cp3b = 7.90; Cp3d= -1.03; @free(Cp3a); @free(Cp3b);
@free(Cp3d);
Cp4a= 25.40; Cp4b = -2.25; Cp4d= 0.16; @free(Cp4a); @free(Cp4b);
@free(Cp4d);
Cp5a= -99.86; Cp5b = 71.89; Cp5d= -7.70; @free(Cp5a); @free(Cp5b);
@free(Cp5d);
Cp6a= -2.21; Cp6b = 30.79; Cp6d= -1.98; @free(Cp6a); @free(Cp6b);
@free(Cp6d);
Cp7a= 69.38; Cp7b = -2.63; Cp7d= 1.91; @free(Cp7a); @free(Cp7b);
@free(Cp7d);
Cp8a= 32.92; Cp8b = 10.22; Cp8d= -1.96; @free(Cp8a); @free(Cp8b);
@free(Cp8d);
Cp9a= 21.08; Cp9b = 14.60; Cp9d= -0.71; @free(Cp9a); @free(Cp9b);
@free(Cp9d);
Cp10a= 41.12; Cp10b = 6.56; Cp10d= -1.16; @free(Cp10a);
@free(Cp10b); @free(Cp10d);
Cp11a= 15.13; Cp11b = 9.02; Cp11d= 0.99; @free(Cp11a);
@free(Cp11b); @free(Cp11d);
Cp12a= 48.82; Cp12b = 4.92; Cp12d= -0.40; @free(Cp12a);
@free(Cp12b); @free(Cp12d);
Cp13a= 66.98; Cp13b = -9.64; Cp13d= 0.60; @free(Cp13a);
@free(Cp13b); @free(Cp13d);
Cp14a= 34.25; Cp14b = 35.65; Cp14d= -5.17; @free(Cp14a);
@free(Cp14b); @free(Cp14d);

!Calculate for Tb in C;
!Tb constant,tb0 in K;
tb0 = 244.5165;
Tbcelcius = @log(tb_total)*tb0 -273.15; @free(Tbcelcius);

T= Tbcelcius + 273.15 + 5; @free(T); !T=evaporator temp;

Cp0 = Cp0a + Cp0b*(T/100) + Cp0d*(T/100)^2; @free(Cp0);
Cp1 = Cp1a + Cp1b*(T/100) + Cp1d*(T/100)^2; @free(Cp1);
Cp2 = Cp2a + Cp2b*(T/100) + Cp2d*(T/100)^2; @free(Cp2);
Cp3 = Cp3a + Cp3b*(T/100) + Cp3d*(T/100)^2; @free(Cp3);
Cp4 = Cp4a + Cp4b*(T/100) + Cp4d*(T/100)^2; @free(Cp4);
Cp5 = Cp5a + Cp5b*(T/100) + Cp5d*(T/100)^2; @free(Cp5);
Cp6 = Cp6a + Cp6b*(T/100) + Cp6d*(T/100)^2; @free(Cp6);
Cp7 = Cp7a + Cp7b*(T/100) + Cp7d*(T/100)^2; @free(Cp7);
Cp8 = Cp8a + Cp8b*(T/100) + Cp8d*(T/100)^2; @free(Cp8);
Cp9 = Cp9a + Cp9b*(T/100) + Cp9d*(T/100)^2; @free(Cp9);
Cp10 = Cp10a + Cp10b*(T/100) + Cp10d*(T/100)^2; @free(Cp10);
Cp11 = Cp11a + Cp11b*(T/100) + Cp11d*(T/100)^2; @free(Cp11);
Cp12 = Cp12a + Cp12b*(T/100) + Cp12d*(T/100)^2; @free(Cp12);
Cp13 = Cp13a + Cp13b*(T/100) + Cp13d*(T/100)^2; @free(Cp13);
Cp14 = Cp14a + Cp14b*(T/100) + Cp14d*(T/100)^2; @free(Cp14);

Tref = 35 + 273.15; @free(Tref);

!Cp at Tref;
Cp0f = Cp0a + Cp0b*(Tref/100) + Cp0d*(Tref/100)^2; @free(Cp0f);

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```

Cp1f = Cp1a + Cp1b*(Tref/100) + Cp1d*(Tref/100)^2; @free(Cp1f);
Cp2f = Cp2a + Cp2b*(Tref/100) + Cp2d*(Tref/100)^2; @free(Cp2f);
Cp3f = Cp3a + Cp3b*(Tref/100) + Cp3d*(Tref/100)^2; @free(Cp3f);
Cp4f = Cp4a + Cp4b*(Tref/100) + Cp4d*(Tref/100)^2; @free(Cp4f);
Cp5f = Cp5a + Cp5b*(Tref/100) + Cp5d*(Tref/100)^2; @free(Cp5f);
Cp6f = Cp6a + Cp6b*(Tref/100) + Cp6d*(Tref/100)^2; @free(Cp6f);
Cp7f = Cp7a + Cp7b*(Tref/100) + Cp7d*(Tref/100)^2; @free(Cp7f);
Cp8f = Cp8a + Cp8b*(Tref/100) + Cp8d*(Tref/100)^2; @free(Cp8f);
Cp9f = Cp9a + Cp9b*(Tref/100) + Cp9d*(Tref/100)^2; @free(Cp9f);
Cp10f = Cp10a + Cp10b*(Tref/100) + Cp10d*(Tref/100)^2;
@free(Cp10f);
Cp11f = Cp11a + Cp11b*(Tref/100) + Cp11d*(Tref/100)^2;
@free(Cp11f);
Cp12f = Cp12a + Cp12b*(Tref/100) + Cp12d*(Tref/100)^2;
@free(Cp12f);
Cp13f = Cp13a + Cp13b*(Tref/100) + Cp13d*(Tref/100)^2;
@free(Cp13f);
Cp14f = Cp14a + Cp14b*(Tref/100) + Cp14d*(Tref/100)^2;
@free(Cp14f);

!Equation for heat capacity (CP) in J/K mol;
CP_total =
n1*Cp1+n2*Cp2+n3*Cp3+n4*Cp4+n5*Cp5+n6*Cp6+n7*Cp7+n8*Cp8+n9*Cp9+
n10*Cp10+n11*Cp11+n12*Cp12+n13*Cp13+n14*Cp14+Cp0;
@free(CP_total);

!Equation for heat capacity (CP) in Tref in J/K mol;
CPf_total =
n1*Cp1f+n2*Cp2f+n3*Cp3f+n4*Cp4f+n5*Cp5f+n6*Cp6f+n7*Cp7f+n8*Cp8f
+n9*Cp9f+n10*Cp10f+n11*Cp11f+n12*Cp12f+n13*Cp13f+n14*Cp14f+ Cp0f;
@free(CPf_total);

!Hv0=9.6127;

!Equation for heat of vaporisation (Hv) in KJ/mol;
Hv_total =
n1*Hv1+n2*Hv2+n3*Hv3+n4*Hv4+n5*Hv5+n6*Hv6+n7*Hv7+n8*Hv8+n9*Hv9+
n10*Hv10+n11*Hv11+n12*Hv12+n13*Hv13+n14*Hv14+9.6127;
@free(Hv_total);

!Equation for molecular weight (mw);
mw_total =
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13+n14*mw14;

!Equation for flash point (fp);
fp_total =
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13+n14*fp14; @free(fp_total);

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

fp > 242;

fpcelcius = fp - 273.15; @free(fpcelcius);

!Equation for aquatic toxicity (LC50);

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LC50_total
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013+n
14*LC5014; @free(LC50_total);

!Equation for terrestrial toxicity (LD50);
LD50_total
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013+n
14*LD5014; @free(LD50_total);

!Equation for photochemical oxidation potential (PCO);
PCO_total
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13+n14*PCO14;
@free(PCO_total);

!Equation for bioconcentration factor (BCF);
BCF_total
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13+n14*BCF14;
@free(BCF_total);

BCF_total < 3.3;

!Equation for octanol-water partition coefficient (logKow);
logkow_total
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13+n14*logkow14; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

!Equation for permissible exposure limit (PEL);
PEL_total
n1*PEL1+n2*PEL2+n3*PEL3+n4*PEL4+n5*PEL5+n6*PEL6+n7*PEL7+n8*PEL8
+n9*PEL9+n10*PEL10+n11*PEL11+n12*PEL12+n13*PEL13+n14*PEL14;
@free(PEL_total);

!Calculate PEL in ppm;
!molar volume of gas, Vgas, in dm3/mol, Note that 1L=1dm3;
Vgas = 24.45;
PEL = Vgas*1000*10^(-PEL_total);

!Calculate for oxygen stoichiometric coefficient, Co;
Co = C_number + (H_number/4) - (O_number/2);

!Calculate for Lower explosion limit, LEL;
LEL = (100/(1+9.045*Co));

!Calculate for Upper explosion limit, UEL;
UEL = (100/(1+1.1843*Co));

!Calculate explosiveness, Iex using S= (UEL - LEL)vol%;
S = UEL - LEL;

!Disjunctive equation for explosiveness, Iex;

```

```

Iex = Iex1 + Iex2 + Iex3 + 1; @bin(Iex1); @bin(Iex2); @bin(Iex3);
(0-20)*(1-Iex1) < S - 20;
S - 20 <= (100 - 20)*(Iex1);
(0-45)*(1-Iex2) < S - 45;
S - 45 <= (100 - 45)*(Iex2);
(0-70)*(1-Iex3) < S - 70;
S - 70 <= (100 - 70)*(Iex3);

!!Disjunctive equation for acute health hazard;
IAH = IAH1 + IAH2 + IAH3 + IAH4; @bin(IAH1); @bin(IAH2);
@bin(IAH3); @bin(IAH4);
(0.00001-2000)*(IAH1) < LD50_mg- 2000;
LD50_mg- 2000 <= (10000 - 2000)*(1-IAH1);
(0.00001-500)*(IAH2) < LD50_mg - 500;
LD50_mg- 500 <= (10000 - 500)*(1-IAH2);
(0.00001-50)*(IAH3) < LD50_mg - 50;
LD50_mg - 50 <= (10000 - 50)*(1-IAH3);
(0.00001-5)*(IAH4) < LD50_mg- 5;
LD50_mg - 5 <= (10000 - 5)*(1-IAH4);

!Disjunctive equation for volatility;
!Iv = Iv1 + Iv2 + Iv3; !@bin(Iv1); !@bin(Iv2); !@bin(Iv3);
!(-10000-150)*Iv1 < Tbcelsius - 150;
!Tbcelsius - 150 <= (10000 - 150)*(1-Iv1);
!(-10000-50)*Iv2 < Tbcelsius - 50;
!Tbcelsius - 50 <= (10000 - 50)*(1-Iv2);
!(-10000-0)*Iv3 < Tbcelsius - 0;
!Tbcelsius - 0 <= (10000 - 0)*(1-Iv3);

!Disjunctive equation for material phase;
! To ensure solvent boiling pt in between (40-80C) and it should
be a liquid;
!Ims = Ims1 + 1; !@bin (Ims1);
!(39.99-80)*Ims1 < Tbcelsius - 80;
!Tbcelsius - 80 <= (10000 - 80)* (1-Ims1);

!Disjunctive equation for flammability. Ifl;
Ifl = Ifl1 + Ifl2 + Ifl5 + 1; @bin(Ifl1); @bin(Ifl2); @bin(Ifl3);
@bin(Ifl4); @bin(Ifl5);
(-1000-93.4)*(Ifl1) < Fpcelsius - 93.4;
Fpcelsius - 93.4 <= (10000-93.4)*(1-Ifl1);
(-1000-37.8)*(Ifl2) < Fpcelsius - 37.8;
Fpcelsius - 37.8 <= (10000-37.8)*(1-Ifl2);
(-1000-22.8)*(Ifl3) < Fpcelsius - 22.8;
Fpcelsius - 22.8 <= (10000-22.8)*(1-Ifl3);
(-1000-37.8)*(Ifl4) < Tbcelsius - 37.8;
Tbcelsius - 37.8 <= (10000-37.8)*(1-Ifl4);
Ifl3 + Ifl4 = g;
(0-2)*(1-Ifl5) < g- 2;
g - 2 <= (5-2)*Ifl5;

!Disjunctive equation for exposure limit, Iel;
Iel = Iel1 + Iel2 + Iel3 + Iel4; @bin(Iel1); @bin(Iel2);
@bin(Iel3); @bin(Iel4);
(0.0001-1000)*(Iel1) < PEL -1000;
PEL - 1000 <= (10000 - 1000)*(1-Iel1);
(0.0001-100)*(Iel2) < PEL -100;
PEL - 100 <= (10000 - 100)*(1-Iel2);
(0.0001-10)*(Iel3) < PEL -10;
PEL - 10 <= (10000 - 10)*(1-Iel3);
(0.0001-1)*(Iel4) < PEL -1;

```

```

PEL - 1 <= (10000 - 1)*(1-Iel4);

!Mass and Energy balance around the evaporator;
!Evaporator feed stream temperature = 35C;
!Evaporator outlet stream temperature based on boiling point of
solvent added by 5 degree celsius to ensure complete vaporisation;
!Mass of solvent entering evaporator, Ms = 0.15kg;
!Mass of oil entering evaporator, Mo = 0.05kg;
!Mass of solvent vapour, Msv = 0.149 kg;
!Mass of solvent at the bottom, Msb = 0.001 kg;
!Mass of oil at the bottom, Mob = 0.05 kg;

Ms = 0.15;
Mo = 0.05;
Msv = 0.149;
Msb = 0.001;
Mob = 0.05;

!Cp in kJ/kg C;
Cpoil = 1.902;

!Treference = lowest temperature of the system, which is the feed
temperature;
!Tfeed = 35 + 273.15;
!Enthalpy for feed of evaporator, deltaHf = mCPdeltaT;
!Enthalpy for vapor stream of evaporator, deltaHv = mCPdeltaT +
m*hv;
!Enthalpy for vapor stream of evaporator, deltaHb = mCPdeltaT;
!Total energy requirement = deltaHv + deltaHb;

!average Cp = (cp at 308.15K + cp at T)/ 2;
averageCp = (Cpf_total + Cp_total)/2;

deltaHv = Msv*(averageCp/Mw_total)*(T - Tref) +
Msv*Hv_total*1000/Mw_total;
deltaHb = Msb*(averageCp/Mw_total)*(T - Tref) + Mob*Cpoil*(T -
Tref);

energyrequirement = deltaHv + deltaHb;

!8 bar steam latent heat = 2046.53;

!amount_steam in kg= energyrequirement/2046.53;

!amount of steam in MJ, amt_steam;

amt_steam = energyrequirement/1000;

!1MJ of steam will produce emissions as below (From GREET MODEL
2016): (in grams);
co2_steam = 78.36;
VOC_steam = 0.01527;
CO_steam = 0.06771;
NOx_steam = 0.09647;
SOx_steam = 0.01417;
CH4_steam = 0.34;
N2O_steam = 0.0021;

```

```

!1MJ of electricity will produce emissions as below (From GREET
MODEL 2016): (in grams), assume electricity from NGCC;
!co2_electricity = 120;
!VOC_electricity = 0.01635;
!CO_electricity = 0.06962;
!NOx_electricity = 0.08701;
!SOx_electricity = 0.02163;
!CH4_electricity = 0.46;
!N2O_electricity = 0.0017;

!Amount of gas produced;
CO2_total = amt_steam*78.36 ;
VOC_total = amt_steam * 0.01527 ;
CO_total = amt_steam * 0.06771 ;
NOx_total = amt_steam * 0.09647 ;
SOx_total = amt_steam * 0.01417 ;
CH4_total = amt_steam * 0.34 ;
N2O_total = amt_steam * 0.0021 ;

!CO2_total = amt_steam*78.36 + amt_electricity*120;
!VOC_total = amt_steam * 0.01527 + amt_electricity*0.01635;
!CO_total = amt_steam * 0.06771 + amt_electricity*0.06962;
!NOx_total = amt_steam * 0.09647 + amt_electricity*0.08701;
!SOx_total = amt_steam * 0.01417 + amt_electricity*0.02163;
!CH4_total = amt_steam * 0.34 + amt_electricity*0.46;
!N2O_total = amt_steam * 0.0021 + amt_electricity*0.0017;

!Icheme Index;
!Global Warming Potency factor;
co2_GWP = 1;
VOC_GWP = 11;
CO_GWP = 3;
NOx_GWP = 40;
SOx_GWP = 0;
CH4_GWP = 21;
N2O_GWP = 310;

!Global warming environmental burden;
GWP = CO2_total*co2_GWP + VOC_total*VOC_GWP + CO_total*CO_GWP +
NOx_total*NOx_GWP + SOx_total*SOx_GWP + CH4_total*CH4_GWP +
N2O_total*N2O_GWP;

!Photochemical smog Potency factor;
co2_PCO = 0;
VOC_PCO = 0;
CO_PCO = 0.027;
NO2_PCO = 0.028;
SOx_PCO = 0;
CH4_PCO = 0.034;
N2O_PCO = 0;

!Photochemical smog environmental burden;
PCOp= CO2_total*co2_PCO + VOC_total*VOC_PCO + CO_total*CO_PCO +
NOx_total*NO2_PCO + SOx_total*SOx_PCO + CH4_total*CH4_PCO +
N2O_total*N2O_PCO;

!Eutrophication potency factor;
NOx_EU = 0.13;

!Photochemical smog environmental burden;
EU = NOx_total*NOx_EU;

```

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!Atmospheric Acidification potency factor (assume NO will form
NO2 which is more stable);
NO2_AA = 0.7;

!Atmospheric Acidification environmental burden;
AA = NOx_total*NO2_AA;

!Total environmental burden;
EB_total = GWP + PCOp + EU + AA;

end

```

Appendix D: Lingo Coding (Chapter 7)

Part A: Evaporation under normal condition

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model:

max = objectivefunction;

!when consider only yield and energy, by assuming both of them
equal importance;
!objectivefunction      =      0.5*Fyield+0.5*EReq;      !@free
(objectivefunction);

!Exclude Tb as objective function;
objectivefunction = 0.03105*sol + 0.0621*st + 0.0621*vis +
0.0077*LC50 + 0.0278*PCO + 0.0034*BCF + 0.0034*KOW +
0.1302*Iflfinal + 0.1302*Iex + 0.0211*Ielfinal + 0.0211*IAHfinal
+ 0.25*Fyield + 0.25*finalcost;

!For acyclic compound;

!sol = (2.697 - Diff_car)/(2.697 - 0.0822);@free(sol);

!st = (26.0327 - st_total)/(26.0327- 20.1833);@free(st);

!vis = (2.8845- vis_total)/(2.8845 + 1.1851);@free(vis);

!LC50 = (1.9761 - LC50_total)/(1.9761 + 1.236);@free(LC50);

!LD50 = (0.2165 - LD50_total)/(0.2165 + 0.2253);@free(LD50);

!PCO= (PCO_total + 0.4427)/(0.5548 + 0.4427);@free(PCO);

!BCF = (1.6047 - BCF_total)/(1.6047 - 0.2037);@free(BCF);

!KOW = (0.7499- logkow_total)/(0.7499 + 0.6804);@free(KOW);

!Iflfinal = Ifl/3; @free(Iflfinal);

!Ielfinal = (4-Iel)/(4-1); @free(Ielfinal);

!IAHfinal = (2 -IAH)/(2-1); @free(IAHfinal);

!FYield = (Yield - 0.378583)/(1-0.378583); @free(Fyield);

!finalcost = (30.44256 - cost)/(30.44256 - 16.06097);
@free(finalcost);

```



```

!For monocyclic compound;

sol = (2.7895 - Diff_car)/(2.7895 - 0.0104);!@free(sol);

st = (9.014 - st_total)/(9.014- 1.7853);!@free(st);

vis = (4.3483 - vis_total)/(4.3483 - 1.067);!@free(vis);

LC50 = (3.1332 - LC50_total)/(3.1332+ 1.6118);!@free(LC50);

LD50 = (0.947 - LD50_total)/(0.947 - 0.0611);!@free(LD50);

PCO = (PCO_total + 0.9224)/(0.6671 + 0.9224);!@free(PCO);

BCF = (1.1159 - BCF_total)/(1.1159 + 0.2181);!@free(BCF);

KOW = (3.6594 - logkow_total)/(3.6594 - 0.5966);!@free(KOW);

Iflfinal = Ifl/3; !@free(Iflfinal);

Ielfinal = (4-Iel)/(4-0); !@free(Ielfinal);

IAHfinal = (2-IAH)/(2-1); !@free(IAHfinal);

FYield = (Yield - 0.372005)/(1-0.372005); !@free(Fyield);

finalcost = (17.12801- cost)/(17.12801-
14.03574); !@free(finalcost);

!Defining the chemical building blocks
n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O, n14 = CH3COO;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13); @GIN (n14);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13+n14*2;
H_number = n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13+n14*3;
O_number = n5+n6*2+n7+n8+n9+n12+n13+n14*2;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
O_number <2;

!Free bonds for each group;
val1 = 1;
val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;
val8 = 1;

```

```

val9 = 1;
val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;
val14 = 1;

!Structural constraint, the molecule generated must not contain
free bonds;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1))      -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14) + 2
= 0; !monocyclic compound;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1))      -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14)    =
0; !acyclic compound;

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);
tb14 = 2.5805; @free(tb14);

!Property Constraints;
!Equation for normal boiling point;
tb_total =
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13+n14*tb14; @free(tb_total);

!B.pt constraint value, where Tb > 40C, Tb < 95C (due to
degradation kinetics data up to 100C);
tb_total > 3.59912;
tb_total < 4.50697;

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;
mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;
mw14 = 59.044;

```

```

!Equation for molecular weight (mw);
mw_total
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13+n14*mw14;

mw_total <150;

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);
sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);
sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);
sol14 = -0.6905; @free(sol14);

!Equation for solubility (sol);
sol_total
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13+n14*sol14;
@free(sol_total);

!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacglycerol = 17.1822MPa;
!sol0= 21.6654 MPa (sol0 = solubility constant);

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

!constaint on solubility;
sol_final < 20.6;

```

```

sol_final > 14.4;

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);
vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);
vis14 = -0.0358; @free(vis14);

!Equation for viscosity (vis);
vis_total =
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13+n14*vis14;
@free(vis_total);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);
st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);
st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);
st14 = 14.8168; @free(st14);

!Equation for surface tension (st);
st_total =
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13+n14*st14; @free(st_total);

!Group contribution for heat of vaporisation(Hv);
Hv1 = 2.2643; @free(Hv1);
Hv2 = 4.7607; @free(Hv2);
Hv3 = 5.0336; @free(Hv3);
Hv4 = 5.1448; @free(Hv4);
Hv5 = 24.1639; @free(Hv5);
Hv6 = 20.4196; @free(Hv6);
Hv7 = 15.1303; @free(Hv7);
Hv8 = 13.2496; @free(Hv8);
Hv9 = 7.8029; @free(Hv9);
Hv10 = 17.5679; @free(Hv10);
Hv11 = 5.4644; @free(Hv11);
Hv12 = 8.5931; @free(Hv12);
Hv13 = 9.1274; @free(Hv13);
Hv14 = 20.0986; @free(Hv14);

```

```

!Hv0=9.6127;

!Equation for heat of vaporisation (Hv) in KJ/mol;
Hv_total =
n1*Hv1+n2*Hv2+n3*Hv3+n4*Hv4+n5*Hv5+n6*Hv6+n7*Hv7+n8*Hv8+n9*Hv9+
n10*Hv10+n11*Hv11+n12*Hv12+n13*Hv13+n14*Hv14+9.6127;
@free(Hv_total);

!Group contribution for heat capacity (CP);
Cp0a= 89.53; Cp0b = -40.13; Cp0d= 5.19; @free(Cp0a); @free(Cp0b);
@free(Cp0d);
Cp1a= 1.04; Cp1b = 8.29; Cp1d= 0.76; @free(Cp1a); @free(Cp1b);
@free(Cp1d);
Cp2a= 19.64; Cp2b = 0.78; Cp2d= 0.80; @free(Cp2a); @free(Cp2b);
@free(Cp2d);
Cp3a= 12.20; Cp3b = 7.90; Cp3d= -1.03; @free(Cp3a); @free(Cp3b);
@free(Cp3d);
Cp4a= 25.40; Cp4b = -2.25; Cp4d= 0.16; @free(Cp4a); @free(Cp4b);
@free(Cp4d);
Cp5a= -99.86; Cp5b = 71.89; Cp5d= -7.70; @free(Cp5a); @free(Cp5b);
@free(Cp5d);
Cp6a= -2.21; Cp6b = 30.79; Cp6d= -1.98; @free(Cp6a); @free(Cp6b);
@free(Cp6d);
Cp7a= 69.38; Cp7b = -2.63; Cp7d= 1.91; @free(Cp7a); @free(Cp7b);
@free(Cp7d);
Cp8a= 32.92; Cp8b = 10.22; Cp8d= -1.96; @free(Cp8a); @free(Cp8b);
@free(Cp8d);
Cp9a= 21.08; Cp9b = 14.60; Cp9d= -0.71; @free(Cp9a); @free(Cp9b);
@free(Cp9d);
Cp10a= 41.12; Cp10b = 6.56; Cp10d= -1.16; @free(Cp10a);
@free(Cp10b); @free(Cp10d);
Cp11a= 15.13; Cp11b = 9.02; Cp11d= 0.99; @free(Cp11a);
@free(Cp11b); @free(Cp11d);
Cp12a= 48.82; Cp12b = 4.92; Cp12d= -0.40; @free(Cp12a);
@free(Cp12b); @free(Cp12d);
Cp13a= 66.98; Cp13b = -9.64; Cp13d= 0.60; @free(Cp13a);
@free(Cp13b); @free(Cp13d);
Cp14a= 34.25; Cp14b = 35.65; Cp14d= -5.17; @free(Cp14a);
@free(Cp14b); @free(Cp14d);

!Calculate for Tb in C;
!Tb constant,tb0 in K;
tb0 = 244.5165;
Tbcelcius = @log(tb_total)*tb0 -273.15; @free(Tbcelcius);

T= Tbcelcius + 273.15 + 5; @free(T); !T=evaporator temp;

!Cp at Tevalp;
Cp0 = Cp0a + Cp0b*(T/100) + Cp0d*(T/100)^2; @free(Cp0);
Cp1 = Cp1a + Cp1b*(T/100) + Cp1d*(T/100)^2; @free(Cp1);
Cp2 = Cp2a + Cp2b*(T/100) + Cp2d*(T/100)^2; @free(Cp2);
Cp3 = Cp3a + Cp3b*(T/100) + Cp3d*(T/100)^2; @free(Cp3);
Cp4 = Cp4a + Cp4b*(T/100) + Cp4d*(T/100)^2; @free(Cp4);
Cp5 = Cp5a + Cp5b*(T/100) + Cp5d*(T/100)^2; @free(Cp5);
Cp6 = Cp6a + Cp6b*(T/100) + Cp6d*(T/100)^2; @free(Cp6);
Cp7 = Cp7a + Cp7b*(T/100) + Cp7d*(T/100)^2; @free(Cp7);
Cp8 = Cp8a + Cp8b*(T/100) + Cp8d*(T/100)^2; @free(Cp8);
Cp9 = Cp9a + Cp9b*(T/100) + Cp9d*(T/100)^2; @free(Cp9);
Cp10 = Cp10a + Cp10b*(T/100) + Cp10d*(T/100)^2; @free(Cp10);
Cp11 = Cp11a + Cp11b*(T/100) + Cp11d*(T/100)^2; @free(Cp11);
Cp12 = Cp12a + Cp12b*(T/100) + Cp12d*(T/100)^2; @free(Cp12);

```

```
Cp13 = Cp13a + Cp13b*(T/100) + Cp13d*(T/100)^2; @free(Cp13);
Cp14 = Cp14a + Cp14b*(T/100) + Cp14d*(T/100)^2; @free(Cp14);
```

```
Tref = 35 + 273.15; @free(Tref);
```

```
!Cp at Tref;
```

```
Cp0f = Cp0a + Cp0b*(Tref/100) + Cp0d*(Tref/100)^2; @free(Cp0f);
Cp1f = Cp1a + Cp1b*(Tref/100) + Cp1d*(Tref/100)^2; @free(Cp1f);
Cp2f = Cp2a + Cp2b*(Tref/100) + Cp2d*(Tref/100)^2; @free(Cp2f);
Cp3f = Cp3a + Cp3b*(Tref/100) + Cp3d*(Tref/100)^2; @free(Cp3f);
Cp4f = Cp4a + Cp4b*(Tref/100) + Cp4d*(Tref/100)^2; @free(Cp4f);
Cp5f = Cp5a + Cp5b*(Tref/100) + Cp5d*(Tref/100)^2; @free(Cp5f);
Cp6f = Cp6a + Cp6b*(Tref/100) + Cp6d*(Tref/100)^2; @free(Cp6f);
Cp7f = Cp7a + Cp7b*(Tref/100) + Cp7d*(Tref/100)^2; @free(Cp7f);
Cp8f = Cp8a + Cp8b*(Tref/100) + Cp8d*(Tref/100)^2; @free(Cp8f);
Cp9f = Cp9a + Cp9b*(Tref/100) + Cp9d*(Tref/100)^2; @free(Cp9f);
Cp10f = Cp10a + Cp10b*(Tref/100) + Cp10d*(Tref/100)^2;
@free(Cp10f);
Cp11f = Cp11a + Cp11b*(Tref/100) + Cp11d*(Tref/100)^2;
@free(Cp11f);
Cp12f = Cp12a + Cp12b*(Tref/100) + Cp12d*(Tref/100)^2;
@free(Cp12f);
Cp13f = Cp13a + Cp13b*(Tref/100) + Cp13d*(Tref/100)^2;
@free(Cp13f);
Cp14f = Cp14a + Cp14b*(Tref/100) + Cp14d*(Tref/100)^2;
@free(Cp14f);
```

```
!Equation for heat capacity (CP) in J/K mol;
```

```
CP_total =
n1*Cp1+n2*Cp2+n3*Cp3+n4*Cp4+n5*Cp5+n6*Cp6+n7*Cp7+n8*Cp8+n9*Cp9+
n10*Cp10+n11*Cp11+n12*Cp12+n13*Cp13+n14*Cp14+Cp0;
@free(CP_total);
```

```
!Equation for heat capacity (CP) in Tref in J/K mol;
```

```
CPF_total =
n1*Cp1f+n2*Cp2f+n3*Cp3f+n4*Cp4f+n5*Cp5f+n6*Cp6f+n7*Cp7f+n8*Cp8f
+n9*Cp9f+n10*Cp10f+n11*Cp11f+n12*Cp12f+n13*Cp13f+n14*Cp14f+ Cp0f;
@free(CPF_total);
```

```
!Group contribution for flash point;
```

```
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);
fp14 = 73.7; @free(fp14);
```

```
!Equation for flash point (fp);
```

```
fp_total =
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13+n14*fp14; @free(fp_total);
```

```

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

fp > 242;

fpcelcius = fp - 273.15; @free(fpcelcius);

!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);
logkow14 = -0.4615; @free(logkow14);

!Equation for octanol-water partition coefficient (logKow);
logkow_total =
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13+n14*logkow14; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);
LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);
LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);
LC5014 = 0.4393; @free(LC5014);

!Equation for aquatic toxicity (LC50);
LC50_total =
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013+n
14*LC5014; @free(LC50_total);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);

```

```

LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);
LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);
LD5014 = -0.1734; @free(LD5014);

!Equation for terrestrial toxicity (LD50);
LD50_total =
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013+n
14*LD5014; @free(LD50_total);

!constant for LD50;
A= 1.9372;
B= 0.0016;

!calculate for LD50 in mol/kg;
LD50_mol = 10^(-(LD50_total + A + B*mw_total)); @free(LD50_mol);

!Calculate for LD50 in mg/kg;
LD50_mg = LD50_mol*mw_total*1000; @free(LD50_mg);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);
PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);
PCO14 = 0.3858; @free(PCO14);

!Equation for photochemical oxidation potential (PCO);
PCO_total =
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13+n14*PCO14;
@free(PCO_total);

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);
BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);
BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);

```



```

BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);
BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);
BCF14 = 0.3988; @free(BCF14);

!Equation for bioconcentration factor (BCF);
BCF_total =
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13+n14*BCF14;
@free(BCF_total);

BCF_total < 3.3;

!Group contribution for permissible exposure limit (PEL);
PEL1 = 0.7723; @free(PEL1);
PEL2 = 0.0727; @free(PEL2);
PEL3 = -0.6557; @free(PEL3);
PEL4 = -1.3404; @free(PEL4);
PEL5 = 1.3612; @free(PEL5);
PEL6 = 2.3281; @free(PEL6);
PEL7 = 1.4016; @free(PEL7);
PEL8 = 2.3662; @free(PEL8);
PEL9 = 2.1251; @free(PEL9);
PEL10 = 2.0449; @free(PEL10);
PEL11 = 2.2638; @free(PEL11);
PEL12 = 0.9276; @free(PEL12);
PEL13 = -0.7462; @free(PEL13);
PEL14 = 1.2544; @free(PEL14);

!Equation for permissible exposure limit (PEL);
PEL_total =
n1*PEL1+n2*PEL2+n3*PEL3+n4*PEL4+n5*PEL5+n6*PEL6+n7*PEL7+n8*PEL8
+n9*PEL9+n10*PEL10+n11*PEL11+n12*PEL12+n13*PEL13+n14*PEL14;
@free(PEL_total);

!Calculate PEL in ppm;
!molar volume of gas, Vgas, in dm3/mol, Note that 1L=1dm3;
Vgas = 24.45;
PEL = Vgas*1000*10^(-PEL_total);

!Calculate for oxygen stoichiometric coefficient, Co;
Co = C_number + (H_number/4) - (O_number/2);

!Calculate for Lower explosion limit, LEL;
LEL = (100/(1+9.045*Co));

!Calculate for Upper explosion limit, UEL;
UEL = (100/(1+1.1843*Co));

!Calculate explosiveness, Iex using S= (UEL - LEL)vol%;
S = UEL - LEL;

!Disjunctive equation for explosiveness, Iex;
Iex = Iex1 + Iex2 + Iex3 +1; @bin(Iex1); @bin(Iex2); @bin(Iex3);
(0-20)*(1-Iex1) < S - 20;
S - 20 <= (100 - 20)*(Iex1);
(0-45)*(1-Iex2) < S - 45;
S - 45 <= (100 - 45)*(Iex2);
(0-70)*(1-Iex3) < S - 70;

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```

S - 70 <= (100 - 70)*(Iex3);

!!Disjunctive equation for acute health hazard;
IAH = IAH1 + IAH2 + IAH3 + IAH4; @bin(IAH1); @bin(IAH2);
@bin(IAH3); @bin(IAH4);
(0.00001-2000)*(IAH1) < LD50_mg- 2000;
LD50_mg- 2000 <= (10000 - 2000)*(1-IAH1);
(0.00001-500)*(IAH2) < LD50_mg - 500;
LD50_mg- 500 <= (10000 - 500)*(1-IAH2);
(0.00001-50)*(IAH3) < LD50_mg - 50;
LD50_mg - 50 <= (10000 - 50)*(1-IAH3);
(0.00001-5)*(IAH4) < LD50_mg- 5;
LD50_mg - 5 <= (10000 - 5)*(1-IAH4);

!Disjunctive equation for flammability. Ifl;
Ifl = Ifl1 + Ifl2 + Ifl5 + 1; @bin(Ifl1); @bin(Ifl2); @bin(Ifl3);
@bin(Ifl4); @bin(Ifl5);
(-1000-93.4)*(Ifl1) < Fpcelcius - 93.4;
Fpcelcius - 93.4 <= (10000-93.4)*(1-Ifl1);
(-1000-37.8)*(Ifl2) < Fpcelcius - 37.8;
Fpcelcius - 37.8 <= (10000-37.8)*(1-Ifl2);
(-1000-22.8)*(Ifl3) < Fpcelcius - 22.8;
Fpcelcius - 22.8 <= (10000-22.8)*(1-Ifl3);
(-1000-37.8)*(Ifl4) < Tbcelcius - 37.8;
Tbcelcius - 37.8 <= (10000-37.8)*(1-Ifl4);
Ifl3 + Ifl4 = g;
(0-2)*(1-Ifl5) < g- 2;
g - 2 <= (5-2)*Ifl5;

!Disjunctive equation for exposure limit, Iel;
Iel = Iel1 + Iel2 + Iel3 + Iel4; @bin(Iel1); @bin(Iel2);
@bin(Iel3); @bin(Iel4);
(0.0001-1000)*(Iel1) < PEL -1000;
PEL - 1000 <= (10000 - 1000)*(1-Iel1);
(0.0001-100)*(Iel2) < PEL -100;
PEL - 100 <= (10000 - 100)*(1-Iel2);
(0.0001-10)*(Iel3) < PEL -10;
PEL - 10 <= (10000 - 10)*(1-Iel3);
(0.0001-1)*(Iel4) < PEL -1;
PEL - 1 <= (10000 - 1)*(1-Iel4);

!Mass and Energy balance around the evaporator;
!Evaporator feed stream temperature = 35C;
!Evaporator outlet stream temperature based on boiling point of
solvent added by 5 degree celsius to ensure complete vaporisation;
!Mass of solvent entering evaporator, Ms = 750;
!Mass of oil entering evaporator, Mo = 250 kg;
!Mass of solvent vapour, Msv = 745 kg;
!Mass of solvent at the bottom, Msb = 5 kg;
!Mass of oil at the bottom, Mob = 250 kg;

Ms = 750;
Mo = 250;
Msv = 745;
Msb = 5;
Mob = 250;

!Cp in kJ/kg C; !Assume cp oil constant over temperature;
Cpoil = 1.902;

```

```

!Treference = lowest temperature of the system, which is the feed
temperature;
!Tfeed = 35 + 273.15;
!Enthalpy for feed of evaporator, deltaHf = mCPdeltaT;
!Enthalpy for vapor stream of evaporator, deltaHv = mCPdeltaT +
m*hv;
!Enthalpy for vapor stream of evaporator, deltaHb = mCPdeltaT;
!Total energy requirement = deltaHv + deltaHb;

!average Cp = (cp at 308.15K + cp at T)/ 2;
averageCp = (Cpf_total + Cp_total)/2;

deltaHv = Msv*(averageCp/Mw_total)*(T - Tref) +
Msv*Hv_total*1000/Mw_total;
deltaHb = Msb*(averageCp/Mw_total)*(T - Tref) + Mob*Cpoil*(T -
Tref);

!energyrequirement, ERhot to vapourize solvent;
ERhot = deltaHv + deltaHb; @free(ERhot);

!8 bar steam latent heat = 2046.53;

!amount_steam in kg= energyrequirement/2046.53;

amt_steam = ERhot/2046.53;

!energy required to condense the solvent to 35C for recycle
purpose, ERcold;
-ERcold = Msv*(averageCp/Mw_total)*(Tref - T) -
Msv*Hv_total*1000/Mw_total; @free(ERcold);

!utility cost = cost; !steam cost = RM70.21/1000kg; !cooling
water cost = RM 1.44/GJ;

heatingcost = amt_steam*70.21/1000;
coolingcost = ERcold/100000*1.44;

cost = amt_steam*70.21/1000 + ERcold/100000*1.44; @free(cost);

k=@exp((-3231.7/T)+3.8708); @free(k);

!degradation kinetics;
!c/co=exp(-kt);
! t = heating time (min), assume 2 hours = 120min;
!co= initial carotene concentration (mg/kg);
!c = final carotene concentration (mg/kg);
!Assume co = 5000ppm = 5000 mg/kg;
cf = (@exp(-k*time)*5000); @free(cf);
time=120;
c1=5000;

!Disjunctive equation for concentration;
C = IC1*c1 + Cf*(1-IC1);@bin(IC1);

(0-343.15)*(IC1)<= T - 343.15;
T - 343.15 < (1000-343.15)*(1-IC1);

Yield = C/c1;

```

End

Part B: Evaporation under vacuum condition

model:

```
max = objectivefunction;
!when consider only yield and energy, by assuming both of them
equal importance;
!objectivefunction                                     =
0.5*Fyield+0.5*EReq; !@free(objectivefunction);

!Exclude Tb as objective function;
objectivefunction = 0.03105*sol + 0.0621*st + 0.0621*vis +
0.0077*LC50 + 0.0278*PCO + 0.0034*BCF + 0.0034*KOW +
0.1302*Iflfinal + 0.1302*Iex + 0.0211*Ielfinal + 0.0211*IAHfinal
+0.5*finalcost ;

!For acyclic compound;

!sol = (2.697 - Diff_car)/(2.697 - 0.0022);@free(sol);
!st = (27.4799 - st_total)/(27.4799 - 20.8046);@free(st);
!vis = (2.8845- vis_total)/(2.8845 + 1.1851);@free(vis);
!LC50 = (2.9129 - LC50_total)/(2.9129 + 1.236);@free(LC50);
!LD50 = (0.3994 - LD50_total)/(0.3944 + 0.2253);@free(LD50);
!PCO= (PCO_total + 0.7789)/(0.6011 + 0.7789);@free(PCO);
!BCF = (1.7102 - BCF_total)/(1.7102 - 0.1706);@free(BCF);
!KOW = (1.1851- logkow_total)/(1.1851 + 0.6804);@free(KOW);
!Iflfinal = Ifl/3; @free(Iflfinal);
!Ielfinal = (4-Iel)/(4-1); @free(Ielfinal);
!IAHfinal = (2 -IAH)/(2-1); @free(IAHfinal);
!finalcost = (152.2367 - cost)/(152.2367 - 53.02582);
@free(finalcost);

!For monocyclic compound;

sol = (2.7895 - Diff_car)/(2.7895 - 0.0104);!@free(sol);
st = (10.2261 - st_total)/(10.2261- 2.4066);!@free(st);
vis = (4.3483 - vis_total)/(4.3483 - 1.067);!@free(vis);
LC50 = (3.4217 - LC50_total)/(3.4217+ 1.3233);!@free(LC50);
LD50 = (0.947 - LD50_total)/(0.947 - 0.0611);!@free(LD50);
PCO = (PCO_total + 0.9224)/(0.6671 + 0.9224);!@free(PCO);
```

```

BCF = (1.1159 - BCF_total)/(1.1159 + 0.1442);!@free(BCF);

KOW = (3.8453 - logkow_total)/(3.8453 - 0.6772);!@free(KOW);

Iflfinal = Ifl/3; !@free(Iflfinal);

Ielfinal = (4-Iel)/(4-0); !@free(Ielfinal);

IAHfinal = (2-IAH)/(2-1); !@free(IAHfinal);

finalcost      =      (131.381      -      cost)/(131.381      -
45.47011); !@free(finalcost);

!Defining the chemical building blocks
n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O, n14 = CH3COO;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13); @GIN (n14);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13+n14*2;
H_number      =
n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13+n14*3;
O_number = n5+n6*2+n7+n8+n9+n12+n13+n14*2;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
O_number <2;

!Free bonds for each group;
val1 = 1;
val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;
val8 = 1;
val9 = 1;
val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;
val14 = 1;

!Structural constraint, the molecule generated must not contain
free bonds;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14) + 2
= 0; !monocyclic compound;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1)) -
(n1*val1+n2*val2+n3*val3+n4*val4+n5*val5+n6*val6+n7*val7+n8*val
8+n9*val9+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14) =
0; !acyclic compound;

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```

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);
tb14 = 2.5805; @free(tb14);

!Property Constraints;
!Equation for normal boiling point;
tb_total =
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13+n14*tb14; @free(tb_total);

!B.pt constraint value, where Tb > 65C;
tb_total > 3.9866;

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;
mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;
mw14 = 59.044;

!Equation for molecular weight (mw);
mw_total =
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13+n14*mw14;

mw_total <150;

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);
sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);

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sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);
sol14 = -0.6905; @free(sol14);

!Equation for solubility (sol);
sol_total
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13+n14*sol14;
@free(sol_total);

!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacglycerol = 17.1822MPa;
!sol0= 21.6654 MPa (sol0 = solubility constant);

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

!constaint on solubility;
sol_final < 20.6;
sol_final > 14.4;

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);
vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);
vis14 = -0.0358; @free(vis14);

!Equation for viscosity (vis);

```

```

vis_total
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13+n14*vis14;
@free(vis_total);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);
st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);
st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);
st14 = 14.8168; @free(st14);

!Equation for surface tension (st);
st_total
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13+n14*st14; @free(st_total);

!Group contribution for heat of vaporisation(Hv);
Hv1 = 2.2643; @free(Hv1);
Hv2 = 4.7607; @free(Hv2);
Hv3 = 5.0336; @free(Hv3);
Hv4 = 5.1448; @free(Hv4);
Hv5 = 24.1639; @free(Hv5);
Hv6 = 20.4196; @free(Hv6);
Hv7 = 15.1303; @free(Hv7);
Hv8 = 13.2496; @free(Hv8);
Hv9 = 7.8029; @free(Hv9);
Hv10 = 17.5679; @free(Hv10);
Hv11 = 5.4644; @free(Hv11);
Hv12 = 8.5931; @free(Hv12);
Hv13 = 9.1274; @free(Hv13);
Hv14 = 20.0986; @free(Hv14);

!Hv0=9.6127;

!Equation for heat of vaporisation (Hv) in KJ/mol;
Hv_total
n1*Hv1+n2*Hv2+n3*Hv3+n4*Hv4+n5*Hv5+n6*Hv6+n7*Hv7+n8*Hv8+n9*Hv9+
n10*Hv10+n11*Hv11+n12*Hv12+n13*Hv13+n14*Hv14+9.6127;
@free(Hv_total);

!Group contribution for heat capacity (CP);
Cp0a= 89.53; Cp0b = -40.13; Cp0d= 5.19; @free(Cp0a); @free(Cp0b);
@free(Cp0d);
Cp1a= 1.04; Cp1b = 8.29; Cp1d= 0.76; @free(Cp1a); @free(Cp1b);
@free(Cp1d);
Cp2a= 19.64; Cp2b = 0.78; Cp2d= 0.80; @free(Cp2a); @free(Cp2b);
@free(Cp2d);
Cp3a= 12.20; Cp3b = 7.90; Cp3d= -1.03; @free(Cp3a); @free(Cp3b);
@free(Cp3d);
Cp4a= 25.40; Cp4b = -2.25; Cp4d= 0.16; @free(Cp4a); @free(Cp4b);
@free(Cp4d);

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Cp5a= -99.86; Cp5b = 71.89; Cp5d= -7.70; @free(Cp5a); @free(Cp5b);
@free(Cp5d);
Cp6a= -2.21; Cp6b = 30.79; Cp6d= -1.98; @free(Cp6a); @free(Cp6b);
@free(Cp6d);
Cp7a= 69.38; Cp7b = -2.63; Cp7d= 1.91; @free(Cp7a); @free(Cp7b);
@free(Cp7d);
Cp8a= 32.92; Cp8b = 10.22; Cp8d= -1.96; @free(Cp8a); @free(Cp8b);
@free(Cp8d);
Cp9a= 21.08; Cp9b = 14.60; Cp9d= -0.71; @free(Cp9a); @free(Cp9b);
@free(Cp9d);
Cp10a= 41.12; Cp10b = 6.56; Cp10d= -1.16; @free(Cp10a);
@free(Cp10b); @free(Cp10d);
Cp11a= 15.13; Cp11b = 9.02; Cp11d= 0.99; @free(Cp11a);
@free(Cp11b); @free(Cp11d);
Cp12a= 48.82; Cp12b = 4.92; Cp12d= -0.40; @free(Cp12a);
@free(Cp12b); @free(Cp12d);
Cp13a= 66.98; Cp13b = -9.64; Cp13d= 0.60; @free(Cp13a);
@free(Cp13b); @free(Cp13d);
Cp14a= 34.25; Cp14b = 35.65; Cp14d= -5.17; @free(Cp14a);
@free(Cp14b); @free(Cp14d);

!Calculate for Tb in C;
!Tb constant, tb0 in K;
tb0 = 244.5165;
Tbcelcius = @log(tb_total)*tb0 -273.15; @free(Tbcelcius);

T1= Tbcelcius + 273.15; @free(T1); !T1=normal boiling point (K);

!clausius clayperson eqn: hv at kJ/mol, R= 0.008314 kJ/K mol, Tb
at K;
!P1 = 750.062; !1 bar = 750.062 torr;
!R = 0.008314; @free(R);

P2 = 750.062*@exp((Hv_total/0.008314)*((1/T1)-(1/T2)));
@free(P2);

T2 = T3 - 5; !T3= evaporator temperature; @free(T2);

T3 = 338.15;

!suction gas temperature, Tsg = T3 (degree celcius);
Tsg = T3 - 273.15;

!Cp at Tevap;
Cp0 = Cp0a + Cp0b*(T3/100) + Cp0d*(T3/100)^2; @free(Cp0);
Cp1 = Cp1a + Cp1b*(T3/100) + Cp1d*(T3/100)^2; @free(Cp1);
Cp2 = Cp2a + Cp2b*(T3/100) + Cp2d*(T3/100)^2; @free(Cp2);
Cp3 = Cp3a + Cp3b*(T3/100) + Cp3d*(T3/100)^2; @free(Cp3);
Cp4 = Cp4a + Cp4b*(T3/100) + Cp4d*(T3/100)^2; @free(Cp4);
Cp5 = Cp5a + Cp5b*(T3/100) + Cp5d*(T3/100)^2; @free(Cp5);
Cp6 = Cp6a + Cp6b*(T3/100) + Cp6d*(T3/100)^2; @free(Cp6);
Cp7 = Cp7a + Cp7b*(T3/100) + Cp7d*(T3/100)^2; @free(Cp7);
Cp8 = Cp8a + Cp8b*(T3/100) + Cp8d*(T3/100)^2; @free(Cp8);
Cp9 = Cp9a + Cp9b*(T3/100) + Cp9d*(T3/100)^2; @free(Cp9);
Cp10 = Cp10a + Cp10b*(T3/100) + Cp10d*(T3/100)^2; @free(Cp10);
Cp11 = Cp11a + Cp11b*(T3/100) + Cp11d*(T3/100)^2; @free(Cp11);
Cp12 = Cp12a + Cp12b*(T3/100) + Cp12d*(T3/100)^2; @free(Cp12);
Cp13 = Cp13a + Cp13b*(T3/100) + Cp13d*(T3/100)^2; @free(Cp13);
Cp14 = Cp14a + Cp14b*(T3/100) + Cp14d*(T3/100)^2; @free(Cp14);

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Tref = 35 + 273.15; @free(Tref);

!Cp at Tref;
Cp0f = Cp0a + Cp0b*(Tref/100) + Cp0d*(Tref/100)^2; @free(Cp0f);
Cp1f = Cp1a + Cp1b*(Tref/100) + Cp1d*(Tref/100)^2; @free(Cp1f);
Cp2f = Cp2a + Cp2b*(Tref/100) + Cp2d*(Tref/100)^2; @free(Cp2f);
Cp3f = Cp3a + Cp3b*(Tref/100) + Cp3d*(Tref/100)^2; @free(Cp3f);
Cp4f = Cp4a + Cp4b*(Tref/100) + Cp4d*(Tref/100)^2; @free(Cp4f);
Cp5f = Cp5a + Cp5b*(Tref/100) + Cp5d*(Tref/100)^2; @free(Cp5f);
Cp6f = Cp6a + Cp6b*(Tref/100) + Cp6d*(Tref/100)^2; @free(Cp6f);
Cp7f = Cp7a + Cp7b*(Tref/100) + Cp7d*(Tref/100)^2; @free(Cp7f);
Cp8f = Cp8a + Cp8b*(Tref/100) + Cp8d*(Tref/100)^2; @free(Cp8f);
Cp9f = Cp9a + Cp9b*(Tref/100) + Cp9d*(Tref/100)^2; @free(Cp9f);
Cp10f = Cp10a + Cp10b*(Tref/100) + Cp10d*(Tref/100)^2;
@free(Cp10f);
Cp11f = Cp11a + Cp11b*(Tref/100) + Cp11d*(Tref/100)^2;
@free(Cp11f);
Cp12f = Cp12a + Cp12b*(Tref/100) + Cp12d*(Tref/100)^2;
@free(Cp12f);
Cp13f = Cp13a + Cp13b*(Tref/100) + Cp13d*(Tref/100)^2;
@free(Cp13f);
Cp14f = Cp14a + Cp14b*(Tref/100) + Cp14d*(Tref/100)^2;
@free(Cp14f);

!Equation for heat capacity (CP) in J/K mol;
CP_total =
n1*Cp1+n2*Cp2+n3*Cp3+n4*Cp4+n5*Cp5+n6*Cp6+n7*Cp7+n8*Cp8+n9*Cp9+
n10*Cp10+n11*Cp11+n12*Cp12+n13*Cp13+n14*Cp14+Cp0;
@free(CP_total);

!Equation for heat capacity (CP) in Tref in J/K mol;
CPf_total =
n1*Cp1f+n2*Cp2f+n3*Cp3f+n4*Cp4f+n5*Cp5f+n6*Cp6f+n7*Cp7f+n8*Cp8f
+n9*Cp9f+n10*Cp10f+n11*Cp11f+n12*Cp12f+n13*Cp13f+n14*Cp14f+ Cp0f;
@free(CPf_total);

!Group contribution for flash point;
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);
fp14 = 73.7; @free(fp14);

!Equation for flash point (fp);
fp_total =
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13+n14*fp14; @free(fp_total);

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

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fp > 242;

fpcelcius = fp - 273.15; @free(fpcelcius);

!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);
logkow14 = -0.4615; @free(logkow14);

!Equation for octanol-water partition coefficient (logKow);
logkow_total =
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13+n14*logkow14; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);
LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);
LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);
LC5014 = 0.4393; @free(LC5014);

!Equation for aquatic toxicity (LC50);
LC50_total =
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013+n
14*LC5014; @free(LC50_total);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);
LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);

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LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);
LD5014 = -0.1734; @free(LD5014);

!Equation for terrestrial toxicity (LD50);
LD50_total =
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013+n
14*LD5014; @free(LD50_total);

!constant for LD50;
A= 1.9372;
B= 0.0016;

!calculate for LD50 in mol/kg;
LD50_mol = 10^(-(LD50_total + A + B*mw_total)); @free(LD50_mol);

!Calculate for LD50 in mg/kg;
LD50_mg = LD50_mol*mw_total*1000; @free(LD50_mg);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);
PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);
PCO14 = 0.3858; @free(PCO14);

!Equation for photochemical oxidation potential (PCO);
PCO_total =
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13+n14*PCO14;
@free(PCO_total);

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);
BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);
BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);
BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);

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BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);
BCF14 = 0.3988; @free(BCF14);

!Equation for bioconcentration factor (BCF);
BCF_total
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13+n14*BCF14;
@free(BCF_total);

BCF_total < 3.3;

!Group contribution for permissible exposure limit (PEL);
PEL1 = 0.7723; @free(PEL1);
PEL2 = 0.0727; @free(PEL2);
PEL3 = -0.6557; @free(PEL3);
PEL4 = -1.3404; @free(PEL4);
PEL5 = 1.3612; @free(PEL5);
PEL6 = 2.3281; @free(PEL6);
PEL7 = 1.4016; @free(PEL7);
PEL8 = 2.3662; @free(PEL8);
PEL9 = 2.1251; @free(PEL9);
PEL10 = 2.0449; @free(PEL10);
PEL11 = 2.2638; @free(PEL11);
PEL12 = 0.9276; @free(PEL12);
PEL13 = -0.7462; @free(PEL13);
PEL14 = 1.2544; @free(PEL14);

!Equation for permissible exposure limit (PEL);
PEL_total
n1*PEL1+n2*PEL2+n3*PEL3+n4*PEL4+n5*PEL5+n6*PEL6+n7*PEL7+n8*PEL8
+n9*PEL9+n10*PEL10+n11*PEL11+n12*PEL12+n13*PEL13+n14*PEL14;
@free(PEL_total);

!Calculate PEL in ppm;
!molar volume of gas, Vgas, in dm3/mol, Note that 1L=1dm3;
Vgas = 24.45;
PEL = Vgas*1000*10^(-PEL_total);

!Calculate for oxygen stoichiometric coefficient, Co;
Co = C_number + (H_number/4) - (O_number/2);

!Calculate for Lower explosion limit, LEL;
LEL = (100/(1+9.045*Co));

!Calculate for Upper explosion limit, UEL;
UEL = (100/(1+1.1843*Co));

!Calculate explosiveness, Iex using S= (UEL - LEL)vol%;
S = UEL - LEL;

!Disjunctive equation for explosiveness, Iex;
Iex = Iex1 + Iex2 + Iex3 +1; @bin(Iex1); @bin(Iex2); @bin(Iex3);
(0-20)*(1-Iex1) < S - 20;
S - 20 <= (100 - 20)*(Iex1);
(0-45)*(1-Iex2) < S - 45;
S - 45 <= (100 - 45)*(Iex2);
(0-70)*(1-Iex3) < S - 70;
S - 70 <= (100 - 70)*(Iex3);

!!Disjunctive equation for acute health hazard;

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IAH = IAH1 + IAH2 + IAH3 + IAH4; @bin(IAH1); @bin(IAH2);
@bin(IAH3); @bin(IAH4);
(0.00001-2000)*(IAH1) < LD50_mg- 2000;
LD50_mg- 2000 <= (10000 - 2000)*(1-IAH1);
(0.00001-500)*(IAH2) < LD50_mg - 500;
LD50_mg- 500 <= (10000 - 500)*(1-IAH2);
(0.00001-50)*(IAH3) < LD50_mg - 50;
LD50_mg - 50 <= (10000 - 50)*(1-IAH3);
(0.00001-5)*(IAH4) < LD50_mg- 5;
LD50_mg - 5 <= (10000 - 5)*(1-IAH4);

!Disjunctive equation for flammability. Ifl;
Ifl = Ifl1 + Ifl2 + Ifl5 + 1; @bin(Ifl1); @bin(Ifl2); @bin(Ifl3);
@bin(Ifl4); @bin(Ifl5);
(-1000-93.4)*(Ifl1) < Fpcelcius - 93.4;
Fpcelcius - 93.4 <= (10000-93.4)*(1-Ifl1);
(-1000-37.8)*(Ifl2) < Fpcelcius - 37.8;
Fpcelcius - 37.8 <= (10000-37.8)*(1-Ifl2);
(-1000-22.8)*(Ifl3) < Fpcelcius - 22.8;
Fpcelcius - 22.8 <= (10000-22.8)*(1-Ifl3);
(-1000-37.8)*(Ifl4) < Tbcelsius - 37.8;
Tbcelsius - 37.8 <= (10000-37.8)*(1-Ifl4);
Ifl3 + Ifl4 = g;
(0-2)*(1-Ifl5) < g- 2;
g - 2 <= (5-2)*Ifl5;

!Disjunctive equation for exposure limit, Iel;
Iel = Iel1 + Iel2 + Iel3 + Iel4; @bin(Iel1); @bin(Iel2);
@bin(Iel3); @bin(Iel4);
(0.0001-1000)*(Iel1) < PEL -1000;
PEL - 1000 <= (10000 - 1000)*(1-Iel1);
(0.0001-100)*(Iel2) < PEL -100;
PEL - 100 <= (10000 - 100)*(1-Iel2);
(0.0001-10)*(Iel3) < PEL -10;
PEL - 10 <= (10000 - 10)*(1-Iel3);
(0.0001-1)*(Iel4) < PEL -1;
PEL - 1 <= (10000 - 1)*(1-Iel4);

!Mass and Energy balance around the evaporator;
!Evaporator feed stream temperature = 35C;
!Evaporator outlet stream temperature based on boiling point of
solvent added by 5 degree celsius to ensure complete vaporisation;
!Mass of solvent entering evaporator, Ms = 0.15kg;
!Mass of oil entering evaporator, Mo = 0.05kg;
!Mass of solvent vapour, Msv = 0.149 kg;
!Mass of solvent at the bottom, Msb = 0.001 kg;
!Mass of oil at the bottom, Mob = 0.05 kg;

Ms = 750;
Mo = 250;
Msv = 745;
Msb = 5;
Mob = 250;

!Cp in kJ/kg C; !Assume cp oil constant over temperature;
Cpoil = 1.902;

!Treference = lowest temperature of the system, which is the feed
temperature;
!Tfeed = 35 + 273.15;

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!Enthalpy for feed of evaporator, deltaHf = mCPdeltaT;
!Enthalpy for vapor stream of evaporator, deltaHv = mCPdeltaT +
m*hv;
!Enthalpy for vapor stream of evaporator, deltaHb = mCPdeltaT;
!Total energy requirement = deltaHv + deltaHb;

!average Cp = (cp at 308.15K + cp at T)/ 2;
averageCp = (Cpf_total + Cp_total)/2;

deltaHv = Msv*(averageCp/Mw_total)*(T3 - Tref) +
Msv*Hv_total*1000/Mw_total; @free(deltaHv);
deltaHb = Msb*(averageCp/Mw_total)*(T3 - Tref) + Mob*Cpoil*(T3 -
Tref); @free(deltaHb);

!energyrequirement to vaporize solvent, ERhot;
ERhot = deltaHv + deltaHb;

!8 bar steam latent heat = 2046.53;

!amount_steam in kg= ERhot/2046.53;

amt_steam = ERhot/2046.53; @free(amt_steam);

!energy requirement to condense solvent, ERcold;
-ERcold = Msv*(averageCp/Mw_total)*(Tref - T3) -
Msv*Hv_total*1000/Mw_total; @free(ERcold);

!entrainment ratio, TCA;

TCA = (-4*10^-10)*Tsg^3+(3*10^-7)*Tsg^2 -0.0005*Tsg + 1.0131;
@free(TCA);
!TCA = 0.982;

molwt1 = 1*10^-5*(mw_total)^3 - 0.0013*(mw_total)^2 +
0.0642*mw_total + 0.0161; @free(molwt1);

Molwt2 = 2*10^-5*(mw_total)^2 + 0.0077*mw_total + 0.9464;
@free(molwt2);

MWg = M1*molwt1 + Molwt2 ; @bin(M1); @free(mwg);

(0-60)*(M1) < mw_total - 60;
mw_total - 60 < (1000-60)*(1-M1);

DAE = Msv/(TCA*mwg); @free(DAE); !wog = solvent flowrate;

P2 > 75; !single stage ejector can create vacuum up to 75 mm Hg;
Pd = 1125.093; !Pd = discharge pressure in torr, Pd = 1.5 bar;
Pd < 15*P2;

Ra = (Pd/P2)*((0.434-1.338/P2+0.475*10^-3*(P2))-
0.187)*(1.31); !use 8 barg steam; @free(Ra);

ejectorsteam = DAE*Ra; @free(ejectorsteam);

```

```

!totalcost = hot utility cost + cold utility cost + ejector
steam cost;
hotcost = amt_steam*70.21/1000;
coldcost = ERcold/1000000*1.44; @free(coldcost);
ejectorsteamcost = ejectorsteam*70.21/1000;

cost = (hotcost + coldcost + ejectorsteamcost); @free(cost);

!integer cut;

end

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Part C: Cooling Crystallisation

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model:

max = objectivefunction;

!Exclude Tb and yield as objective function; !because yield is
always 1; @free(objectivefunction);
objectivefunction = 0.03105*sol + 0.0621*st + 0.0621*vis +
0.0077*LC50 + 0.0278*PCO + 0.0034*BCF + 0.0034*KOW +
0.1302*Iflfinal + 0.1302*Iexfinal + 0.0211*Ielfinal +
0.0211*IAHfinal + 0.5*finalcost;

!For acyclic compound;

!sol = (2.7954 - Diff_car)/(2.7954 - 0.0022);@free(sol);

!st = (33.0008- st_total)/(33.0008- 20.1833);@free(st);

!vis = (4.6837 - vis_total)/(4.6837 + 1.1851);@free(vis);

!LC50 = (3.9917 - LC50_total)/(3.9917 + 1.4238);@free(LC50);

!LD50 = (1.1536 - LD50_total)/(1.1536 + 0.2253);@free(LD50);

!PCO= (PCO_total+ 1.4889)/(0.74 + 1.4889);@free(PCO);

!BCF = (1.9106 - BCF_total)/(1.9106 - 0.1706);@free(BCF);
!
KOW = (2.9334- logkow_total)/(2.9334 + 0.6804);@free(KOW);

!Iflfinal = (3-Ifl)/(3-1); @free(Iflfinal);

!Iexfinal = 1; @free(Iexfinal);

!Ielfinal = (4-Iel)/(4-1); @free(Ielfinal);

!IAHfinal = (2 -IAH)/(2-1); @free(IAHfinal);

!finalcost = (3.180435 - cost)/(3.180435 - 2.632213) ;
@free(finalcost);

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!For monocyclic compound;

sol = (2.7987 - Diff_car)/(2.7987 - 0.0104);!@free(sol);

st = (14.2929 - st_total)/(14.2929 - 1.7853);!@free(st);

vis = (6.6708 - vis_total)/(6.6708 - 1.067);!@free(vis);

LC50 = (3.8088 - LC50_total)/(3.8088 + 1.806);!@free(LC50);

LD50 = (0.963 - LD50_total)/(0.963 - 0.0611);!@free(LD50);

PCO = (PCO_total + 1.2466)/(0.7134 + 1.2466);!@free(PCO);

BCF = (1.2 - BCF_total)/(1.2 + 0.5042);!@free(BCF);

KOW = (4.352 - logkow_total)/(4.352 - 0.5966);!@free(KOW);

Iflfinal = (3-Ifl)/(3-2); !@free(Iflfinal);

Iexfinal = 1;

Ielfinal = (4-Iel)/(4-0); !@free(Ielfinal);

IAHfinal = (2-IAH)/(2-1); !@free(IAHfinal);

finalcost      =      (3.00865      -      cost)/(3.00865      -
2.588456) ; !@free(finalcost);

!Defining the chemical building blocks
n1 = CH3, n2 = CH2, n3 = CH, n4 = C, n5 = OH, n6 = COOH, n7 =
CH3CO, n8 = CHO, n9 = CH3O, n10 = NH2, n11 = CH2=CH, n12 = CH2O,
n13 = CH-O, n14 = CH3COO;

@GIN (n1); @GIN (n2); @GIN (n3); @GIN (n4); @GIN (n5); @GIN (n6);
@GIN (n7); @GIN (n8); @GIN (n9); @GIN (n10); @GIN (n11); @GIN
(n12); @GIN (n13); @GIN (n14);

n_total = n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14;
C_number = n1+n2+n3+n4+n6+n7*2+n8+n9+n11*2+n12+n13+n14*2;
H_number      =
n1*3+n2*2+n3+n5+n6+n7*3+n8+n9*3+n10*2+n11*3+n12*2+n13+n14*3;
O_number = n5+n6*2+n7+n8+n9+n12+n13+n14*2;
N_number = n10;

!molecular structure constraints;
n_total > 0;
n_total <15;
O_number <2;

!Free bonds for each group;
val1 = 1;
val2 = 2;
val3 = 3;
val4 = 4;
val5 = 1;
val6 = 1;
val7 = 1;
val8 = 1;
val9 = 1;

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val10 = 1;
val11 = 1;
val12 = 2;
val13 = 3;
val14 = 1;

!Structural constraint, the molecule generated must not contain
free bonds;
(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1))      -
(n1*val11+n2*val12+n3*val13+n4*val14+n5*val15+n6*val16+n7*val17+n8*val
8+n9*val19+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14) + 2
= 0; !monocyclic compound;
!(2*(n1+n2+n3+n4+n5+n6+n7+n8+n9+n10+n11+n12+n13+n14-1))      -
(n1*val11+n2*val12+n3*val13+n4*val14+n5*val15+n6*val16+n7*val17+n8*val
8+n9*val19+n10*val10+n11*val11+n12*val12+n13*val13+n14*val14)    =
0; !acyclic compound;

!Group contribution for normal boiling point;
tb1 = 0.8853; @free(tb1);
tb2 = 0.5815; @free(tb2);
tb3 = -0.0039; @free(tb3);
tb4 = -0.4985; @free(tb4);
tb5 = 2.1385; @free(tb5);
tb6 = 4.0158; @free(tb6);
tb7 = 2.6245; @free(tb7);
tb8 = 2.1663; @free(tb8);
tb9 = 1.5724; @free(tb9);
tb10 = 1.8748; @free(tb10);
tb11 = 1.4381; @free(tb11);
tb12 = 0.9999; @free(tb12);
tb13 = 0.4724; @free(tb13);
tb14 = 2.5805; @free(tb14);

!Property Constraints;
!Equation for normal boiling point;
tb_total =
n1*tb1+n2*tb2+n3*tb3+n4*tb4+n5*tb5+n6*tb6+n7*tb7+n8*tb8+n9*tb9+
n10*tb10+n11*tb11+n12*tb12+n13*tb13+n14*tb14; @free(tb_total);

!B.pt constraint value, where Tb > 40C; !solvent must be liquid
in extractor; !extractor temperature set at 35C;
tb_total > 3.59912;

!Group contribution for melting point;
tm_total =
n1*tm1+n2*tm2+n3*tm3+n4*tm4+n5*tm5+n6*tm6+n7*tm7+n8*tm8+n9*tm9+
n10*tm10+n11*tm11+n12*tm12+n13*tm13+n14*tm14; @free(tm_total);

!Group contribution for melting point;
tm1 = 0.6699; @free(tm1);
tm2 = 0.2992; @free(tm2);
tm3 = -0.2943; @free(tm3);
tm4 = -0.043; @free(tm4);
tm5 = 3.2702; @free(tm5);
tm6 = 7.1886; @free(tm6);
tm7 = 3.1357; @free(tm7);
tm8 = 2.9884; @free(tm8);
tm9 = 1.5327; @free(tm9);
tm10 = 3.5553; @free(tm10);
tm11 = 1.0511; @free(tm11);
tm12 = 0.7649; @free(tm12);

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tm13 = 0.1817; @free(tm13);
tm14 = 2.4227; @free(tm14);

!tm0 = 143.5706;

tm = @log(tm_total)*143.5706; !kelvin; @free(tm);

!tm of solvent must be less than crystalliser temperature;
!Crystallizer temperature must be less than melting point of
lower melting TAG which is around 15C;

!crystallisationtemp = 10;
tc = 283.15;

tm <= 283.15;

!Group contribution for molecular weight;
mw1 = 15.035;
mw2 = 14.027;
mw3 = 13.019;
mw4 = 12.011;
mw5 = 17.007;
mw6 = 45.017;
mw7 = 43.045;
mw8 = 29.018;
mw9 = 31.034;
mw10 = 16.023;
mw11 = 27.045;
mw12 = 30.026;
mw13 = 29.018;
mw14 = 59.044;

!Equation for molecular weight (mw);
mw_total =
n1*mw1+n2*mw2+n3*mw3+n4*mw4+n5*mw5+n6*mw6+n7*mw7+n8*mw8+n9*mw9+
n10*mw10+n11*mw11+n12*mw12+n13*mw13+n14*mw14;

mw_total < 150;

!Group contribution for hildebrand solubility parameter;
sol1 = -2.1040; @free(sol1);
sol2 = -0.1540; @free(sol2);
sol3 = 1.1153; @free(sol3);
sol4 = 1.9577; @free(sol4);
sol5 = 2.4637; @free(sol5);
sol6 = 3.1694; @free(sol6);
sol7 = -0.1581; @free(sol7);
sol8 = 0.9642; @free(sol8);
sol9 = -1.7006; @free(sol9);
sol10 = 3.7625; @free(sol10);
sol11 = -2.6837; @free(sol11);
sol12 = -0.0286; @free(sol12);
sol13 = 0.5182; @free(sol13);
sol14 = -0.6905; @free(sol14);

!Equation for solubility (sol);
sol_total =
n1*sol1+n2*sol2+n3*sol3+n4*sol4+n5*sol5+n6*sol6+n7*sol7+n8*sol8
+n9*sol9+n10*sol10+n11*sol11+n12*sol12+n13*sol13+n14*sol14;
@free(sol_total);

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!Hildebrand solubility parameter for hexane= 14.9MPa;
!Hildebrand solubility parameter for Linoleic acid= 16.07763MPa;
!Hildebrand solubility parameter for Palmitic acid= 16.138995MPa;
!Hildebrand solubility parameter for Oleic acid= 16.17991MPa;
!Hildebrand solubility parameter for carotene = 17.79585MPa;
!Hildebrand solubility parameter for triacglycerol = 17.1822MPa;
!sol0= 21.6654 MPA (sol0 = solubility constant);

sol0 = 21.6654;

sol_final = sol_total + sol0; @free(sol_final);

!Constraints for solubility between solvent and unwanted
component(Linoleic acid (LA), Palmitic acid (PA), oleic acid
(OA)), ie. their difference must be bigger than those of hexane;
Diff_LA = (sol_final - 16.1 );
!@ABS(Diff_LA) > 1.2;

Diff_PA = (sol_final - 16.1);
!@ABS(Diff_PA) > 1.25;

Diff_OA = (sol_final - 16.2);
!@ABS(Diff_OA) > 1.3;

Diff_TAG = (sol_final - 17.2);
!@ABS(Diff_TAG) < 3.4;

Diff_car = (sol_final - 17.8);
!@ABS(Diff_car) < 3.4;

!constaint on solubility;
sol_final < 20.6;
sol_final > 14.4;

!Group contribution for viscosity;
vis1 = -1.0278; @free(vis1);
vis2 = 0.2125; @free(vis2);
vis3 = 1.318; @free(vis3);
vis4 = 2.8147; @free(vis4);
vis5 = 1.3057; @free(vis5);
vis6 = 1.143; @free(vis6);
vis7 = -0.1881; @free(vis7);
vis8 = -0.076; @free(vis8);
vis9 = -0.6902; @free(vis9);
vis10 = 0.0733; @free(vis10);
vis11 = -0.997; @free(vis11);
vis12 = 0.6134; @free(vis12);
vis13 = 3.6344; @free(vis13);
vis14 = -0.0358; @free(vis14);

!Equation for viscosity (vis);
vis_total =
n1*vis1+n2*vis2+n3*vis3+n4*vis4+n5*vis5+n6*vis6+n7*vis7+n8*vis8
+n9*vis9+n10*vis10+n11*vis11+n12*vis12+n13*vis13+n14*vis14;
@free(vis_total);

!Group contribution for surface tension;
st1 = 8.0328; @free(st1);
st2 = 0.6213; @free(st2);
st3 = -7.7843; @free(st3);
st4 = -16.3927; @free(st4);

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st5 = 16.0184; @free(st5);
st6 = 16.93; @free(st6);
st7 = 15.3216; @free(st7);
st8 = 14.574; @free(st8);
st9 = 9.781; @free(st9);
st10 = 17.5324; @free(st10);
st11 = 9.7658; @free(st11);
st12 = 2.3925; @free(st12);
st13 = -7.077; @free(st13);
st14 = 14.8168; @free(st14);

!Equation for surface tension (st);
st_total =
n1*st1+n2*st2+n3*st3+n4*st4+n5*st5+n6*st6+n7*st7+n8*st8+n9*st9+
n10*st10+n11*st11+n12*st12+n13*st13+n14*st14; @free(st_total);

Cp0a= 89.53; Cp0b = -40.13; Cp0d= 5.19; @free(Cp0a); @free(Cp0b);
@free(Cp0d);
Cp1a= 1.04; Cp1b = 8.29; Cp1d= 0.76; @free(Cp1a); @free(Cp1b);
@free(Cp1d);
Cp2a= 19.64; Cp2b = 0.78; Cp2d= 0.80; @free(Cp2a); @free(Cp2b);
@free(Cp2d);
Cp3a= 12.20; Cp3b = 7.90; Cp3d= -1.03; @free(Cp3a); @free(Cp3b);
@free(Cp3d);
Cp4a= 25.40; Cp4b = -2.25; Cp4d= 0.16; @free(Cp4a); @free(Cp4b);
@free(Cp4d);
Cp5a= -99.86; Cp5b = 71.89; Cp5d= -7.70; @free(Cp5a); @free(Cp5b);
@free(Cp5d);
Cp6a= -2.21; Cp6b = 30.79; Cp6d= -1.98; @free(Cp6a); @free(Cp6b);
@free(Cp6d);
Cp7a= 69.38; Cp7b = -2.63; Cp7d= 1.91; @free(Cp7a); @free(Cp7b);
@free(Cp7d);
Cp8a= 32.92; Cp8b = 10.22; Cp8d= -1.96; @free(Cp8a); @free(Cp8b);
@free(Cp8d);
Cp9a= 21.08; Cp9b = 14.60; Cp9d= -0.71; @free(Cp9a); @free(Cp9b);
@free(Cp9d);
Cp10a= 41.12; Cp10b = 6.56; Cp10d= -1.16; @free(Cp10a);
@free(Cp10b); @free(Cp10d);
Cp11a= 15.13; Cp11b = 9.02; Cp11d= 0.99; @free(Cp11a);
@free(Cp11b); @free(Cp11d);
Cp12a= 48.82; Cp12b = 4.92; Cp12d= -0.40; @free(Cp12a);
@free(Cp12b); @free(Cp12d);
Cp13a= 66.98; Cp13b = -9.64; Cp13d= 0.60; @free(Cp13a);
@free(Cp13b); @free(Cp13d);
Cp14a= 34.25; Cp14b = 35.65; Cp14d= -5.17; @free(Cp14a);
@free(Cp14b); @free(Cp14d);

!Calculate for Tb in C;
!Tb constant, tb0 in K;
tb0 = 244.5165;
Tbcelcius = @log(tb_total)*tb0 -273.15; @free(Tbcelcius);

!Cp at Tc;
Cp0 = Cp0a + Cp0b*(Tc/100) + Cp0d*(Tc/100)^2; @free(Cp0);
Cp1 = Cp1a + Cp1b*(Tc/100) + Cp1d*(Tc/100)^2; @free(Cp1);
Cp2 = Cp2a + Cp2b*(Tc/100) + Cp2d*(Tc/100)^2; @free(Cp2);
Cp3 = Cp3a + Cp3b*(Tc/100) + Cp3d*(Tc/100)^2; @free(Cp3);
Cp4 = Cp4a + Cp4b*(Tc/100) + Cp4d*(Tc/100)^2; @free(Cp4);
Cp5 = Cp5a + Cp5b*(Tc/100) + Cp5d*(Tc/100)^2; @free(Cp5);
Cp6 = Cp6a + Cp6b*(Tc/100) + Cp6d*(Tc/100)^2; @free(Cp6);

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Cp7 = Cp7a + Cp7b*(Tc/100) + Cp7d*(Tc/100)^2; @free(Cp7);
Cp8 = Cp8a + Cp8b*(Tc/100) + Cp8d*(Tc/100)^2; @free(Cp8);
Cp9 = Cp9a + Cp9b*(Tc/100) + Cp9d*(Tc/100)^2; @free(Cp9);
Cp10 = Cp10a + Cp10b*(Tc/100) + Cp10d*(Tc/100)^2; @free(Cp10);
Cp11 = Cp11a + Cp11b*(Tc/100) + Cp11d*(Tc/100)^2; @free(Cp11);
Cp12 = Cp12a + Cp12b*(Tc/100) + Cp12d*(Tc/100)^2; @free(Cp12);
Cp13 = Cp13a + Cp13b*(Tc/100) + Cp13d*(Tc/100)^2; @free(Cp13);
Cp14 = Cp14a + Cp14b*(Tc/100) + Cp14d*(Tc/100)^2; @free(Cp14);

Tref = 35 + 273.15; @free(Tref);

!Cp at Tref;
Cp0f = Cp0a + Cp0b*(Tref/100) + Cp0d*(Tref/100)^2; @free(Cp0f);
Cp1f = Cp1a + Cp1b*(Tref/100) + Cp1d*(Tref/100)^2; @free(Cp1f);
Cp2f = Cp2a + Cp2b*(Tref/100) + Cp2d*(Tref/100)^2; @free(Cp2f);
Cp3f = Cp3a + Cp3b*(Tref/100) + Cp3d*(Tref/100)^2; @free(Cp3f);
Cp4f = Cp4a + Cp4b*(Tref/100) + Cp4d*(Tref/100)^2; @free(Cp4f);
Cp5f = Cp5a + Cp5b*(Tref/100) + Cp5d*(Tref/100)^2; @free(Cp5f);
Cp6f = Cp6a + Cp6b*(Tref/100) + Cp6d*(Tref/100)^2; @free(Cp6f);
Cp7f = Cp7a + Cp7b*(Tref/100) + Cp7d*(Tref/100)^2; @free(Cp7f);
Cp8f = Cp8a + Cp8b*(Tref/100) + Cp8d*(Tref/100)^2; @free(Cp8f);
Cp9f = Cp9a + Cp9b*(Tref/100) + Cp9d*(Tref/100)^2; @free(Cp9f);
Cp10f = Cp10a + Cp10b*(Tref/100) + Cp10d*(Tref/100)^2;
@free(Cp10f);
Cp11f = Cp11a + Cp11b*(Tref/100) + Cp11d*(Tref/100)^2;
@free(Cp11f);
Cp12f = Cp12a + Cp12b*(Tref/100) + Cp12d*(Tref/100)^2;
@free(Cp12f);
Cp13f = Cp13a + Cp13b*(Tref/100) + Cp13d*(Tref/100)^2;
@free(Cp13f);
Cp14f = Cp14a + Cp14b*(Tref/100) + Cp14d*(Tref/100)^2;
@free(Cp14f);

!Equation for heat capacity (CP) in J/K mol;
CP_total =
n1*Cp1+n2*Cp2+n3*Cp3+n4*Cp4+n5*Cp5+n6*Cp6+n7*Cp7+n8*Cp8+n9*Cp9+
n10*Cp10+n11*Cp11+n12*Cp12+n13*Cp13+n14*Cp14+Cp0;
@free(CP_total);

!Equation for heat capacity (CP) in Tref in J/K mol;
CPf_total =
n1*Cp1f+n2*Cp2f+n3*Cp3f+n4*Cp4f+n5*Cp5f+n6*Cp6f+n7*Cp7f+n8*Cp8f
+n9*Cp9f+n10*Cp10f+n11*Cp11f+n12*Cp12f+n13*Cp13f+n14*Cp14f+ Cp0f;
@free(CPf_total);

!Group contribution for flash point;
fp1 = 21.7458; @free(fp1);
fp2 = 11.5194; @free(fp2);
fp3 = -5.1205; @free(fp3);
fp4 = -19.7535; @free(fp4);
fp5 = 78.5878; @free(fp5);
fp6 = 115.3016; @free(fp6);
fp7 = 70.9382; @free(fp7);
fp8 = 62.3286; @free(fp8);
fp9 = 41.9635; @free(fp9);
fp10 = 65.5706; @free(fp10);
fp11 = 32.1079; @free(fp11);
fp12 = 32.914; @free(fp12);
fp13 = -8.9309; @free(fp13);
fp14 = 73.7; @free(fp14);

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!Equation for flash point (fp);
fp_total =
n1*fp1+n2*fp2+n3*fp3+n4*fp4+n5*fp5+n6*fp6+n7*fp7+n8*fp8+n9*fp9+
n10*fp10+n11*fp11+n12*fp12+n13*fp13+n14*fp14; @free(fp_total);

fp0 = 170.7058; @free(fp0);

fp = fp_total + fp0; @free(fp);

fp > 242;

fpcelcius = fp - 273.15; @free(fpcelcius);

!Group contribution for octanol-water partition coefficient
(logKow);
logkow1 = 0.3008; @free(logkow1);
logkow2 = 0.4352; @free(logkow2);
logkow3 = 0.3837; @free(logkow3);
logkow4 = 0.6325; @free(logkow4);
logkow5 = -1.0185; @free(logkow5);
logkow6 = -0.9393; @free(logkow6);
logkow7 = -0.3774; @free(logkow7);
logkow8 = -0.7850; @free(logkow8);
logkow9 = -0.3030; @free(logkow9);
logkow10 = -0.7775; @free(logkow10);
logkow11 = 0.5059; @free(logkow11);
logkow12 = -0.1449; @free(logkow12);
logkow13 = 0.165; @free(logkow13);
logkow14 = -0.4615; @free(logkow14);

!Equation for octanol-water partition coefficient (logKow);
logkow_total =
n1*logkow1+n2*logkow2+n3*logkow3+n4*logkow4+n5*logkow5+n6*logko
w6+n7*logkow7+n8*logkow8+n9*logkow9+n10*logkow10+n11*logkow11+n
12*logkow12+n13*logkow13+n14*logkow14; @free(logkow_total);

kow0 = 0.4876;

logkow_final = logkow_total + 0.4876; @free(logkow_final);

logkow_final < 5;

!Group contribution for terrestrial toxicity potential (LC50);
LC501 = 0.0972; @free(LC501);
LC502 = 0.2885; @free(LC502);
LC503 = 0.2441; @free(LC503);
LC504 = -0.3822; @free(LC504);
LC505 = -0.6115; @free(LC505);
LC506 = -0.1104; @free(LC506);
LC507 = 0.0835; @free(LC507);
LC508 = 0.6008; @free(LC508);
LC509 = -0.5209; @free(LC509);
LC5010 = 0.1130; @free(LC5010);
LC5011 = 1.0340; @free(LC5011);
LC5012 = -0.2160; @free(LC5012);
LC5013 = -0.8189; @free(LC5013);
LC5014 = 0.4393; @free(LC5014);

!Equation for aquatic toxicity (LC50);

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LC50_total =
n1*LC501+n2*LC502+n3*LC503+n4*LC504+n5*LC505+n6*LC506+n7*LC507+
n8*LC508+n9*LC509+n10*LC5010+n11*LC5011+n12*LC5012+n13*LC5013+n
14*LC5014; @free(LC50_total);

!Group contribution for aquatic toxicity potential (LD50);
LD501 = -0.0742; @free(LD501);
LD502 = 0.0223; @free(LD502);
LD503 = 0.1335; @free(LD503);
LD504 = 0.2641; @free(LD504);
LD505 = -0.1955; @free(LD505);
LD506 = 0.0320; @free(LD506);
LD507 = -0.0172; @free(LD507);
LD508 = -0.1338; @free(LD508);
LD509 = -0.0259; @free(LD509);
LD5010 = 0.0130; @free(LD5010);
LD5011 = 0.1087; @free(LD5011);
LD5012 = 0.0974; @free(LD5012);
LD5013 = 0.4987; @free(LD5013);
LD5014 = -0.1734; @free(LD5014);

!Equation for terrestrial toxicity (LD50);
LD50_total =
n1*LD501+n2*LD502+n3*LD503+n4*LD504+n5*LD505+n6*LD506+n7*LD507+
n8*LD508+n9*LD509+n10*LD5010+n11*LD5011+n12*LD5012+n13*LD5013+n
14*LD5014; @free(LD50_total);

!constant for LD50;
A= 1.9372;
B= 0.0016;

!calculate for LD50 in mol/kg;
LD50_mol = 10^(-(LD50_total + A + B*mw_total)); @free(LD50_mol);

!Calculate for LD50 in mg/kg;
LD50_mg = LD50_mol*mw_total*1000; @free(LD50_mg);

!Group contribution for photochemical oxidation potential (PCO);
PCO1 = 0.1227; @free(PCO1);
PCO2 = 0.0463; @free(PCO2);
PCO3 = -0.079; @free(PCO3);
PCO4 = -0.0434; @free(PCO4);
PCO5 = 0.0359; @free(PCO5);
PCO6 = -0.0379; @free(PCO6);
PCO7 = 0.1409; @free(PCO7);
PCO8 = -0.1855; @free(PCO8);
PCO9 = 0.1499; @free(PCO9);
PCO10 = -0.4319; @free(PCO10);
PCO11 = -0.2572; @free(PCO11);
PCO12 = -0.1226; @free(PCO12);
PCO13 = -0.2064; @free(PCO13);
PCO14 = 0.3858; @free(PCO14);

!Equation for photochemical oxidation potential (PCO);
PCO_total =
n1*PCO1+n2*PCO2+n3*PCO3+n4*PCO4+n5*PCO5+n6*PCO6+n7*PCO7+n8*PCO8
+n9*PCO9+n10*PCO10+n11*PCO11+n12*PCO12+n13*PCO13+n14*PCO14;
@free(PCO_total);

!Group contribution for bioconcentration factor (BCF);
BCF1 = 0.6657; @free(BCF1);

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BCF2 = 0.0948; @free(BCF2);
BCF3 = -0.3921; @free(BCF3);
BCF4 = -0.9137; @free(BCF4);
BCF5 = -0.0340; @free(BCF5);
BCF6 = -0.8830; @free(BCF6);
BCF7 = 0.6654; @free(BCF7);
BCF8 = -0.3560; @free(BCF8);
BCF9 = 0.2530; @free(BCF9);
BCF10 = -0.1643; @free(BCF10);
BCF11 = 0.7712; @free(BCF11);
BCF12 = -0.106; @free(BCF12);
BCF13 = -0.3114; @free(BCF13);
BCF14 = 0.3988; @free(BCF14);

!Equation for bioconcentration factor (BCF);
BCF_total =
n1*BCF1+n2*BCF2+n3*BCF3+n4*BCF4+n5*BCF5+n6*BCF6+n7*BCF7+n8*BCF8
+n9*BCF9+n10*BCF10+n11*BCF11+n12*BCF12+n13*BCF13+n14*BCF14;
@free(BCF_total);

BCF_total < 3.3;

!Group contribution for permissible exposure limit (PEL);
PEL1 = 0.7723; @free(PEL1);
PEL2 = 0.0727; @free(PEL2);
PEL3 = -0.6557; @free(PEL3);
PEL4 = -1.3404; @free(PEL4);
PEL5 = 1.3612; @free(PEL5);
PEL6 = 2.3281; @free(PEL6);
PEL7 = 1.4016; @free(PEL7);
PEL8 = 2.3662; @free(PEL8);
PEL9 = 2.1251; @free(PEL9);
PEL10 = 2.0449; @free(PEL10);
PEL11 = 2.2638; @free(PEL11);
PEL12 = 0.9276; @free(PEL12);
PEL13 = -0.7462; @free(PEL13);
PEL14 = 1.2544; @free(PEL14);

!Equation for permissible exposure limit (PEL);
PEL_total =
n1*PEL1+n2*PEL2+n3*PEL3+n4*PEL4+n5*PEL5+n6*PEL6+n7*PEL7+n8*PEL8
+n9*PEL9+n10*PEL10+n11*PEL11+n12*PEL12+n13*PEL13+n14*PEL14;
@free(PEL_total);

!Calculate PEL in ppm;
!molar volume of gas, Vgas, in dm3/mol, Note that 1L=1dm3;
Vgas = 24.45;
PEL = Vgas*1000*10^(-PEL_total); @free(PEL);

!Calculate for oxygen stoichiometric coefficient, Co;
Co = C_number + (H_number/4) - (O_number/2);

!Calculate for Lower explosion limit, LEL;
LEL = (100/(1+9.045*Co)); @free(LEL);

!Calculate for Upper explosion limit, UEL;
UEL = (100/(1+1.1843*Co)); @free(UEL);

!Calculate explosiveness, Iex using S= (UEL - LEL)vol%;
S = UEL - LEL; @free(S);

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!Disjunctive equation for explosiveness, Iex;
Iex = Iex1 + Iex2 + Iex3 + 1; @bin(Iex1); @bin(Iex2); @bin(Iex3);
(0-20)*(1-Iex1) < S - 20;
S - 20 <= (100 - 20)*(Iex1);
(0-45)*(1-Iex2) < S - 45;
S - 45 <= (100 - 45)*(Iex2);
(0-70)*(1-Iex3) < S - 70;
S - 70 <= (100 - 70)*(Iex3);

!!Disjunctive equation for acute health hazard;
IAH = IAH1 + IAH2 + IAH3 + IAH4; @bin(IAH1); @bin(IAH2);
@bin(IAH3); @bin(IAH4);
(0.00001-2000)*(IAH1) < LD50_mg- 2000;
LD50_mg- 2000 <= (10000 - 2000)*(1-IAH1);
(0.00001-500)*(IAH2) < LD50_mg - 500;
LD50_mg- 500 <= (10000 - 500)*(1-IAH2);
(0.00001-50)*(IAH3) < LD50_mg - 50;
LD50_mg - 50 <= (10000 - 50)*(1-IAH3);
(0.00001-5)*(IAH4) < LD50_mg- 5;
LD50_mg - 5 <= (10000 - 5)*(1-IAH4);

!Disjunctive equation for flammability. Ifl;
Ifl = Ifl1 + Ifl2 + Ifl5 + 1; @bin(Ifl1); @bin(Ifl2); @bin(Ifl3);
@bin(Ifl4); @bin(Ifl5);
(-1000-93.4)*(Ifl1) < Fpcelcius - 93.4;
Fpcelcius - 93.4 <= (10000-93.4)*(1-Ifl1);
(-1000-37.8)*(Ifl2) < Fpcelcius - 37.8;
Fpcelcius - 37.8 <= (10000-37.8)*(1-Ifl2);
(-1000-22.8)*(Ifl3) < Fpcelcius - 22.8;
Fpcelcius - 22.8 <= (10000-22.8)*(1-Ifl3);
(-1000-37.8)*(Ifl4) < Tbcelsius - 37.8;
Tbcelsius - 37.8 <= (10000-37.8)*(1-Ifl4);
Ifl3 + Ifl4 = g;
(0-2)*(1-Ifl5) < g- 2;
g - 2 <= (5-2)*Ifl5;

!Disjunctive equation for exposure limit, Iel;
Iel = Iel1 + Iel2 + Iel3 + Iel4; @bin(Iel1); @bin(Iel2);
@bin(Iel3); @bin(Iel4);
(0.0001-1000)*(Iel1) < PEL -1000;
PEL - 1000 <= (10000 - 1000)*(1-Iel1);
(0.0001-100)*(Iel2) < PEL -100;
PEL - 100 <= (10000 - 100)*(1-Iel2);
(0.0001-10)*(Iel3) < PEL -10;
PEL - 10 <= (10000 - 10)*(1-Iel3);
(0.0001-1)*(Iel4) < PEL -1;
PEL - 1 <= (10000 - 1)*(1-Iel4);

!Mass and Energy balance around the crystallizer;
!Crystallizer feed stream temperature = 35C;
!Mass of solvent entering crystallizer, Ms = 750kg;
!Mass of oil entering crystallizer, Mo = 250kg;
!Mass of oil crystal, Mo;
!Mass of solvent at the bottom, Ms;

Ms = 750;
Mo = 250;

!Cp in kJ/kg C; !Assume cp oil constant over temperature;
Cpoil = 1.902;

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!heat of fusion of oil, kJ/kg;
Hfoil = -91.3; @free(Hfoil);

!Treference = lowest temperature of the system, which is the feed
temperature;
!Tfeed = 35 + 273.15;
!Enthalpy for feed of evaporator, deltaHf = mCPdeltaT;
!Enthalpy for oil crystals, deltaHo = Mo*Cpoil*(Tc - Tref) +
Mo*Hfoil;
!Enthalpy for solvent, deltaHs = Msb*(averageCp/Mw_total)*(Tc -
Tref);
!Energy required to crystallize the oil, -ERcold = deltaHo +
deltaHs;

!average Cp = (cp at 308.15K + cp at Tc)/ 2;
averageCp = (Cpf_total + Cp_total)/2; @free(averageCP);

deltaHo = Mo*Cpoil*(Tc - Tref) + Mo*Hfoil; @free(deltaHo);
deltaHs = Ms*(averageCp/Mw_total)*(Tc - Tref); @free(deltaHs);

!Energy required to crystallize the oil, ERcold; !ER at kJ;
-ERcold = deltaHo + deltaHs; @free(ERcold);

!Energy required to heat the solvent for recovery;
ERhot = Ms*(averageCp/Mw_total)*(Tref - Tc); @free(ERhot);
amtofsteam = ERhot/2046.53; !steam at kg;

!Refrigerant comes in at 5C, goes out at 15C;
!cost of refrigerant = RM 20.45233/GJ;
!cost of MPsteam = RM 70.21/1000 kg;

Cost = (ERcold/1000000)*20.45233 + amtofsteam*70.21/1000;

end

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