Life cycle analysis of graphene in a supercapacitor application

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Abstract

The aim of this thesis is to undertake a life cycle analysis to identify the environmental impact of using graphene to manufacture supercapacitors. It was part of a larger project to develop supercapacitors using graphene in place of activated carbon.

The first part of this work focuses on production of graphene in the laboratory. Data were directly measured in different laboratories to perform a comparative life cycle analysis in order to evaluate the environmental performance of several graphene synthesis methods including graphite electrochemical exfoliation, graphite chemical oxidation with subsequent chemical or thermal reduction and chemical vapour deposition. One electrochemical exfoliation technique, one chemical oxidation followed by two different reduction routes were selected on the base of their environmental performance and their measured specific capacitance and used as electrode materials for supercapacitors.

The second part of the thesis is a comparative life cycle assessment involving three supercapacitors having the electrodes made of graphene synthesised via the three shortlisted production routes and one state of the art activated carbon based supercapacitor commercially available. A commercial-scale graphene production process is simulated using a process simulation tool in order to minimise the process inefficiencies inherent to laboratory processes and to compare it with a commercial-scale activated carbon production process. The results showed a large reduction of the graphene environmental impact of around 50% in most of the environmental impact categories analysed but also proved that the activated carbon supercapacitor is currently the technology with the lowest impact for all categories. They also showed that graphene production needs more research to improve its efficiency and efficacy as it is the operation with the highest environmental impact in the supercapacitor manufacturing for most of the analysed impact categories.

In the third part of this study the use-phase and end-of-life of supercapacitors is evaluated in which the supercapacitors are used to power a car door mirror and are finally recycled. The results showed that over the lifetime of a vehicle (150,000 km), the graphene based supercapacitors have a lower impact (10% less) during the use-phase as they are lighter. The recycling process is also simulated to be scaled up to a commercial-scale with minimised heat losses for both graphene and activated carbon based supercapacitors. Recycling proved to be the key to reduce the environmental impact of the graphene supercapacitor. As graphene proved to be the most problematic material for the environment and the recycled graphene proved to be of a quality similar to pristine material, its recovery generates an environmental credit that is 90% of the production burden for all categories by displacing the production of new graphene for polymer reinforcement applications.

Sensitivity analysis is performed and various scenarios generated to evaluate potential variations in specific capacitance of all active materials and subsequently the impact of these variations on the manufacture of supercapacitors. The results are normalised and weighted according to the latest EU requirements. Aggregating the weighted results proved that the activated carbon and the graphene based supercapacitors could have similar impacts. This is a very encouraging result considering that the graphene synthesis process is still at its infancy while the activated carbon production is a well-established industrial process. When a more efficient graphene production can be industrialised, graphene supercapacitors will have the potential to become the future technology with the lowest environmental impact.

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CHAPTER 1: Introduction

Graphene was obtained for the first time in 2004 using simple sticky tape on graphite. Since then the research on this new material and especially on its possible applications has grown significantly with several research groups focusing on a multitude of different graphene related areas (e.g.: graphene as semiconductor [1], as energy storage [2], as structural reinforcement [3, 4] and as membrane for liquids [5] or gas [6] separation). Graphene showed indeed very promising qualities ranging from its great strength to its unusual electronic properties and for this reason it seems likely that it will replace several materials commonly used in today's devices in the near future.

Even though only a few companies claim to use graphene in their products (e.g.: Head for rackets [7] and skis [8]) more and more goods might be marketed starting from flexible touch-panels for mobile devices [9] to Li-Ion batteries [10] (and their thermal management systems [11]), from very sturdy helmets [12] to sensors capable of detecting single atoms of selected substances [13, 14], from more efficient solar panels [15, 16] to bendable supercapacitors [17] with very large capacitance [18].

Graphene might play an important role for energy storage devices that are often coupled with sustainable energy production. In fact, batteries and supercapacitors are gaining momentum as the share of power generated using renewable energies is growing and there is a need for backup systems to cope with the fluctuation of renewable sources. Supercapacitors are often a key technology in this scenario as they operate as a "bridge" from the main power source to the backup while the latter starts and reaches its full power. Graphene in supercapacitors could potentially store a lot more energy compared to current devices using activated carbon due to graphene having a higher surface area per unit volume. This means that even if occupying a small volume, the surface available to store charges can be large, increasing by several times the storage capacity of current devices.

Graphene is used for electrodes also in lithium-ion batteries where it can shorten the recharge time and increase the power output aiding the lithium-ion adsorption and diffusion. Though, it does not improve the long term irreversibility of the reactions between lithium and solid electrolyte interface formation that is the cause of the limited number of cycles that a battery can withstand [19].

Graphene is also used in power generation, for example showing interesting results in improving organic solar cells that are generally seen as a less expensive alternative to the inorganic cells. Graphene can enhance the efficiency of those materials for both photon-charge conversion and charge transportation. Fuel cells also could benefit from graphene where platinum based electrodes are used as catalysts to enhance the oxygen reduction at the cathode. Graphene is used as highly conductive substrate, with high specific surface area, where platinum nanoparticles are immobilised. This solution showed 50% higher electrochemical activity than commercial platinum electrodes and it is potentially a cheaper solution than the current platinum based electrodes as it reduces the platinum used [19, 20]. Nitrogen-doped graphene is also tested for metal-free catalysts [21].

With the threat of the global warming and climate change the technological advancement is no longer the only priority as there is now a necessity of minimising the environmental impacts and risks associated with emerging technologies. In this view, the introduction of graphene in the day to day life is a fact that must be investigated to understand what impacts it has on the health and safety of living organisms and the environment. Using, producing and disposing/recycling this new material might raise some environmental concerns and in this perspective, life cycle assessment (LCA) is a tool that can give an answer to these concerns.

The LCA approach is to analyse all inputs outputs wastes and emissions related to a product or a process starting from the raw material extraction, including the manufacturing processes and finishing with the product use and disposal (or recycling/reuse) at the end of its life. This holistic and comprehensive approach aims at avoiding the environmental burdens shifting from one stage of the life cycle to another. For example, with graphene is theoretically possible to produce very light and small energy storage devices. This is a benefit for non-stationary applications (e.g.: hybrid engines for all sort of vehicles) as transporting a lighter device saves fuel, but, for the time being, the graphene production is energy intensive and it might require more energy than that saved in the use-phase. Moreover, the LCA approach avoids also shifting the environmental burden from one impact category to another, for example when finding a solution that might lead to a reduction of CO_2 emissions but to an increase of carcinogenic emissions or of particulate matter or others.

On top of this, the LCA allows the comparisons between two (or more) different products on the ground of a common function or functional unit making it a very powerful tool especially when a lot of impact categories are included in the analysis. The comparative holistic approach is important during the design phase or research phase of a material or a component because it can give early indications on where the analysed product or process is going from an environmental perspective, especially if benchmarked against the latest technology on the market. This technique can be also used to evaluate the weak points of this new product/material highlighting which are the main causes of impacts and helping to put in place corrective actions before final products reach the market.

For these reasons and to provide a clear answer to the environmental concerns revolving around the development of graphene the LCA technique was selected and applied. It provided an overview on the production, use and end-of-life of this material, a comparison between state of the art supercapacitor on the market (activated carbon based electrodes) and a prototype with graphene-based electrodes and a rank of the environmental impacts in order of importance used to create a list of corrective actions.

1.1 Objectives of the thesis

The aim of this thesis is to quantify the environmental impacts of graphene, with specific application to supercapacitor production. It also includes a comparative analysis with a current state of the art activated carbon based supercapacitor to give some indication on how to make them less impacting.

The first objective of the research is to offer an overview of the environmental impacts connected to some common laboratory processes to synthesise graphene. In this way a short list of least impacting materials is created based on the results of a preliminary LCA. Secondly, to simulate commercial-scale graphene productions based on the shortlisted synthesis methods and subsequently develop the LCA models. A third objective is to compare those materials when used as electrodes in supercapacitors with the state of the art commercial activated carbon based supercapacitors. The last objective is to extend the comparative LCA to the use-phase and end-of-life recovery for a selected case study involving a car door mirror achieving a cradle-to-grave LCA study.

This research is part of an EU project called “ElectroGraph”. The ElectroGraph project was part of the European Union 7th Framework Programme for Research and Technological Development. The project aim was to create a new type of supercapacitor having the electrodes made of graphene instead of activated carbon (generally in use today). For this purpose, ElectroGraph was set up as a consortium involving four universities (Nottingham, Exeter, Paris Diderot and Trinity College Dublin), three research centres (Fraunhofer IPA Institute, Institute of Occupational Medicine (IOM) and Instituto Nacional del Carbon (INCAR)), a multinational company (Maxwell Technologies Inc.), an industrial research centre (Centro Ricerche FIAT) and a start-up company (Danubia Nanotech). The workload was roughly distributed in the following way: synthesis of graphene (Diderot University Paris, Fraunhofer Institute, Trinity College Dublin, Danubia Nanotech), characterisation of graphene (INCAR), health and safety risk assessments (IOM), industrialization (Maxwell Technologies Inc.), use-phase and implementation (Centro Ricerche FIAT), recycling/reuse (University of Nottingham, University of Exeter) and Life Cycle Assessment (University of Nottingham).

This thesis is divided into six chapters, including this introduction.

Chapter 2 introduces key topics relevant to the research. As very little research has been conducted assessing the life cycle impacts of graphene production and use, the literature review focuses on the state of the art of graphene production, supercapacitor research, graphene in supercapacitors and LCA of nano materials.

Chapter 3 investigates the lab-scale synthesis of graphene. Electrochemical exfoliation, chemical, thermal, and chemical vapour deposition routes are considered. Life cycle inventory models are developed and used to shortlist the most promising production processes for further analysis in subsequent chapters.

In Chapter 4, commercial-scale graphene production is simulated for the shortlisted production routes. A case study is then proposed in which the graphene is used as electrode material for supercapacitors. A cradle to gate LCA is performed comparing a graphene-based supercapacitor prototype and the state of the art commercial activated carbon based supercapacitor.

Chapter 5 introduces a case study in which the supercapacitors are placed in a car door mirror to power the motors used to adjust it. This configuration is used to perform a cradle to grave LCA of the best performing supercapacitors selected from the previous chapter. This LCA takes into consideration the whole life cycle of the devices from raw material extraction to the recycling process including the use-phase. The effect of the use-phase per kilometre driven is also evaluated. In both the fourth and fifth chapters, some sensitivity analysis is performed to evaluate the effect on the environmental impacts of the variation of key parameters. Normalisation and weighting of impacts are considered in order to prioritise the hazards to the ecosphere and the potential corrective actions.

Chapter 6 summarises the conclusions drawn from the proposed research. It also includes some discussion on future prospects for supercapacitors and graphene including suggestions for further studies and gaps to be covered.

The LCA is based on the ILCD guidelines developed by the Joint Research Centre (JRC) of the EU Commission and is performed using GaBi 6 (developed by Thinkstep). GaBi is a piece of software that supports and facilitates the LCA study. It includes a vast database of materials and their related environmental impacts (reviewed by the scientific community) allowing for fast and intuitive modelling of the system under study.

Process simulation is instead performed using SuperPro Designer (SPD – developed by Intelligen) a tool that facilitates the modelling and optimisation of a variety of industrial processes. It is used as a source of data for GaBi when performing the life cycle assessment of the commercial-scale production of graphene.

1.2 References

1. Pathipati, S.R., et al., *Graphene flakes at the SiO2/organic-semiconductor interface for high-mobility field-effect transistors.* Organic Electronics, 2015. **27**: p. 221-226.
2. Yang, Y., et al., *Graphene-based materials with tailored nanostructures for energy conversion and storage.* Materials Science and Engineering: R: Reports, 2016. **102**: p. 1-72.
3. Li, X., et al., *In-situ polymerization of polyaniline on the surface of graphene oxide for high electrochemical capacitance.* Thin Solid Films, 2015. **584**(0): p. 348-352.
4. Lian, M., et al., *Kevlar®-functionalized graphene nanoribbon for polymer reinforcement.* Polymer, 2014. **55**(10): p. 2578-2587.
5. Ali, M.E.A., et al., *Thin film composite membranes embedded with graphene oxide for water desalination.* Desalination, 2016. **386**: p. 67-76.
6. Jiang, D.-e., V.R. Cooper, and S. Dai, *Porous Graphene as the Ultimate Membrane for Gas Separation.* Nano Letters, 2009. **9**(12): p. 4019-4024.
7. HEAD. *Raquet*. [cited 2015 06]; Available from: http://www.head.com/tennis/products/racquets/tour-prestige/graphene-prestige-pro/7053/?region=it.
8. HEAD. *Ski*. [cited 2015 06]; Available from: http://www.graphene-info.com/head-launches-super-joy-line-graphene-enhanced-skis.
9. Wang, J., et al., *Rod-Coating: Towards Large-Area Fabrication of Uniform Reduced Graphene Oxide Films for Flexible Touch Screens.* Advanced Materials, 2012. **24**(21): p. 2874-2878.
10. Qu, Q., et al., *Graphene oxides-guided growth of ultrafine Co3O4 nanocrystallites from MOFs as high-performance anode of Li-ion batteries.* Carbon, 2015. **92**: p. 119-125.
11. Brooks, L. and D. Scheffer, *Graphene Based Thermal Management Devices*, 2015.
12. CATLIKE. *Graphene-enhanced Helmet*. 2014; Available from: http://www.graphene-info.com/graphene-enhanced-cycling-helmets-catlike.
13. Graphene-info. *Graphene based sensors*. [cited 2015 06]; Available from: http://www.graphene-info.com/graphene-sensors
14. Abdulkader Tawfik, S., et al., *Sensing sulfur-containing gases using titanium and tin decorated zigzag graphene nanoribbons from first-principles.* Physical Chemistry Chemical Physics, 2015. **17**(10): p. 6925-6932.
15. Graphene-info. *Solar panels*. [cited 2015 06]; Available from: http://www.graphene-info.com/graphene-solar-panels.
16. Xin, G., et al., *Efficient photovoltaic conversion of graphene–carbon nanotube hybrid films grown from solid precursors.* 2D Materials, 2015. **2**(3): p. 034003.
17. Shao, Y., et al., *Graphene-based materials for flexible supercapacitors.* Chemical Society Reviews, 2015. **44**(11): p. 3639-3665.
18. Huang, G., et al., *High-performance all-solid-state yarn supercapacitors based on porous graphene ribbons.* Nano Energy, 2015. **12**: p. 26-32.

19. Liu, J., et al., *Graphene-based materials for energy applications.* MRS bulletin, 2012. **37**(12): p. 1265-1272.
20. Kou, R., et al., *Enhanced activity and stability of Pt catalysts on functionalized graphene sheets for electrocatalytic oxygen reduction.* Electrochemistry Communications, 2009. **11**(5): p. 954-957.
21. Imran Jafri, R., N. Rajalakshmi, and S. Ramaprabhu, *Nitrogen doped graphene nanoplatelets as catalyst support for oxygen reduction reaction in proton exchange membrane fuel cell.* Journal of Materials Chemistry, 2010. **20**(34): p. 7114-7117.

CHAPTER 2: Literature review

2.1 The Life Cycle Assessment in brief

This section contains a brief overview of the LCA process starting from its definition and purpose and discussing its methodology and limitations. It also includes a brief summary of the ILCD handbook for the parts concerning this particular LCA project described in the following chapters.

2.1.1 Origin of the Life Cycle Assessment (LCA)

In the last two centuries, the improvements in comfort, and therefore in the quality of life, had been associated with the economic growth. However, in the last decades, it became more and more clear that this link between material wealth and happiness was not as appropriate This awareness started in the late 50s and early 60s when studies showed the severity of the world pollution (for example linked to the extensive use of pesticides) and the high risk of running out of important natural resources (Hubbert Peak Oil theory – 1959). In 1972 the famous "the limits of growth", a report of The Club of Rome commissioned to the MIT, was published. It clearly stated that a world with finite resources cannot experience an exponential growth without collapsing [1].

A lot of conferences and forums were held after the publication of "the limit of growth" to discuss new models of economic development. In this period the origin of the Life Cycle Assessment (LCA) technique can be set at the Midwest Research Institute. It stemmed from the energy analysis studies but including environmental and sustainability criteria [2] and considering the whole life cycle in order to organically understand the real impact of a product/system/service on the environment by avoiding to focus only on one stage of its life (e.g.: production, use-phase or disposal).

In this background the Life Cycle Assessment evolved and in 2006 it was defined in the ISO standards. It is now becoming a tool, with many others, to support decision making by helping in understanding and analysing the sustainability in a structured quantitative manner.

2.1.2 The Life Cycle Assessment (LCA)

An LCA is defined in the 14040 ISO standards as a way of addressing "the environmental impacts (e.g. use of resources and the environmental consequences of releases) throughout a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal (i.e. cradle-to-grave)". The word "product" it is used in this case in its broadest meaning and it embraces physical goods as well as services and processes. It is a systematic and structured technique to measure and quantify all energies and materials inputs and outputs including emissions and wastes. Those quantities are then translated with mathematical models into environmental impacts related to several different impact categories [3].

An LCA is generally based on quantitative data, but when not available, qualitative aspects can and must be taken into consideration so to have a more complete picture of the environmental impact of the product analysed. Always concerning completeness, the cradle-to-grave approach prevents from moving possible problems a step backward or forward in the production/process chain. For example, turning all cars into electric cars will certainly reduce their emissions, as cars will not burn fossil fuels any more, but the electricity needed to charge their batteries might be still provided by fossil sources and therefore the overall environmental impact becomes uncertain. Only after performing the LCA analysis it is possible to indicate which solution is more ecological [4]. The same goes for the cases when the environmental burdens could be shifted from one medium to another, for instance when a lower rate of emissions in the air corresponds to an increase in solid waste (Figure 2.1).

As a general rule, the LCA is often a comparative analysis as it is used to assess which, among several options, is the most environmentally friendly and it is frequently used to compare the present system versus a new and upgraded one. Therefore, sometimes there is no need to cover the complete cradle-to-grave analysis, but only the significant parts that usually are those where the considered systems differ [5]. Due to its comparative nature the LCA is often used for decision making and for clarifying environmental disputes [6].

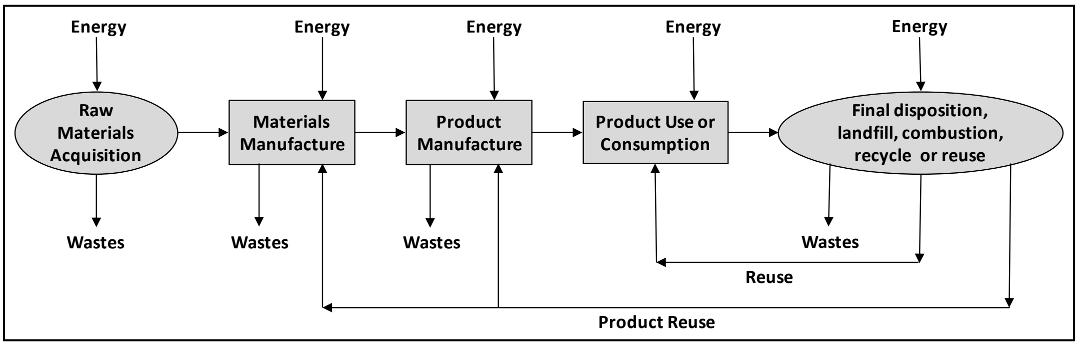

Figure 2.1 – Simplified product/system life cycle [7]

In a broader prospective the LCA has multiple potential purposes [8] such as :

- a base for environmental strategies,
- environmental product declarations and eco-labelling,
- product improvement (weak point analysis),
- assessment of new and cleaner technologies,
- identification of knowledge gaps,
- policy development and information,
- a systematic organisation of information for environmental impact assessment,

and many others, however most of the times this type of analysis is used to [9]:

- decide whether a product, process or service is reducing the environmental burden or simply transferring it to another part of its life cycle,
- establish where the highest environmental load is located in a process,
- make quantitative comparisons between competing alternative technologies concerning their environmental impacts.

It should be noted that LCA only takes into consideration impacts related to normal and abnormal operation of processes and products and not those coming from accidents, spills, and similar [10].

2.1.3 LCA limitations

An LCA has several implicit constraints and some of them are defined already by the ISO standard 14040 such as the limit of assessing completely all environmental impacts of a product/system. This happens because of the nature of the LCA itself as it focuses only on a particular usage of the system under examination (e.g. a life cycle for a light bulb for home applications might be considerably different from an industrial one). A lack of reliability of data can also lay in the way data are aggregated[1] [11] and allocated when they are gathered due to the fact that all processes are considered linear (e.g. fuel consumption and distance travelled) [12]. Moreover, as this is a data intensive process, it can happen that not all the data is available or reliable, which generates gaps and cut-offs in some inputs/outputs of the life cycle under examination (Figure 2.1). Many databases and datasets were however created in recent years with a constant increase in number and quality. The purpose is to expand the availability of the data and, even if the proposed values are usually the average values for goods and services, they come as a great support in performing an LCA [12], especially while coupled with LCA computer software (e.g.: SimaPro, GaBi, Open LCA and many others).

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[1] E.g. the energy production in databases or datasets is generally reported as a single process instead of a combination of steps.

Nevertheless, the lack of available data requires simplifications, estimations, assumptions and those are generally the weakest point of all LCA results.

Another limitation of this tool, stated in the ISO 14040, is the lack of spatial and temporal dimensions as most of the time the environmental impacts of a system can be dependent on the geographical location[2] [12] and dynamically change in time. Especially it is not possible to use the LCA as a tool to predict future developments of the analysis even if some studies are being carried out to propose possible solutions [13].

Additionally, an LCA does not take into consideration any cost or financial aspect of the system under examination and of its possible improvements. This is a significant weak point that might discourage decision and policy makers to use this tool as a fundamental part of their decision process [14] (even though the life cycle costing can give an indication). Moreover, it is difficult for companies, corporations and bodies to fully implement the LCA approach in their business for the difficulty of highlighting and measuring some key performance indicators. There is a need for indices that can be used to evaluate the real performances versus the expected goals. An LCA is time consuming and resource demanding, therefore a lot of development is happening in this area to enhance its user-friendliness and employability such as smart and careful techniques for selection and calculation of the parameters to measure [14], the possible combination of several environment related tools (to fill the gaps where possible) [4] or to simplify the model in order to perform an approximate but reliable LCA using some advanced algorithms [15].

The LCA is an appropriate tool for mature products when a lot of data are available to collect and analyse. On the other hand, for new and emerging processes, during their development phase when data is often insufficient, it is a good tool to set environmental targets for the product in an eco-design exercise.

2.1.4 A structured approach for LCA

Even if some early scientific publications appeared in the beginning of the nineties (e.g. [16]) and the LCA concept was generating high expectations, the outcomes were often criticized (e.g. [17-20]) and mostly for the lack of a standardized approach resulting in different ways of interpreting data and therefore deducing results.

For this reason, a lot of work has been carried on in the past years (and still is) to develop and harmonise the LCA methodology starting from the ISO standards (ISO

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[2] E.g.: different ways of producing energy in different countries, but also different receiving environment in the same country.

14040-14044:2006) to some published guidelines [21] and textbooks. Several international bodies and societies are helping in harmonising the LCA process proposing recommendations and rising awareness towards it via several events and initiatives (e.g.: the Life Cycle Initiative of the United Nations Environment Program (UNEP), the Society of Environmental Toxicology and Chemistry (SETAC) and others).

For example the British standard institution published in 2008 the PAS 2050 (Publicly Available Specifications 2050:2008, specification for the assessment of the life cycle greenhouse gas emissions of goods and services) a specification addressing only the global warming potential in order to offer a simplified approach to assess greenhouse gasses emissions [22].

The European Commission Joint Research Centre is also tried to regiment the LCA process in 2010 issuing the International reference Life Cycle Data system or ILCD handbook [10] (http://lct.jrc.ec.europa.eu/assessment/publications) that is a detailed guide for performing LCA and, quoting from its preface, “The international Reference Life Cycle Assessment Data System (ILCD) Handbook provides governments and businesses with a basis for assuring quality and consistency of life cycle data, methods and assessments”. It provides guidelines not only with a step by step approach to LCA practice (data gathering, report structuring, data quality and completeness assessment and many others) but also on the impacts methodologies to be used and procedures to adopt depending on the nature of the LCA (attributional/consequential with large or small impacts on current situation, comparative or non-comparative, others) Following the ILCD handbook also ensures compliancy with the ISO standards that are the base on which it is built [10].

2.2 Supercapacitors in brief

This section gives a brief description of what is a supercapacitor, how it works, and where it is generally used. It also touches very briefly the status of current research in the field and its future development.

2.2.1 General characteristics

A supercapacitor (Figure 2.2) is an electrochemical device that stores electricity through capacitive charging and is capable of providing high power in a compact size and mass [23]. It is constituted of two electrodes attached to current collectors. The electrodes are submerged in an electrolyte and they are separated by a separator. The supercapacitor is similar to a normal capacitor (Figure 2.3) where two electrical conductive elements are separated by an insulator (dielectric). In a capacitor, when a potential difference is applied across the conductors, it generates a static electric field across the dielectric that causes positive charge to collect on one conductive element and negative on the other. Energy is therefore stored as an electrostatic field [24]. No chemical reaction is involved and this makes the capacitor very fast in charge/discharge and makes its lifetime almost unlimited.

A supercapacitor has the same positive aspects but it can store much more energy than a normal capacitor by crossing over with battery technology adopting special electrodes and an electrolyte. They are called electrochemical double layer capacitors because there is formation of a double layer when the electronic conductor (electrode) gets in contact with an ionic conductor (electrolyte). Consequently a charge separation occurs on either side of the surface of contact forming a double layer that, like for the standard capacitors, does not imply any chemical reaction. The rearrangement of charges, when a voltage is applied, generates a current. It is clear that the more surface area there is, the more charge can be stored [25].

It is important to underline how the behaviour of the supercapacitor differs from the standard capacitor due to the double layer formed at each electrode. This makes the two electrodes behave as two supercapacitors connected in series and therefore the total capacitance is given by the formula [26]:

$$\frac{1}{C_{tot}} = \frac{1}{C_{anode}} + \frac{1}{C_{cathode}} \tag{1}$$

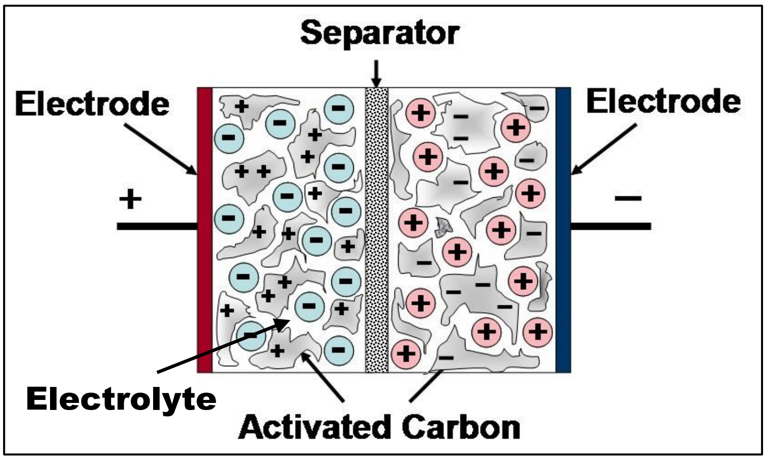

Figure 2.2 – Supercapacitor (modified from [27]). On each side of the separator there are positive and negative charges forming the so called double layer between the carbon and the electrolyte

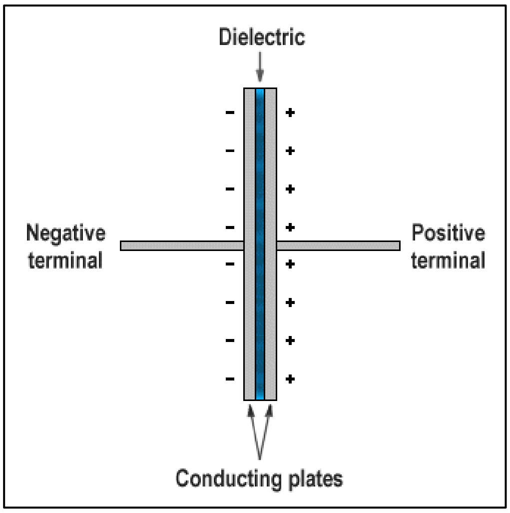

Figure 2.3 – Capacitor [28]

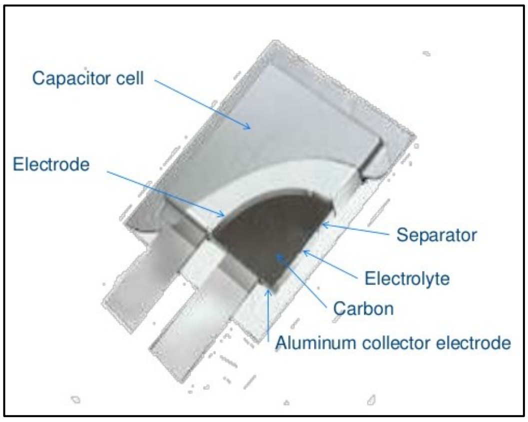

Figure 2.4 – supercapacitor: stacked structure (flat) [29]

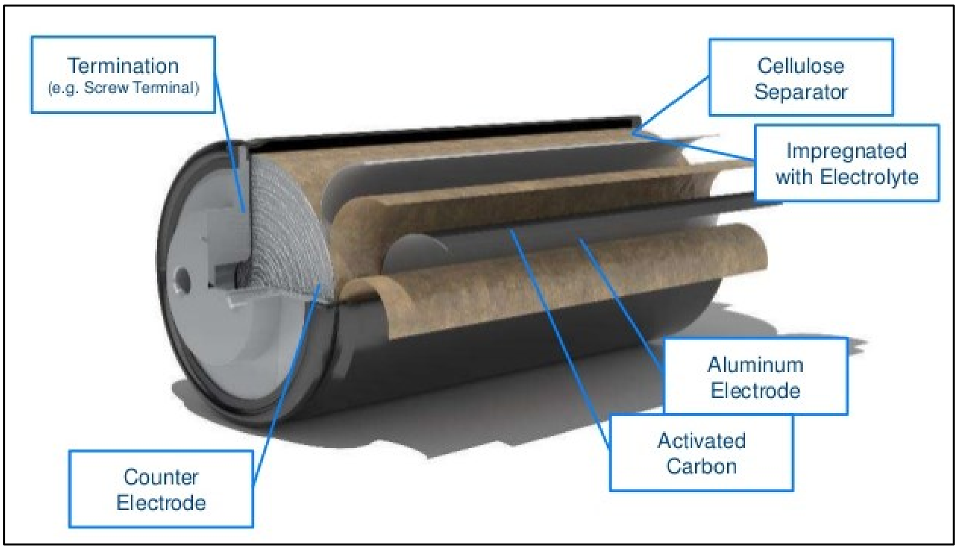

Figure 2.5 – Supercapacitor: rolled structure (cylindrical) [30]

Following the same logic it is possible to derive that the specific capacitance (F/g) of each electrode is 4 times bigger than the specific capacitance of the supercapacitor. This is because the electrode has twice the capacitance of the supercapacitor but it has half the mass of active material. This is an important relation that is used in Chapter 4 in order to calculate the specific capacitance of supercapacitors when only the specific capacitance of synthesised materials was measured

Supercapacitors can have different shapes and generally they are either cylindrical, presenting a rolled structure (details in Figure 2.5) or flat, having a stacked structure (Figure 2.4). In a supercapacitor, the parameters that are generally considered fundamental to vary the energy density and the power density are the specific surface area (SSA) and the pores size distribution (PSD). Large SSA increase the quantity of ions that can be adsorbed [31] , while the PSD can impact on the energy density and power density [32]. Moreover, other important parameters are the good electrical conductivity and wettability by the electrolyte.

Pseudocapacitors are another family of supercapacitors similar to batteries in which redox reactions happen. A third class of supercapacitor is the hybrid solution between the two. Supercapacitors have electrodes made of carbon materials and pseudocapacitors use metal oxides or conducting polymers as materials for electrodes [33]. Both of them are not part of this research.

The activated carbon electrodes are generally cheap and widely used due to their accessibility, high chemical stability, non-toxicity and wide temperature range of operation [34]. They store the charged ions as they accumulate in the pores of the activated carbon (generally obtained by pyrolysis of several different carbon sources, from petroleum coke to wood) [35].

Metal oxides are considered the best materials due to their high specific capacitance and low resistance, hence high power density, but the materials employed are quite rare and expensive. Some recent discoveries seem to have found interesting solutions for cost effective large scale supercapacitors as the cauliflower-like CuO (copper oxide) [36]. Another approach involves the metal oxide and multi walled nanotubes and in some cases with good results. For example using TiO_2/MWNTs it was possible to obtain great capacitance with a good potential for scalability [37].

Conductive polymers, instead, are relatively cheap, have a suitable morphology, a fast doping-undoping process (through which they store the charges) and are easy to manufacture, nevertheless they have problems in long term stability and degrade during cycling [38].

Carbon nanotubes and especially graphene are the latest materials applied to supercapacitors. Generally, carbon nanotubes are used as additives for the electrodes in order to reduce the equivalent series resistance (ESR) as they have a high conductivity and hence enhancing the electrode performance [39]. Graphene also looks very promising due to its high electrical and thermal conductivity and large surface area. So far the cheapest and easier to scale up process that showed promising properties is the chemical exfoliation/oxidation and consequential reduction of graphite. Several other types of graphene based materials are under development, such as graphene based hydrogel, activated graphene, graphene sheets intercalated (generally with platinum) and many others [40], but this research focuses on the former. Graphene is also used in combination with conductive polymers (e.g.: [41]) and with metal oxides as well (e.g.: [42]).

The electrolytes consist of a solvent and a salt that dissociates in positive and negative ions allowing electrons mobility. Operating voltage, ESR (equivalent series resistance), temperature range of operation and capacitance of the device are also connected to the electrolyte performance [43].

Electrolytes are mainly of two main categories: organic or aqueous. Organic electrolytes allow to achieve a higher voltage and this compensates the fact that they have a higher specific resistance that reduces the maximum usable power while allows for a larger energy density[3] [44]. Acetonitrile is commonly used as solvent and this limits their range of applications due to its flammability and consequential release of toxic elements. For this reason ionic liquids constitute a third category that is under development as alternative to organic electrolytes [45]. Aqueous electrolytes can withstand a lower voltage (narrower electrochemical window, need a lower voltage to dissociate) but have a higher conductance, therefore higher power densities and lower costs [44].

It is important to select the right electrolyte to combine with the electrodes material, not only to match the material properties, but also to tailor the dimensions of the porous material to the size of the ions and the properties (e.g. wettability) of the electrolyte [46]. For example, carbon composite electrode are generally coupled with organic electrolyte or and carbon/metal fibre composite with aqueous electrolyte achieve higher energy densities [47].

2.2.2 Applications and future developments

It is straightforward that a combination of supercapacitors coupled with batteries is used to obtain more optimized backup systems to manage the power demand. Supercapacitors reduce the number of battery cycles as they can provide the power needed for peak shaving or short power cuts [48]. This extends the batteries life time relieving them from severe loads and pulsed current requests. This is not only valid for backup systems or distributed renewable energy generation but also in consumer electronics [49]. They are used for power quality absorbing voltage fluctuations [50], in hybrid vehicles or trains (for peak demand and recharged while braking), to power actuators in emergency applications, where the subsystem must work even when the main one has failed (e.g. aircraft doors, pitch system for windmills, elevators, power steering, electro-hydraulic brake systems), or to provide peak power to several devices (e.g. forklifts, cranes, elevators as well as flashes for mobile handsets or wireless communications) [51].

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[3] $E = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2$ where $Q = CV$ with C = capacitance and Q = quantity of charge

A reason to consider supercapacitors for particular applications is their long life cycle time and zero maintenance as (ideally) there is no chemical reaction/change at the electrodes under normal operations [38]. For the same reason, if a supercapacitor is left unused, there is no material deterioration and it can be charged to its full potential after self-discharging, while batteries degrade over time even if unused due to corrosion effects [52].

The future development of supercapacitors is linked to the development of better performing electrodes materials and electrolytes. Several studies are carried on in these fields aiming at, increasing the specific capacitance, incrementing voltage to boost the energy density, reduce the weight of current collectors and binder of active material. For the carbon electrodes, in general, the future research is focused on obtaining higher specific surface area, rational pore distribution and a smaller internal resistance. For the metal oxide electrodes it is crucial to reduce costs, while for polymeric ones, that are cheaper and easily manufactured, the research focuses more in extending their lifetime [38, 53].

While this research is going on, industry is still inclined to use organic electrolytes (generally acetonitrile) and cheap materials for electrodes, such as activated carbon, with the intention of keeping a low manufacturing cost. A lot of research is still going on in the activated carbon development because, most of the alternative materials including carbon nanotubes and graphene have not achieved a large scale production and long term stability. In addition their production processes use a lot of toxic chemicals that further slowdown their adoption [54].

2.3 Graphene in brief

This section discussed briefly the development of graphene and some of the production routes focusing mostly on those that have been measured and analysed in the following chapters: electrochemical exfoliation, chemical and thermal reduction of graphite/graphene oxide and chemical vapour deposition. It also touches the problem of lack of standards in the field and scalability to industrial volumes.

2.3.1 General background

For many years graphene was considered only as a purely theoretical material and even early prediction about two dimensional materials assessed their instability due to thermal fluctuations. Supporting this theory there were some cases of thin films becoming unstable as their thickness was reduced [55]. In the early 2000s, however, Geim and Novoselov, managed to show very thin layers of carbon and monolayer graphene simply using scotch tape [56, 57].

Even if this material has been synthesised only 10 years ago for the first time, after this discovery, a lot of research focused on exploring the physical and chemical properties of this new material fostering all types of possible applications from reinforcement for different materials [58-60], flexible displays [61], membranes [62], transistors [63], solar cells [64] and many others. The reason why this material has sparked a lot of new ideas and applications is linked with its peculiar properties in almost all aspects: physical, electrical, mechanical thermal and magnetic.

Graphene is a single layer of carbon atoms arranged hexagonally with an hybridized sp^2 electronic configuration [65]. It offers both high thermal conductivity [66] and high mechanical properties [67] being very strong but also flexible [68]. It also offers a superior carrier mobility, higher than in known superconductors enabling the possibility of operating at higher frequencies and, therefore, generating much faster electronic devices.

Strictly speaking, only a single monoatomic layer of carbon should be called graphene [69] and thus few stacked layers of carbon should be defined as graphene nanoplatelets (GNP). Nevertheless, many papers refer to GNP as graphene and moreover, there is no common agreement about how many layers of carbon can still be called graphene/GNP or it becomes normal graphite. Some papers define say that graphene/GNPs are generally between few and ten layers of graphene [70] while some other call nanoplatelets also particles made of more than 10 layers [71]. This uncertainty is also linked to the fact that the graphene layers can be stacked in several ways (atom above atom, atom above an empty area but also in a totally asymmetric and random way) and the different staking exhibit different properties. This also means that nanoparticles with different types of staking behave very differently [72] making it difficult to create a standard based on number of layers.

2.3.2 Graphene in supercapacitors

Graphene also offers a unique specific surface (2630 m^2/g), bigger than that of carbon nanotubes and normal graphite [73]. It also offers high electrical conductivity (around 64 mS/cm) that is about 60 times more than carbon nanotubes and remains stable at a wide range of temperature. This is important for energy related applications especially as an electrode material and this makes graphene an ideal candidate material to be placed in a supercapacitor.

Several studies have been carried out on about this topic and with some interesting results [74-76] with specific capacitance above 200 F/g and cycling ability larger than a thousand cycles. This proves that graphene is a good alternative to the activated carbon even though scalability could be an issue.

Nevertheless, these values fall short from the graphene theoretical value of 550 F/g [77] and for this reason research has moved into hybrid materials through which higher capacitances and cycling capabilities are achieved especially using polyaniline (PANI – a conductive polymer) [77-81], metal oxides [82-84] or with inorganic nanomaterial anchored on the graphene surface [85-88].

It is important to mention, though, that having graphitic structures of a single layer is not always good. It was demonstrated how multilayer graphene (>10 layers) exhibit a higher capacitance than few layers and a far larger capacitance than a single layer with the same dimension [89]. This is most likely due to the increase of the area of the edge plane (due for example to stacking of several planes that increases the thickness and therefore the edge plane, due to defects like holes or wrinkles that generate internal edges or due to random orientation of planes) that is where graphene layers show its higher electron transfer properties, much higher than on its sides [90]. This also indicates that the best configuration for an electrode is to be made of GNP vertically oriented. In fact they offer a larger edge plane and more space between vertical layers, hence higher space utilisation also if compared to randomly oriented GNPs (that nonetheless have still a higher capacitance than single layer graphene) [91].

2.3.3 Production methods

As vertical or randomly oriented GNPs are more suitable for supercapacitor applications, this section will mostly focus on the graphene production technologies that synthesise nanoplatelets more than single layer graphene and, moreover, only on those methodologies studied in the next chapters. This because there are too many different ways of making graphene and all harvest materials with different properties suitable for different applications. The purpose of this section is to explain in detail the procedures followed later in this thesis and not to give an overall overview on graphene production methods.

2.3.3.1 Electrochemical exfoliation

Electrochemical exfoliation instead offers quite good possibilities for industrial scale up as it produces high-quality graphene. This type of exfoliation happens in an electrolytic cell with two (or three) electrodes and a liquid with a narrow electrochemical window (water) and another liquid with a higher electrochemical window (e.g. salt dissolved, KOH, NaOH, other). When current flows through the electrodes, the electrolysis of water produces hydroxyl and oxygen radicals that initiate the corrosion at the graphite anode on edge sides. This reaction opens the edge planes and allows the salt ions to intercalate between them and to expand the electrode. This weakens the cohesive Van Der Waals forces and leads to a precipitation of electrode material in the form of graphene nanoribbons or graphene sheets (from single to multilayer graphene) in the solution [92].

Something similar is the chemical exfoliation, first reported even before graphene was discovered, but only achieved few layers graphene and not a single one [93]. This method uses the same approach intercalating smaller ions between layers of graphite using alkali metals (like potassium) whose ions are smaller than graphite interlayer distance [94]. Some other methods are used for the exfoliation of graphite rods for example using supercritical fluids [95] but they are not covered in this review.

2.3.3.2 Chemical and thermal routes

Another way of obtaining nanoplatelets is via oxidation and reduction of graphite powder. The oxidation is generally chemical, while the reduction can be either chemical or thermal.

The first step consists in oxidising the graphite powder using three main methods: the Brodie method (1860) [96], the Staudenmaier method (1898) [97] and the Hummers method (1958) [98]. All three methods involve the use of acids and strong oxidants and increase the mass of carbon adding oxygen and hydrogen.

Brodie actually proposed three very similar methods, always involving acids (nitric and sulphuric) and oxidants potassium chlorate or sodium chlorate and with different proportions. However, for this research the Brodie method considered is the following procedure: mix 40 ml of fuming nitric acid (HNO_3) with 2 g of graphite powder at 0 °C for 15 min. Sodium chlorate ($NaClO_3$) is then added slowly in order to avoid over vigorous reactions (this is the case for all methods when adding the oxidising agent) [99] and stirred for 24 h at room temperature. The resulting mix is then filtered and washed with deionised water until the pH is around 7 and dried (better if at temperatures about 50 °C to avoid even minimal thermal reductions).

The Staudenmaier method follows a similar procedure but with different chemicals. In a flask, 18 ml of sulphuric acid (H_2SO_4) is mixed together with 9 ml of fuming nitric acid (HNO_3) at 0-5 °C and stirred for 15 min. Graphite powder is then added (1 g) and stirred for 30 min at 0 °C to avoid agglomeration. 11 g of an oxidative agent, potassium chlorate ($KClO_3$) are added slowly to avoid over vigorous reaction or sudden increase of temperature and the mixture is then stirred for 96 h at room temperature [100]. The reaction releases chlorine dioxide (ClO_2) that must be dispersed as it is explosive at high concentration [101]. The reaction mix is then filtered, washed and dried as in the previous procedure.

The Hummers method includes several variants too. They are all similar to the original but vary in doses and times. The ones considered in this thesis are the Hummers modified Fugetsu, modified Hummers Bangal and modified Hummers Jeong.

Fugetsu proposed the following recipe: 2 g of graphite powder and 1 g of sodium nitrate ($NaNO_3$) are mixed in sulphuric acid (H_2SO_4) in an ice bath. 6 g of potassium permanganate ($KMnO_4$) are added slowly in order to avoid over vigorous reactions and temperature increase. The mix is stirred for 2 h and then the temperature is increased to 35 °C and stirred for 30 min followed by a slow addiction of 100 ml of distilled water to avoid bubbling. The temperature is then risen to just below 100 °C and constantly stirred. After 3h hydrogen peroxide (H_2O_2) is added (5%, 100 ml) to stop the reaction and remove all oxidants, the mixture is filtered and washed and dried [102].

Bangal instead proposed a different procedure using 2 g of graphite powder and 1 g of sodium nitrate ($NaNO_3$) in 46 ml of sulphuric acid (H_2SO_4) stirred in ice bath. 6 g of potassium permanganate ($KMnO_4$) are added slowly in order to avoid over vigorous reactions and temperature increase higher than 20 °C. After 5 min the ice bath is removed and temperature increased to 35 °C and stirred for 30 min. Next, 92 ml of distilled water are added slowly and the mixture is stirred for another 15 min. Then 80 ml of hot water at 60 °C and hydrogen peroxide (H_2O_2) 3% aqueous solution are added to reduce the residual potassium permanganate until bubbling disappears. The mixture is then filtered and washed and dried [103].

The Jeong method starts with 350 ml of sulphuric acid (H_2SO_4) and 2 g of graphite stirred at around 0-5 °C for 15 min. Potassium permanganate ($KMnO_4$), 8 g, and 1 g of sodium nitrate ($NaNO_3$) are added slowly at 0 °C and stirred for 30 min. Then the temperature is increased to 35 °C for another 30 min of stirring. Water (250 ml) is added slowly and the temperature is increased to 98 °C for 3 h. The reaction is terminated adding 500 ml of deionised water and 40 ml of 30% hydrogen peroxide (H_2O_2) aqueous solution. The mix is then filtered and washed with an aqueous solution of 10% hydrochloric acid (HCL) in order to remove metal ions and then washed with distilled water until the PH is about 7 and dried [104].

Hummers introduced potassium permanganate that, when used in combination with sulphuric acid, creates dimanganese heptoxide (Mn_2O_7) that is far more reacting than MnO_4^- and is explosive above 55 °C or when placed in contact with organic compounds [105]. The oxidation of graphite changes the planar sp^2 hybridised structure to a tetrahedral sp^3 and increases the distance between planes of a variable quantity depending on the intercalating chemicals [106], hence the oxidation method. Graphite oxide is reported to be a very promising material for supercapacitors as well as graphene [107].

The structure of graphite (or graphene) oxide has been debated for long time with a great uncertainty about type and distribution of oxygen functional groups. Late studies have proposed a model with hydroxyl and epoxy functional groups on the basal plane. Most likely carbonyl groups are present at the edge plane in the form of carboxylic acids, however further studies are needed [108].

Until standards and standard measurements/characterisation methods are not defined, all these materials will be similar but with different properties. Wastes and emissions will be different for different methodologies [109], but also for the same methodology as the level of oxidation is slightly different at every batch. Quality standards are needed to set some material properties and tolerances in order to be able to define a class of material with common performances and structures.

The reduction of the GO material, changes the structure of GO eliminating the oxygen groups from the material and liberating the flakes of graphene generating the so called reduced graphene oxide (rGO). There are several ways of reducing the GO but in this review only two are analysed in detail. The first one is the chemical reduction with hydrazine. After sonication of 1 g of GO, the material is mixed with ammonia (1.5 ml) and hydrazine monohydrate (3 ml) at 85 °C for 24 h under reflux condenser. The solution was then filtered, washed with 500 ml of deionised water 50 ml of methanol and dried at 75 °C for 24 h [110]. There are some other ways of reducing the GO chemically, for example with sodium borohydride [111], vitamin C [112] and even bacteria [113], however these are not part of this analysis.

The thermal reaction (or annealing) happens in a vacuumed environment in which some inert gas is flowing to clean it from the oxygen released by the reaction. The temperatures used can vary from slightly above 100 °C [114] to above 1000 °C [106] producing material with different characteristics and properties, and their increase must be controlled as the reduction reaction can be explosive [115]. For example, the thermal reduction analysed in the following chapter is performed at 700 °C in argon [116] however, to reach 700 °C it needs more than 15 h as the ramp up is divided into three main stages: up to 140 °C the heating rate is 1.5 °C per minute, then the sample is kept at 140 °C for 30 min. The second part of the ramp up is performed with a reduced heating rate of 0.3 °C/min until 350 °C then the sample is kept at this temperature for 30 min. In the last stage, from 350 °C to 700 °C, the heating rate is again set at 1.5 °C per minute and the sample is kept at 700 °C for 2 h before turning off the furnace and let the sample cool down.

This material obtained with both chemical or thermal reduction does not appear to be free of all oxygen (with thermal annealing performing better in this respect) and has therefore different properties if compared to the pristine graphene and for this reason is called rGO [117]. Moreover, the reduction of GO introduces defects to the graphene sheets as some atoms of carbon leave together with oxygen during the reduction or some functional groups remaining after reduction. It has been shown, however, that rGO can be repaired introducing some carbon source (for example ethylene) at high temperature (800°C) [118]. Also for the reduction, the uncertainty of reaction mechanism generates uncertainties [119]. Some other routes to reduce GO are investigated such as electrochemical reduction [120], photocatalytic reduction [121], reduction using photographic flash [122] and “light-scribed” [123].

2.3.3.3 Chemical vapour deposition (CVD)

The CVD process produces a thin film of graphene over a metallic substrate and seems to be the most promising technology to be scaled up industrially. The mechanism through with CVD works is to let a precursor gas, usually methane or ethane, flow inside a vessel preheated at elevated temperature where it reacts with a catalyst substrate forming graphene on its surface. The temperatures at which the reaction can happen vary from some hundreds degrees to almost the melting point of the substrate [124]. To transfer the catalyst onto other materials, the graphene layer is generally coated with a polymer (e.g. PMMA) and the catalyst is subsequently etched and dissolved. The graphene sheet on the new substrate is then deposited on the new material (for example silicon wafer) and the polymer is dissolved using acetone and IPA (isopropyl alcohol) to rinse [125].

Among the most suitable catalysts are copper and nickel as the strength of their interaction with carbon is moderate and their lattice match with graphite. Force of interaction can be seen as the solubility of carbon in these metals [126]. Nickel has a higher interaction with carbon and therefore, at high temperature, carbon is dissolved in the metal. When the substrate is cooled, the solubility of carbon decreases and therefore the carbon first separates from the metal and then grows on nickel surface. For this reason the cooling must be fast to avoid the deposition of many layers of carbon. On copper, instead, the solubility is negligible and the carbon layer grows directly on the surface even at high temperature and therefore there is no need to control the cooling rate. Moreover, on copper, once the monolayer of graphene has been created, there is a self-blocking mechanisms that avoids the deposition of other layers [127] even if some cases of multilayer graphene are reported [128].

Despite a lot of research going on about CVD and supercapacitors, during the ElectroGraph FP7 EU project on which this thesis is based, this technology was declared not suitable for supercapacitors by the partners involved as it did not show enough specific capacitance. For this reason also this review is limited to the basic principles of CVD and does not investigate further.

2.3.4 Graphene production scalability

There are a lot of potential processes ready to be scaled up at industrial level; however, the market of graphene is driven by the type of graphene produced and the properties appropriate for each application. At present stage, the material does not seem to match the market requirements for quality and costs.

The chemical route, with oxidation and reduction, already offers good potential for scalability and an important variation to be used in industry could be the thermal shock procedure that combines oxidation and reduction in one unique step. The graphene obtained may contain nanoplatelets of several layers as well, however, one single step procedure is generally cheaper and, moreover, the material preserves very good properties (e.g.: only single layer flakes) [129]. This type of graphene is already produced in large quantity with several different methodologies, generally following the chemical route or mechanical grinding and some simple products like graphene paints or inks will be soon on the market [130]. For supercapacitor applications it is more difficult for graphene to reach the market as it needs to compete against activated carbon that is a quite cheap and well performing solution (e.g.: 100 F/g is available already on the market, see Chapter 4). Electrolytes are also another key area of research for graphene supercapacitors. Until a real competitive advantage in term of costs or performances (e.g.: specific capacitance much higher of 100 F/g) is achieved the breakthrough of graphene in this market remains quite far ahead in time.

2.4 LCA and graphene

In recent times, as the manufacture of nanomaterials increases, public concern about their environmental burden and their effect on human health has become a notable issue. It is already known that emissions of nanomaterials occur from some products (textiles, paints, etc.) into the environment. However, the main difficulty is to quantify those emissions especially because the material released may be very different from the material that constituted the product; it might be altered (e.g. while washing textile products) or it might be still in the matrix that contains it and therefore not released individually [131]. This generates a need for mathematical simulation of environmental exposure routes that are relevant for some nanomaterials. For example, it is found in [132] that nano-Ag and nano-TiO_2 may constitute a risk for aquatic organisms, nano ZnO can be emitted in wastewater treatment effluents and nano-Ag for surface waters.

Nevertheless, even if this type of modelling defines a quantitative starting point in the discussion about environmental and human risks of nanoparticles and might set a term of comparison for other toxicological data [133], the research is still at an early stage. Even if toxicological studies are performed on graphene [134], the recent LCIA methods do not take into consideration the toxicological effects of nanomaterials [135].

Several features of nanoparticles contribute to their possible toxicological effects:

- Nanoscale particles have modified properties compared with the basic material increasing the interaction with biological tissue
- Surface area can influence the exposure as the same mass of smaller particles have generally a larger surface area thus possibly reacting at greater rates with the environment
- Shape, aggregation, coating and solubility could affect psychochemical and transport properties [136]

The application of the LCA methodology on these types of materials is hence a possible way of determining these aspects; however, the lack of reliable data related to both exposure/toxicology and production/use-phase/end-of-life prevents it from being an exhaustive tool.

To be significant and reliable an LCA needs a broad set of information and data to be inventoried and for nanomaterials, they are mostly missing. The data are generally covering areas such as the material production, use and end-of-life, its level of exposure to the environment and human beings and the effects of this exposure on them. For this reason some studies welcome a change in the approach that the society has towards development by looking at it with a life cycle thinking perspective. In such way, it would be easier to close general information gaps and in a much quicker way. For this purpose it is recommended that the LCA is performed already at an early stage of development for all new technologies. Moreover, the life cycle thinking approach could contribute in setting the guiding principles for a more sustainable development [137].

As there are no dedicated impact-assessment factors related to the emission of nanoparticles (linked with each specific type of nanomaterial) [138], using the current impact factors will not be sufficient in the future [139] and for this reason several toxicological studies and exposure models are proposed. A first attempt to define characterisation factors for carbon nanotube has been proposed lately [140] but for graphene nothing is available yet.

To date, only one LCA study of graphene production has been published in peer-reviewed literature, which involves a comparison of graphene produced by ultrasound and chemical reduction processes [141]. The study considers “cradle to gate” activities (e.g.: graphene use and end-of-life are excluded) and models graphene production based on literature values for inputs, reaction conditions, and graphene yield.

The study stems from a statement from patent promoting the ultrasound method as an environmentally friendly alternative to the chemical route for graphene production. What at a first look seemed to be a reasonable statement was proven to be wrong, or at least partially wrong demonstrating how important is to perform an LCA at an early stage of product development. While it is true that ultrasound method does not involve toxic or aggressive chemicals, it was demonstrated that it is more problematic for human toxicity and to a lesser extent for ecotoxicity.

This method operates at ambient temperature using solvents to facilitate the exfoliation of carbon layers. In this study diethyl ether is used as solvent and it is the main cause of human toxicity. In detail this result is due to the production of ethylene, from which diethyl ether is produced, that releases mercury into the atmosphere. The same can be said for ecotoxicity as the production of ethylene releases copper in the water. However, even if slightly less impacting, the chemical route shows a comparable ecotoxicity as the production of hydrazine releases vanadium in the water. The chemical route is more impacting in the other two analysed impact categories, energy use, due to the heat needed for the chemical reductions, and blue water footprint, due to the water used to produce sulphuric acid and to wash the GO before it is chemically reduced.

These results cannot be compared with the findings of this thesis as different impact assessment methods are used. Though, it is possible to compare the inventory data for the chemical graphene production as is performed using the Hummers method coupled with a reduction using hydrazine. For the oxidation process the material input, yield and temperature profile are similar. Nothing can be said about the reduction as no details are given.

What is also important is that that published study ([141]) does not take into account any possible application of the material and its quality in this perspective (thus the quantity needed for the selected application). No sensitivity analysis is performed to the graphene properties from each production route. Selecting an application would also allow for a cradle to grave LCA making the study more complete. Even if it can be considered the first LCA on graphene, this study only considers four impact categories and only for its production phase. Secondarily, it is based on numbers found in literature and not on direct measurements therefore its reliability is limited by the transferability of the data from one study to another.

Even if only one study was found in literature about comparative LCA of graphene synthesis processes, it is possible to see that some initial steps were taken in the past few years towards establishing a possible approach to the investigation of nanomaterials from a life cycle assessment prospective.

A study compared the synthesis of 1 kg GNP with 1 kg of epoxy composite loaded with the same GNP (0.058 kg). It showed how, using a cradle to gate approach, hence from raw material extraction, the production of 1 kg GNP is more energy consuming and impacts more on the environment than the production of 1kg of epoxy composite loaded with 0.058 kg of GNP. However, in the composite, the filler (0.058 kg GNPs) uses only 38% of the total energy consumption suggesting that in some particular applications (e.g. aeronautic or aerospace), the increase of energy consumption might be compensated by the lighter weight, making the composite material more energy efficient overall [142].

Although performing this type of study on a new and fast evolving technology of nanomaterial synthesis can be compared to following a moving target [143], several attempts were made to define some major contributors to the environmental impacts for carbon nanotubes (CNT) as well. In their production, the energy consumption is the main driver for their environmental burden [144] and this should be reflected in the graphene synthesis process. From [145] it is also possible to notice that the energy used impacts the fossil fuel consumption that leads to consequences such as climate change among many others.

The electricity consumption varies by several orders of magnitude and ranging from 10^2 to 10^8 MJ/kg [138]. However, concerning the CVD method, the only production method for CNT in common with graphene, the energy consumption ranges from 10^2 MJ/kg when produced on a fluidised/floating bed to 10^5 MJ/kg of fixed bed. In the middle, the carbon nano fibres produced via CVD ranging from 10^3 to 10^4 MJ/kg. The impact related to electricity consumption could be reduced, for example, by using renewable feedstock, by reusing the waste materials as carbon precursors [138] or by reducing the heat losses.

Generally speaking, most of the LCA about nanomaterials found in literature involve production methods that are different from those used to produce graphene, excluding the CVD (chemical vapour deposition) method, and therefore not transferrable. A lot of LCA studies about carbon nanotubes concern CVD as it seems to be the most likely future industrial method for growing nanotubes (ambient pressure and lower temperature than other processes) [146]. On the other side, the CVD method for graphene was discarded during ElectroGraph FP7 EU project as the material produced was declared not suitable for supercapacitor applications by the project members as it did not show interesting values of specific capacitance.

No LCA studies were found involving supercapacitors and graphene and only one was found about supercapacitors using carbon nanotubes to enhance their performance [147]. However, that study covers only the energy consumption and without performing an LCA. In its limited scope it only shows an energy assessment that proves how the production of carbon nanotubes in a laboratory is more energy demanding than the current activated carbon production. It also declares the importance of the scale up activity in reducing the energy consumption of the carbon nanotubes production and consequentially its environmental impact.

Supercapacitors are evaluated with LCA in some studies, mainly involving electrical mobility, but also linked with the penetration of renewable energies in the energy market [148] or even connecting these two aspects when the batteries for electric cars are powered by renewable energies [149]. This is always done to evaluate their environmental impacts over their life cycle in order to understand if the proposed technology is performing better than the current one, however no studies involving only supercapacitors were found.

At last, it is worth to mention that most of the presented studies highlight the presence of several data gaps and uncertainties. To close the gaps there is a need for further research in a lot of different areas [139] and therefore, at present time, the common way to bridge data gaps, besides using literature, is to make educated guesses, to simulate processes or reactions and to transfer data from similar processes. For this thesis, assumptions and simulations are used.

2.5 Process simulation and scale up

Process simulation it is performed using software (e.g.: SuperPro Designer, Aspen Hysys, Aspen Plus and others) offering mathematical algorithms capable of simulating process operations [150]. SuperPro Designer, the software used in this thesis, offers a large database of chemicals and it is used in designing, evaluating and optimising processes in a variety of industrial sectors. It is designed originally to cover process optimisation and scheduling of processes, workforce planning and economic evaluation. Many studies use this software for both process optimisation and economic evaluation [151, 152].

It is now common to use process simulation software to feed LCA models in order to evaluate environmental performances of possible variations to known processes or of newly developed processes [153-156]. However, the software does not offer tools to scale processes up or down as they do not offer any yield/energy optimising algorithm. Therefore the scale up activity is mostly performed using assumptions or estimated as proposed by some LCA studies executed on laboratory process under development [157, 158]. This scale up process is feasible only under some pre-requisites: the analysed process must be already under research and feasible, the basic data on the process must be available and the product has the potential to be industrialised in the future [159].

Based on those methods, a study on hypothetical scale up of carbon nanotubes synthesis proved that the environmental impacts could diminish by a value ranging from 84% to 94% when produced at industrial scale [160]. Uncertainties generated by assumptions or estimations are dealt with sensitivity analysis and scenario modelling [161-163]. However, those studies are generally having a cradle to gate approach and they only compare production routes on the base of a functional unit based on a physical dimension (volume or mass) and not on a function performed. This is a good way to compare production processes, but this approach penalises those routes that can synthesise high quality material. This is because it does not take into consideration the quality of the material that is fundamental to evaluate the quantity needed to perform a selected function.

2.6 References

1. Colombo, U., *The Club of Rome and sustainable development.* Futures, 2001. **33**(1): p. 7-11.
2. Hunt, R.G., J.D. Sellers, and W.E. Franklin, *Resource and environmental profile analysis: A life cycle environmental assessment for products and procedures.* Environmental Impact Assessment Review, 1992. **12**(3): p. 245-269.
3. ISO, *Environmental management - Life cycle assessment - Principles and framework*, EN ISO 14040:2006, European Standard.
4. Hermann, B.G., C. Kroeze, and W. Jawjit, *Assessing environmental performance by combining life cycle assessment, multi-criteria analysis and environmental performance indicators.* Journal of Cleaner Production, 2007. **15**(18): p. 1787-1796.
5. Waldron, K., *Handbook of Waste Management and Co-Product Recovery in Food Processing, Volume 2*, Woodhead Publishing.
6. Goldberg, L.H. and W. Middleton, *Green Electronics/Green Bottom Line - Environmentally Responsible Engineering*, Elsevier.
7. Randall, J.F., *Designing Indoor Solar Products - Photovoltaic Technologies for AES*, John Wiley & Sons.
8. ISO, *Environmental management - Life cycle assessment - Principles and framework*, EN ISO 14044:2006, European Standard.
9. Atlas, R.M. and J. Philp, *Bioremediation - Applied Microbial Solutions for Real-World Environmental Cleanup*, American Society for Microbiology (ASM).
10. JRC, *ILCD handbook*2010: Institute for environment and sustainability European Commission Joint Researc Centre.
11. Bruijn, H., R. Duin, and M. Huijbregts, *Main characteristics of LCA Handbook on Life Cycle Assessment*, J. Guinee, et al., Editors. 2004, Springer Netherlands. p. 5-10.
12. Finnveden, G., et al., *Recent developments in Life Cycle Assessment.* Journal of Environmental Management, 2009. **91**(1): p. 1-21.
13. Alfaro, J.F., B.E. Sharp, and S.A. Miller. *Developing LCA techniques for emerging systems: Game theory, agent modeling as prediction tools*. in *Sustainable Systems and Technology (ISSST), 2010 IEEE International Symposium on*. 2010.
14. De Benedetto, L. and J. Klemeš, *The Environmental Performance Strategy Map: an integrated LCA approach to support the strategic decision-making process.* Journal of Cleaner Production, 2009. **17**(10): p. 900-906.
15. Seo, K.-K. and W.-K. Kim, *Approximate Life Cycle Assessment of Product Concepts Using a Hybrid Genetic Algorithm and Neural Network Approach Advances in Hybrid Information Technology*, M. Szczuka, et al., Editors. 2007, Springer Berlin / Heidelberg. p. 258-268.
16. Guinée, J.B., et al., *Quantitative life cycle assessment of products: 2. Classification, valuation and improvement analysis.* Journal of Cleaner Production, 1993. **1**(2): p. 81-91.

17. Helias A, U.d.H., *Applications of life cycle assessment: expectations, drawbacks and perspectives.* Journal of Cleaner Production, 1993. **1**(3–4): p. 131-137.
18. Ehrenfeld, J.R., *The Importance of LCAs—Warts and All.* Journal of Industrial Ecology, 1997. **1**(2): p. 41-49.
19. Krozer, J. and J.C. Vis, *How to get LCA in the right direction?* Journal of Cleaner Production, 1998. **6**(1): p. 53-61.
20. Finnveden, G., *On the limitations of life cycle assessment and environmental systems analysis tools in general.* The International Journal of Life Cycle Assessment, 2000. **5**(4): p. 229-238.
21. Guinee, J., *Handbook on life cycle assessment operational guide to the ISO standards.* The International Journal of Life Cycle Assessment, 2002. **7**(5): p. 311-313.
22. Sinden, G., *The contribution of PAS 2050 to the evolution of international greenhouse gas emission standards.* The International Journal of Life Cycle Assessment, 2009. **14**(3): p. 195-203.
23. Cleveland, C.J. and C. Morris, *Dictionary of Energy (Expanded Edition)*, Elsevier.
24. Tarter, R.E., *Solid-State Power Conversion Handbook*, 1993, Wiley - IEEE Press.
25. Lota, G., et al., *Improvement of the structural and chemical properties of a commercial activated carbon for its application in electrochemical capacitors.* Electrochimica Acta, 2008. **53**(5): p. 2210-2216.
26. Frackowiak, E., et al., *Supercapacitors based on conducting polymers/nanotubes composites.* Journal of Power Sources, 2006. **153**(2): p. 413-418.
27. *Energy Storage Sense*. 2014 [cited 2015 07/05]; Available from: http://energystoragesense.com/supercapacitors/.
28. *Technology UK*. 2014 [cited 2015 07/05]; Available from: http://www.technologyuk.net/physics/electrical_principles/the_capacitor.shtml.
29. *Supercapacitor application in trasportation (p. 8)*. Kemet Corporation 2014 [cited 2015 05]; Available from: http://www.slideshare.net/KEMETElectronics/supercapacitors-transportation-r2.
30. *Supercapacitor application in trasportation (p. 6)*. Kemet Corporation 2014 [cited 2015 05]; Available from: http://www.slideshare.net/KEMETElectronics/supercapacitors-transportation-r2.
31. Yang, H., et al., *Improvement of Commercial Activated Carbon and Its Application in Electric Double Layer Capacitors.* Electrochemical and Solid-State Letters, 2002. **5**(6): p. A141-A144.
32. Kondrat, S., et al., *Effect of pore size and its dispersity on the energy storage in nanoporous supercapacitors.* Energy & Environmental Science, 2012. **5**(4): p. 6474-6479.

33. Ruiz, V., et al., *Voltage dependence of carbon-based supercapacitors for pseudocapacitance quantification.* Electrochimica Acta, 2013. **95**(0): p. 225-229.
34. Zhang, L.L. and X.S. Zhao, *Carbon-based materials as supercapacitor electrodes.* Chemical Society Reviews, 2009. **38**(9): p. 2520-2531.
35. Wei, L. and G. Yushin, *Nanostructured activated carbons from natural precursors for electrical double layer capacitors.* Nano Energy, 2012. **1**(4): p. 552-565.
36. Dubal, D.P., et al., *CuO cauliflowers for supercapacitor application: Novel potentiodynamic deposition.* Materials Research Bulletin, 2013. **48**(2): p. 923-928.
37. Sankapal, B.R., et al., *Presenting highest supercapacitance for TiO2/MWNTs nanocomposites: Novel method.* Chemical Engineering Journal, 2014. **247**(0): p. 103-110.
38. Zhang, Y., et al., *Progress of electrochemical capacitor electrode materials: A review.* International Journal of Hydrogen Energy, 2009. **34**(11): p. 4889-4899.
39. Huang, C.-W., et al., *Significantly enhanced charge conduction in electric double layer capacitors using carbon nanotube-grafted activated carbon electrodes.* Journal of Power Sources, 2008. **183**(1): p. 406-410.
40. Huang, Y., J. Liang, and Y. Chen, *An Overview of the Applications of Graphene-Based Materials in Supercapacitors.* Small, 2012. **8**(12): p. 1805-1834.
41. Luo, J., et al., *Three-dimensional graphene-polyaniline hybrid hollow spheres by layer-by-layer assembly for application in supercapacitor.* Electrochimica Acta, (0).
42. Zhang, Q., C. Xu, and B. Lu, *Super-Long Life Supercapacitors Based on the Construction of Ni foam/graphene/Co3S4 Composite film hybrid electrodes.* Electrochimica Acta, 2014. **132**(0): p. 180-185.
43. Lu, K., *Materials in Energy Conversion, Harvesting, and Storage* 2014: Wiley. 363 - 365.
44. Miller, J.M., *Energy storage technologies*, in *Propulsion Systems for Hybrid Vehicles (2nd Edition)*2010, Institution of Engineering and Technology. p. 507.
45. Shim, Y., H.J. Kim, and Y. Jung, *Graphene-based supercapacitors in the parallel-plate electrode configuration: Ionic liquids versus organic electrolytes.* Faraday Discussions, 2012. **154**(0): p. 249-263.
46. Kötz, R. and M. Carlen, *Principles and applications of electrochemical capacitors.* Electrochimica Acta, 2000. **45**(15–16): p. 2483-2498.
47. Rashid, M.H., *Power Electronics Handbook - Devices, Circuits, and Applications (3rd Edition)*, 2011, Elsevier.
48. Baxter, R., *Energy Storage - A Nontechnical Guide*, 2007, PennWell.
49. Smith, T.A., J.P. Mars, and G.A. Turner. *Using supercapacitors to improve battery performance*. in *Power Electronics Specialists Conference, 2002. pesc 02. 2002 IEEE 33rd Annual*. 2002.
50. Hingorani, N.G., *Introducing custom power.* Spectrum, IEEE, 1995. **32**(6): p. 41-48.

51. Schneuwly, A., *Charge ahead [ultracapacitor technology and applications].* Power Engineer, 2005. **19**(1): p. 34-37.
52. Eftekhari, A., *Nanostructured Materials in Electrochemistry*, 2008, John Wiley & Sons.
53. Burke, A., *Ultracapacitors: why, how, and where is the technology.* Journal of Power Sources, 2000. **91**(1): p. 37-50.
54. Zhang, X., et al., *Graphene nanostructures toward clean energy technology applications.* Wiley Interdisciplinary Reviews: Energy and Environment, 2012. **1**(3): p. 317-336.
55. Mermin, N.D., *Crystalline Order in Two Dimensions.* Physical Review, 1968. **176**(1): p. 250-254.
56. Novoselov, K.S., et al., *Two-dimensional gas of massless Dirac fermions in graphene.* Nature, 2005. **438**(7065): p. 197-200.
57. Novoselov, K.S., et al., *Electric Field Effect in Atomically Thin Carbon Films.* Science, 2004. **306**(5696): p. 666-669.
58. Young, R.J., et al., *The mechanics of graphene nanocomposites: A review.* Composites Science and Technology, 2012. **72**(12): p. 1459-1476.
59. Xia, H., et al., *Mechanical and thermal properties of reduced graphene oxide reinforced aluminum nitride ceramic composites.* Materials Science and Engineering: A, 2015. **639**(0): p. 29-36.
60. Potts, J.R., et al., *Graphene-based polymer nanocomposites.* Polymer, 2011. **52**(1): p. 5-25.
61. Gee, C.-M., et al., *Flexible transparent electrodes made of electrochemically exfoliated graphene sheets from low-cost graphite pieces.* Displays, 2013. **34**(4): p. 315-319.
62. Hegab, H.M. and L. Zou, *Graphene oxide-assisted membranes: Fabrication and potential applications in desalination and water purification.* Journal of Membrane Science, 2015. **484**(0): p. 95-106.
63. Li, P., et al., *Investigation of the semiconductor/electrode interface in organic thin-film transistor using graphene electrodes.* Synthetic Metals, 2015. **202**(0): p. 103-109.
64. Selopal, G.S., et al., *Graphene as transparent front contact for dye sensitized solar cells.* Solar Energy Materials and Solar Cells, 2015. **135**(0): p. 99-105.
65. Zhu, Y., et al., *Graphene and Graphene Oxide: Synthesis, Properties, and Applications.* Advanced Materials, 2010. **22**(35): p. 3906-3924.
66. Balandin, A.A., et al., *Superior Thermal Conductivity of Single-Layer Graphene.* Nano Letters, 2008. **8**(3): p. 902-907.
67. Lee, C., et al., *Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene.* Science, 2008. **321**(5887): p. 385-388.
68. Frank, I.W., et al., *Mechanical properties of suspended graphene sheets.* Journal of Vacuum Science & Technology B, 2007. **25**(6): p. 2558-2561.
69. Geim, A.K., *Graphene: Status and Prospects.* Science, 2009. **324**(5934): p. 1530-1534.

70. Brownson, D.A.C., D.K. Kampouris, and C.E. Banks, *An overview of graphene in energy production and storage applications.* Journal of Power Sources, 2011. **196**(11): p. 4873-4885.
71. Shao, Y., et al., *Highly durable graphene nanoplatelets supported Pt nanocatalysts for oxygen reduction.* Journal of Power Sources, 2010. **195**(15): p. 4600-4605.
72. Terrones, M., et al., *Graphene and graphite nanoribbons: Morphology, properties, synthesis, defects and applications.* Nano Today, 2010. **5**(4): p. 351-372.
73. Pumera, M., et al., *Graphene for electrochemical sensing and biosensing.* TrAC Trends in Analytical Chemistry, 2010. **29**(9): p. 954-965.
74. Du, X., et al., *Graphene nanosheets as electrode material for electric double-layer capacitors.* Electrochimica Acta, 2010. **55**(16): p. 4812-4819.
75. Wang, Y., et al., *Supercapacitor Devices Based on Graphene Materials.* The Journal of Physical Chemistry C, 2009. **113**(30): p. 13103-13107.
76. Chen, Y., et al., *Electrophoretic deposition of graphene nanosheets on nickel foams for electrochemical capacitors.* Journal of Power Sources, 2010. **195**(9): p. 3031-3035.
77. Zhao, Y., et al., *A Versatile, Ultralight, Nitrogen-Doped Graphene Framework.* Angewandte Chemie, 2012. **124**(45): p. 11533-11537.
78. Wang, H., et al., *Graphene oxide doped polyaniline for supercapacitors.* Electrochemistry Communications, 2009. **11**(6): p. 1158-1161.
79. Wang, W., et al., *Ternary nitrogen-doped graphene/nickel ferrite/polyaniline nanocomposites for high-performance supercapacitors.* Journal of Power Sources, 2014. **269**(0): p. 250-259.
80. Yan, J., et al., *Preparation of a graphene nanosheet/polyaniline composite with high specific capacitance.* Carbon, 2010. **48**(2): p. 487-493.
81. Li, X., et al., *In-situ polymerization of polyaniline on the surface of graphene oxide for high electrochemical capacitance.* Thin Solid Films, 2015. **584**(0): p. 348-352.
82. Srimuk, P., et al., *Solid-type supercapacitor of reduced graphene oxide-metal organic framework composite coated on carbon fiber paper.* Electrochimica Acta, 2015. **157**(0): p. 69-77.
83. Walker, W., et al., *Integrating life cycle assessment into managing potential EHS risks of engineered nanomaterials: reviewing progress to date.* Journal of Nanoparticle Research, 2015. **17**(8): p. 1-16.
84. Lu, T., et al., *Electrochemical behaviors of graphene–ZnO and graphene–SnO2 composite films for supercapacitors.* Electrochimica Acta, 2010. **55**(13): p. 4170-4173.
85. Ghosh, D., et al., *Reduced Graphene Oxide/Manganese Carbonate Hybrid Composite: High Performance Supercapacitor Electrode Material.* Electrochimica Acta, 2014. **147**(0): p. 557-564.
86. Wang, H., et al., *Ni(OH)2 Nanoplates Grown on Graphene as Advanced Electrochemical Pseudocapacitor Materials.* Journal of the American Chemical Society, 2010. **132**(21): p. 7472-7477.

87. Nie, G., et al., *Facile and controlled synthesis of bismuth sulfide nanorods-reduced graphene oxide composites with enhanced supercapacitor performance.* Electrochimica Acta, 2015. **154**(0): p. 24-30.
88. Wu, Z.-S., et al., *Anchoring Hydrous RuO2 on Graphene Sheets for High-Performance Electrochemical Capacitors.* Advanced Functional Materials, 2010. **20**(20): p. 3595-3602.
89. Goh, M.S. and M. Pumera, *Multilayer graphene nanoribbons exhibit larger capacitance than their few-layer and single-layer graphene counterparts.* Electrochemistry Communications, 2010. **12**(10): p. 1375-1377.
90. Wang, Z., et al., *Enhanced performance of multilayer graphene platelet film via three dimensional configuration with efficient exposure of graphitic edge planes.* Electrochemistry Communications, 2014. **47**(0): p. 75-79.
91. Miller, J.R., R.A. Outlaw, and B.C. Holloway, *Graphene electric double layer capacitor with ultra-high-power performance.* Electrochimica Acta, 2011. **56**(28): p. 10443-10449.
92. Skákalová, V. and A.B. Kaiser, *4. Graphene Produced by Electrochemical Exfoliation*, in *Graphene - Properties, Preparation, Characterisation and Devices*2014, Elsevier. p. 3.
93. Viculis, L.M., J.J. Mack, and R.B. Kaner, *A Chemical Route to Carbon Nanoscrolls.* Science, 2003. **299**(5611): p. 1361.
94. Viculis, L.M., et al., *Intercalation and exfoliation routes to graphite nanoplatelets.* Journal of Materials Chemistry, 2005. **15**(9): p. 974-978.
95. Liu, C., G. Hu, and H. Gao, *Preparation of few-layer and single-layer graphene by exfoliation of expandable graphite in supercritical N,N-dimethylformamide.* The Journal of Supercritical Fluids, 2012. **63**(0): p. 99-104.
96. Brodie, B.C., *On the Atomic Weight of Graphite.* Philosophical Transactions of the Royal Society of London, 1859. **149**(ArticleType: research-article / Full publication date: 1859 /): p. 249-259.
97. Staudenmaier, L., *Verfahren zur Darstellung der Graphitsäure.* Berichte der deutschen chemischen Gesellschaft, 1898. **31**(2): p. 1481-1487.
98. Hummers, W.S. and R.E. Offeman, *Preparation of Graphitic Oxide.* Journal of the American Chemical Society, 1958. **80**(6): p. 1339-1339.
99. Kim, H., A.A. Abdala, and C.W. Macosko, *Graphene/Polymer Nanocomposites.* Macromolecules, 2010. **43**(16): p. 6515-6530.
100. Sheshmani, S. and R. Amini, *Preparation and characterization of some graphene based nanocomposite materials.* Carbohydrate Polymers, 2013. **95**(1): p. 348-359.
101. Lopez, M.I., A.E. Croce, and J.E. Sicre, *Explosive decomposition of gaseous chlorine dioxide.* Journal of the Chemical Society, Faraday Transactions, 1994. **90**(22): p. 3391-3396.
102. Sun, L., H. Yu, and B. Fugetsu, *Graphene oxide adsorption enhanced by in situ reduction with sodium hydrosulfite to remove acridine orange from aqueous solution.* Journal of Hazardous Materials, 2012. **203–204**(0): p. 101-110.

103. Chen, W., L. Yan, and P.R. Bangal, *Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves.* Carbon, 2010. **48**(4): p. 1146-1152.
104. Pham, T.A., et al., *One-step reduction of graphene oxide with l-glutathione.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2011. **384**(1–3): p. 543-548.
105. Simon, A., et al., *The Crystal Structure of Mn2O7.* Angewandte Chemie International Edition in English, 1987. **26**(2): p. 139-140.
106. McAllister, M.J., et al., *Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite.* Chemistry of Materials, 2007. **19**(18): p. 4396-4404.
107. Lobato, B., et al., *Graphite Oxide: An Interesting Candidate for Aqueous Supercapacitors.* Electrochimica Acta, 2014. **149**(0): p. 245-251.
108. Cai, W., et al., *Synthesis and Solid-State NMR Structural Characterization of 13C-Labeled Graphite Oxide.* Science, 2008. **321**(5897): p. 1815-1817.
109. Botas, C., et al., *Graphene materials with different structures prepared from the same graphite by the Hummers and Brodie methods.* Carbon, 2013. **65**(0): p. 156-164.
110. Lobato, B., et al., *Reduced graphite oxide in supercapacitor electrodes.* Journal of Colloid and Interface Science, 2015. **446**(0): p. 203-207.
111. Shin, H.-J., et al., *Efficient Reduction of Graphite Oxide by Sodium Borohydride and Its Effect on Electrical Conductance.* Advanced Functional Materials, 2009. **19**(12): p. 1987-1992.
112. Gao, J., et al., *Environment-Friendly Method To Produce Graphene That Employs Vitamin C and Amino Acid.* Chemistry of Materials, 2010. **22**(7): p. 2213-2218.
113. Akhavan, O. and E. Ghaderi, *Escherichia coli bacteria reduce graphene oxide to bactericidal graphene in a self-limiting manner.* Carbon, 2012. **50**(5): p. 1853-1860.
114. Jung, I., et al., *Tunable Electrical Conductivity of Individual Graphene Oxide Sheets Reduced at "Low" Temperatures.* Nano Letters, 2008. **8**(12): p. 4283-4287.
115. Qiu, Y., et al., *Explosive thermal reduction of graphene oxide-based materials: Mechanism and safety implications.* Carbon, 2014. **72**(0): p. 215-223.
116. Skákalová, V., et al., *Electronic transport in composites of graphite oxide with carbon nanotubes.* Carbon, 2014. **72**(0): p. 224-232.
117. Park, S. and R.S. Ruoff, *Chemical methods for the production of graphenes.* Nat Nano, 2009. **4**(4): p. 217-224.
118. López, V., et al., *Chemical Vapor Deposition Repair of Graphene Oxide: A Route to Highly-Conductive Graphene Monolayers.* Advanced Materials, 2009. **21**(46): p. 4683-4686.
119. Gao, X., J. Jang, and S. Nagase, *Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design.* The Journal of Physical Chemistry C, 2009. **114**(2): p. 832-842.

120. Shao, Y., et al., *Facile and controllable electrochemical reduction of graphene oxide and its applications.* Journal of Materials Chemistry, 2010. **20**(4): p. 743-748.
121. Williams, G., B. Seger, and P.V. Kamat, *TiO2-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide.* ACS Nano, 2008. **2**(7): p. 1487-1491.
122. Cote, L.J., R. Cruz-Silva, and J. Huang, *Flash Reduction and Patterning of Graphite Oxide and Its Polymer Composite.* Journal of the American Chemical Society, 2009. **131**(31): p. 11027-11032.
123. Strong, V., et al., *Patterning and Electronic Tuning of Laser Scribed Graphene for Flexible All-Carbon Devices.* ACS Nano, 2012. **6**(2): p. 1395-1403.
124. Frank, O. and M. Kalbac, *2 - Chemical vapor deposition (CVD) growth of graphene films*, in *Graphene*, V. Skákalová and A.B. Kaiser, Editors. 2014, Woodhead Publishing. p. 27-49.
125. McEvoy, N., et al., *Functionalisation of graphene surfaces with downstream plasma treatments.* Carbon, 2013. **54**(0): p. 283-290.
126. Kumar, S., et al., *CVD growth and processing of graphene for electronic applications.* physica status solidi (b), 2011. **248**(11): p. 2604-2608.
127. Li, X., et al., *Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling.* Nano Letters, 2009. **9**(12): p. 4268-4272.
128. Bhaviripudi, S., et al., *Role of Kinetic Factors in Chemical Vapor Deposition Synthesis of Uniform Large Area Graphene Using Copper Catalyst.* Nano Letters, 2010. **10**(10): p. 4128-4133.
129. Schniepp, H.C., et al., *Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide.* The Journal of Physical Chemistry B, 2006. **110**(17): p. 8535-8539.
130. Segal, M., *Selling graphene by the ton.* Nat Nano, 2009. **4**(10): p. 612-614.
131. Gottschalk, F. and B. Nowack, *The release of engineered nanomaterials to the environment.* Journal of Environmental Monitoring, 2011. **13**(5): p. 1145-1155.
132. Gottschalk, F., et al., *Modeled Environmental Concentrations of Engineered Nanomaterials (TiO2, ZnO, Ag, CNT, Fullerenes) for Different Regions.* Environmental Science & Technology, 2009. **43**(24): p. 9216-9222.
133. Nowack, B., *Is anything out there?: What life cycle perspectives of nano-products can tell us about nanoparticles in the environment.* Nano Today, 2009. **4**(1): p. 11-12.
134. Bianco, A., *Graphene: Safe or Toxic? The Two Faces of the Medal.* Angewandte Chemie International Edition, 2013. **52**(19): p. 4986-4997.
135. Bauer, C., et al., *Towards a framework for life cycle thinking in the assessment of nanotechnology.* Journal of Cleaner Production, 2008. **16**(8–9): p. 910-926.
136. Healy, M.L., L.J. Dahlben, and J.A. Isaacs, *Environmental Assessment of Single-Walled Carbon Nanotube Processes.* Journal of Industrial Ecology, 2008. **12**(3): p. 376-393.

137. von Gleich, A., M. Steinfeldt, and U. Petschow, *A suggested three-tiered approach to assessing the implications of nanotechnology and influencing its development.* Journal of Cleaner Production, 2008. **16**(8–9): p. 899-909.
138. Upadhyayula, V.K.K., et al., *Life cycle assessment as a tool to enhance the environmental performance of carbon nanotube products: a review.* Journal of Cleaner Production, 2012. **26**(0): p. 37-47.
139. Hischier, R. and T. Walser, *Life cycle assessment of engineered nanomaterials: State of the art and strategies to overcome existing gaps.* Science of The Total Environment, 2012. **425**(0): p. 271-282.
140. Rodriguez-Garcia, G., B. Zimmermann, and M. Weil, *Nanotoxicity and Life Cycle Assessment: First attempt towards the determination of characterization factors for carbon nanotubes.* IOP Conference Series: Materials Science and Engineering, 2014. **64**(1): p. 012029.
141. Arvidsson, R., et al., *Prospective Life Cycle Assessment of Graphene Production by Ultrasonication and Chemical Reduction.* Environmental Science & Technology, 2014. **48**(8): p. 4529-4536.
142. Pizza, A., et al., *Life cycle assessment of nanocomposites made of thermally conductive graphite nanoplatelets.* The International Journal of Life Cycle Assessment, 2014. **19**(6): p. 1226-1237.
143. Gutowski, T.G., J.Y.H. Liow, and D.P. Sekulic. *Minimum exergy requirements for the manufacturing of carbon nanotubes*. in *Sustainable Systems and Technology (ISSST), 2010 IEEE International Symposium on*. 2010.
144. Isaacs, J.A., A. Tanwani, and M.L. Healy. *Environmental Assessment of SWNT Production*. in *Electronics and the Environment, 2006. Proceedings of the 2006 IEEE International Symposium on*. 2006.
145. Dahlben, L.J. and J.A. Isaacs. *Environmental assessment of manufacturing with carbon nanotubes*. in *Sustainable Systems and Technology, 2009. ISSST '09. IEEE International Symposium on*. 2009.
146. Griffiths, O.G., et al., *Identifying the largest environmental life cycle impacts during carbon nanotube synthesis via chemical vapour deposition.* Journal of Cleaner Production, 2013. **42**(0): p. 180-189.
147. Weil, M., et al., *Ecological assessment of nano-enabled supercapacitors for automotive applications.* IOP Conference Series: Materials Science and Engineering, 2012. **40**(1): p. 012013.
148. Zimmermann, B.M., et al., *Prospective time-resolved LCA of fully electric supercap vehicles in Germany.* Integrated Environmental Assessment and Management, 2015. **11**(3): p. 425-434.
149. Lekakou, C., et al., *AUTOSUPERCAP: Development of High Energy and High Power Density Supercapacitor Cells*, in *Electric Vehicle Batteries: Moving from Research towards Innovation*, E. Briec and B. Müller, Editors. 2015, Springer International Publishing. p. 33-43.
150. Shanklin, T., et al., *Selection of bioprocess simulation software for industrial applications.* Biotechnology and Bioengineering, 2001. **72**(4): p. 483-489.
151. Mabrouki, J., et al., *Simulation of biofuel production via fast pyrolysis of palm oil residues.* Fuel, 2015. **159**: p. 819-827.

152. Brunet, R., et al., *Reducing the cost, environmental impact and energy consumption of biofuel processes through heat integration.* Chemical Engineering Research and Design, 2015. **93**: p. 203-212.
153. Gnansounou, E., P. Vaskan, and E.R. Pachón, *Comparative techno-economic assessment and LCA of selected integrated sugarcane-based biorefineries.* Bioresource Technology, 2015. **196**: p. 364-375.
154. Galera, S. and F.J. Gutiérrez Ortiz, *Life cycle assessment of hydrogen and power production by supercritical water reforming of glycerol.* Energy Conversion and Management, 2015. **96**: p. 637-645.
155. Quintero, J.A., et al., *Fuel ethanol production from sugarcane and corn: Comparative analysis for a Colombian case.* Energy, 2008. **33**(3): p. 385-399.
156. Zhang, Y., et al., *Biodiesel production from waste cooking oil: 1. Process design and technological assessment.* Bioresource Technology, 2003. **89**(1): p. 1-16.
157. Roes, A.L. and M.K. Patel, *Ex-ante environmental assessments of novel technologies – Improved caprolactam catalysis and hydrogen storage.* Journal of Cleaner Production, 2011. **19**(14): p. 1659-1667.
158. Kushnir, D. and B.A. Sandén, *Energy Requirements of Carbon Nanoparticle Production.* Journal of Industrial Ecology, 2008. **12**(3): p. 360-375.
159. Tecchio, P., et al., *Ex-ante Life Cycle Assessment approach developed for a case study on bio-based polybutylene succinate.* Journal of Cleaner Production, 2015.
160. Gavankar, S., S. Suh, and A.A. Keller, *The Role of Scale and Technology Maturity in Life Cycle Assessment of Emerging Technologies: A Case Study on Carbon Nanotubes.* Journal of Industrial Ecology, 2015. **19**(1): p. 51-60.
161. Arvidsson, R., D. Nguyen, and M. Svanström, *Life Cycle Assessment of Cellulose Nanofibrils Production by Mechanical Treatment and Two Different Pretreatment Processes.* Environmental Science & Technology, 2015. **49**(11): p. 6881-6890.
162. Walser, T., et al., *Prospective Environmental Life Cycle Assessment of Nanosilver T-Shirts.* Environmental Science & Technology, 2011. **45**(10): p. 4570-4578.
163. Zhang, Y., et al., *Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis.* Bioresource Technology, 2003. **90**(3): p. 229-240.

CHAPTER 3: Life cycle analysis of graphene synthesis routes

This chapter will investigate a set of graphene synthesis processes, including electrochemical exfoliations of graphite, chemical oxidations of graphite, chemical reduction and thermal reduction of graphite oxide and chemical vapour deposition. Experimental synthesis of graphene via these production routes was performed at the collaborating laboratories.

This initial comparison of processes at laboratory stage is needed to shortlist them and select the most promising in terms of material properties and environmental impacts for further analysis. The material's specific capacitance, measured in Farads per gram (F/g), is used to compare graphene produced by the different routes. For use as electrode material in supercapacitors, specific capacitance should ideally be as high as possible to reduce the weight and size of the final device.

All mass and energy inputs and outputs together with emissions and wastes of each process were measured on site. Those measured values constitute the LCI (Life Cycle Inventory) that is used to calculate the LCIA (Life Cycle Impact Assessment) that provides the impacts associated with the quantities in use.

An "improved lab" scenario is then generated simulating maximised throughput of laboratory-scale processes in order to evaluate the potential of each process of being less impacting when scaled up and therefore to evaluate which process could benefit more from operation at larger capacity in terms of energy and material efficiency.

The LCIA results are then considered alongside measurements of material specific capacitance to select the most promising production routes in terms of environmental impacts and specific capacitance. These processes are investigated further in Chapter 4, which simulates commercial-scale graphene production to better understand environmental impacts of hypothetical graphene production routes.

3.1 Methodology

This section gives an overview of the most important key aspects of the goal and scope of the LCA presented in this chapter and formalises all steps taken to obtain the results presented.

3.1.1 Purpose of this LCA

This preliminary LCA considers and compares some graphene synthesis processes in order to evaluate the least impacting.

The processes analysed consist of:

- six electrochemical exfoliations that differ in batch size, voltage and electrolyte
- five chemical oxidations of graphite using different chemicals, reaction time and temperature,
- one chemical reduction of graphite oxide
- one thermal reduction of graphite oxide
- two chemical vapour depositions of graphene

The intended application of this LCA is then to perform a cradle-to-gate comparative assessment of several graphene synthesis routes in order to select the least impacting route, whilst producing materials showing high values for specific capacitance.

3.1.2 Functional unit, system delimitation, boundaries, impact categories and data quality

The functional unit of the LCA is the production of 1g of graphene. This study is an attributional LCA (rather than consequential LCA) as it only depicts the current situation without predicting any possible future scenario stemming from possible consequences of the adoption of graphene in our society (e.g. possible change in demand of several different products).

The boundaries of this attributional system are set to achieve a cradle to gate LCA and therefore exclude use-phase and end-of-life activities at this stage.

Production processes are analysed using primary data measured directly in the laboratories. Procedures for measurements were put in place in the external labs after the first measurements to guide the collaborators during several rounds of data gathering and refining. They take into consideration inputs, outputs, emissions and wastes, however, emissions and wastes are often calculated or assumed as they were impossible to measure due to lack of proper equipment on site (e.g. mass spectrometer for gaseous emissions).

Upstream activities (e.g., electricity generation) are modelled based on the average European average data (GaBi database) rather than country specific. This approach ensures that processes are assessed in a consistent fashion and that results will not be influenced by the location of specific research activities.

This study covers the standard LCA impact categories suggested in the ILCD methodology (2011 EU standard LCA guidelines) [1]. Those categories fall into three main areas of protection: human health, natural environment and natural resources. Life cycle impact assessment methodologies do not yet include impacts related to emissions of nanoparticles on the environment and their potential environmental or health impacts (see Chapter 2 Section 2.4). Global warming potential is shown more in detail throughout the thesis as it is considered the most important among all impact categories [2].

On this point it is important to highlight that according to measurements performed by IOM (Institute of Occupational Medicine) no airborne particles were detected in all laboratories while synthesising and handling graphene [3].

3.1.3 The improved lab scenario

The "improved lab" scenario is introduced to investigate the maximum potential outputs of the laboratory graphene production processes. This is necessary because the equipment used in the labs consume far more energy than the one needed to produce the small quantities of graphene that were typically synthesised. Maximising the production it is necessary to calculate more precisely the energy consumption per gram of material produced. The maximum graphene production is defined as maximum output achieved with laboratory equipment without significantly varying the energy consumption.

3.2 Electrochemical exfoliation performed at Fraunhofer IPA

The electrochemical exfoliations (see literature review paragraph 2.3.3.1 for the process in detail) performed at Fraunhofer IPA were firstly operated in a small cell using sodium acetate (CH_3COONa) and potassium hydroxide (KOH) as electrolytes. Current flowed through two electrodes made of extruded graphite at a constant voltage (15 V and 9 V). The second set of experiments used a bigger batch in order to increase production. Sodium hydroxide (NaOH) was selected as the electrolyte and the voltage set at 7 V. In this second batch it was possible to reuse the electrodes, as they were bigger than those used for the small configuration. A general diagram of how the experiment set up is shown in Figure 3.1.

A sodium hydroxide batch was never tested at 15 V because the materials synthesised through the electrochemical route showed a low specific capacitance. It must be said, though, that this type of electrochemical exfoliation process, that uses graphite at the anode as precursor, produces graphene oxide and not graphene, therefore a subsequent reduction of the material produced could have been beneficial to enhance its specific capacitance, but it was not tested and it remains a material for further studies.

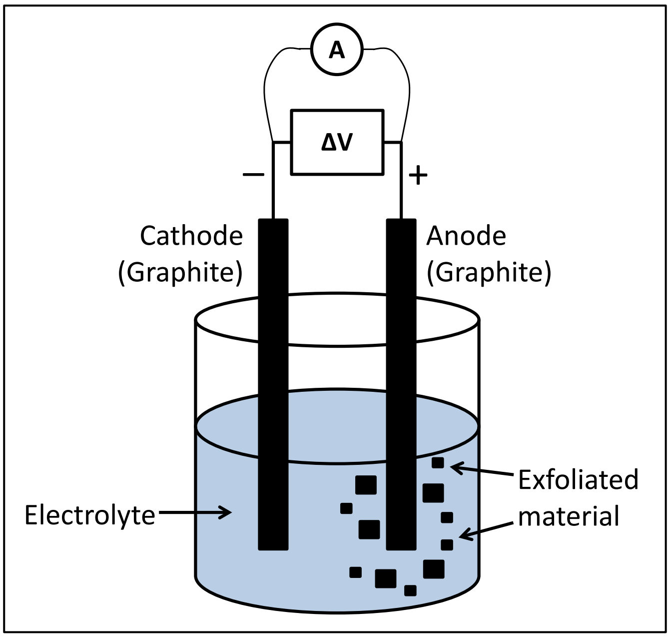


Figure 3.1 – Electrochemical exfoliation set up

The differences in the electrolyte, the voltages applied and the configurations were chosen to understand what impact those variations would have had on the final material in terms of production rate and were chosen among several published configurations [4].

Potassium hydroxide was chosen as it is a good and accessible electrolyte, although it was thought that the potassium ion (K^+) would have recombined again to KOH, once the electrolysis was halted, detaching the hydroxide groups $(OH)^-$ from the graphene planes and therefore reversing the intercalation process. Sodium hydroxide was also chosen because of its low cost and availability but mostly to avoid the problem of graphene planes restacking together back to graphite as it seemed to limit this phenomenon.

The sodium acetate, instead, was selected because it was thought that the acetate ion (CH_3COO^-) would have helped the expansion of the carbon layers intercalating in the electrode [4].

Summarising, the six exfoliations analysed were:

- 9 V and 15 V using potassium hydroxide (KOH)
- 9 V and 15 V using sodium acetate (CH_3COONa)
- 7 V using sodium hydroxide (NaOH) with new and used electrodes (parallel connection with 3 anodes and 4 cathodes)

The first two exfoliation types had the following configuration:

- Two synthetic graphite electrodes (100x10x4.5 mm extruded)
- A beaker containing 200 ml of electrolyte (0.1 mol)
- DC power supply (9 and 15 V)

The third exfoliation type instead used:

- Seven graphite electrodes (100x100x10 mm)
- A beaker containing 1000 ml of electrolyte (0.1 mol)
- DC power with electrodes attached in parallel (7 V)

After exfoliation the solution was filtered at one bar pressure in order to collect the exfoliated particles. In the filtrate, single-layer graphene and multi-layer graphene and some graphite flakes coexist as not all individual graphite planes can be detached [4].

Sonication was the third step where graphene and graphite layers are further detached and dispersed in water. This process generates more graphene by turning the remaining graphite flakes into graphene. This material can still be called graphene as in the scientific community a stack of few layers of carbon is still called graphene even if it is not a single layer of carbon atoms and is addressed indifferently as multi-layer graphene or few-layer graphene [5].

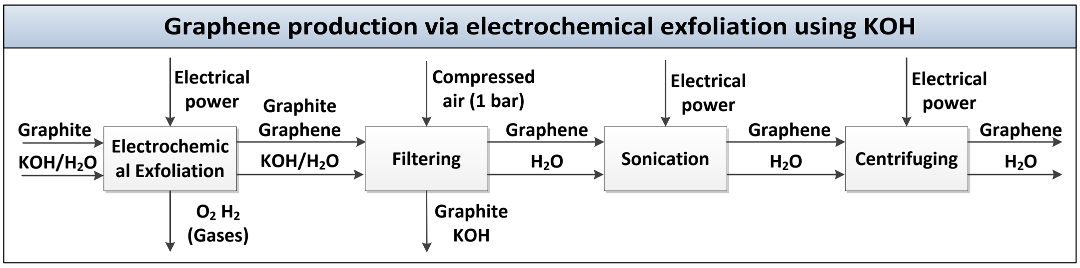


Figure 3.2 – Graphene synthesis with KOH

The last step, centrifuging, was optional and it was used to separate the larger graphene particles from the smaller ones in order to generate a dispersion of graphene of the desired size. The whole process is schematised in Figure 3.2.

3.2.1 Process inventory

Table 3.1 show a summary of what is needed to produce a gram of graphene, including filtering and sonication, for all six electrochemical exfoliations. Electrical measurements were taken at the electrodes in order to avoid including the power supply loss and they are increased by 10% allowing for a typical converter efficiency operating at a predetermined voltage and current.

In the modelling it was possible to use the current measured at the electrodes because the values were quite stable after a short ramp up period. The chart in Figure 3.3 depicts the current measured over a 10 hour period for one of the batches and shows that after one hour, the current remains stable at a level that is ranging from 0.60 to 0.66 A. The visible drop in the current is due to a break in the experiment to refill the beaker with water to compensate for evaporation and adjust the electrodes position. Therefore, once the current stabilises, before the solution saturates, it is possible to use average energy values in the LCA modelling.

Production of 1 g of Graphene	**KOH 15 V**	**KOH 9 V**	**CH_3COO Na 15 V**	**CH_3COO Na 9 V**	**NaOH 7 V new**	**NaOH 7 V used**	
Electricity	1.85	3.88	2.49	3.14	8.30	2.88	MJ
Current density*	0.067	0.047	0.034	0.019	0.014	0.011	A/cm^2
Graphite	3.91	3.01	3.50	3.58	2.29	4.54	g
Potassium hydroxide	1.12	1.12	-	-	-	-	g
Sodium acetate	-	-	1.64	1.64	-	-	g
Sodium hydroxide	-		-	-	1.87	1.87	g
Water (deionised)	0.67	0.5	0.49	0.63	1	1.26	kg

*considering the anodes

Table 3.1 – Electrochemical exfoliations: inventory of inputs for producing 1 g of graphene

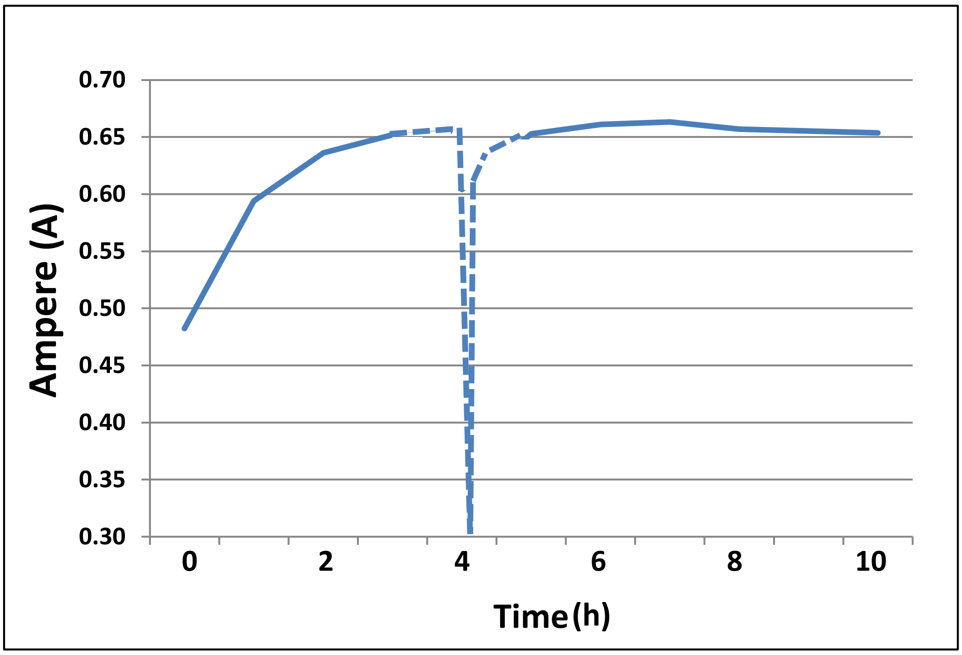


Figure 3.3 – Example of current over time in an electrochemical exfoliation (includes a technical stop)

Figure 3.3 also shows a slow decrease of the current over time after 7 hours of operation and this is thought to be due to a slow but constant decrease of the electrolyte performance caused by the carbon particles slowly saturating the solution [4].

As the small batches were producing much less than a gram over the 10 hours operation, therefore, all their material consumptions are scaled up linearly in order to achieve the desired functional unit as shown in Table 3.1. The only material not scaled up is the electrolyte that is considered the same for all the additional hours of operation needed and then disposed of.

Water, instead, is constantly added in order to keep the surface of the electrodes submerged while it evaporates and dissociates into O_2 and H_2 at the electrodes. The numbers shown in Table 3.1 includes also the initial water as it is completely disposed of as electrolyte at the end of the process. The water consumption is dependent upon the type of salt dissolved in it and the time needed to achieve the desired production quantities. For example the potassium hydroxide (KOH) at 15 V is a fast process in which a lot of water dissociates into oxygen and hydrogen. While, when using sodium acetate at (CH_3COONa) 9 V, the material synthesis is slower and therefore also the water dissociation happens at a slower rate. Nevertheless, it requires much longer time to produce 1 g of graphene, hence the overall energy and materials utilisation increases.

The same table shows electricity consumption that includes the filtering at increased pressure, the sonication and the centrifuging, but those activities account for less than 1% of the total energy consumed. Considering these aggregated values, it is possible to say that, when comparing the processes running at the same voltage, the batches using potassium hydroxide as electrolyte consumes less energy than those using sodium acetate; moreover, that a lower voltage implies higher consumptions per gram of material.

The only exception is the sodium hydroxide batch using used electrodes. This is a particular case where, according to the judgement of Fraunhofer personnel, the electrodes might be already cracked by the previous utilisation and therefore the exfoliation happens quicker than when using new electrodes. In other words, this process produces more material per unit time [6] and this seems to imply that the production rate changes over time while the electrode deteriorates.

On the other hand, this process requires more graphite as the ratio between mass collected from the filter and mass lost from the electrodes is less than half, in percentage, of what can be collected from new electrodes and this also means that more carbon is lost in the solution. It is therefore possible to say that this batch performs better in terms of energy consumption as it takes less time to exfoliate a gram of material, but it is less efficient in terms of material conversion as it uses more graphite.

To draw definite conclusions there is a need for further investigation, but no other experiments were performed with used electrodes and therefore this case is treated as unique but still compared to the others.

Always referring to Table 3.1, the current density values show that, grouping the batches per electrolyte, higher voltages correspond to higher current densities and therefore higher production rates (i.e. less consumption per gram of graphene produced). This is different in the case of the used electrodes that show low current density and high exfoliation rates, but this is most likely due to the previously cracked electrodes that increase the exfoliation rate and also modify the real surface area in contact with the electrolyte.

3.2.2 Impact assessment

Figure 3.4 shows the global warming potential of the six exfoliation procedures under examination. It shows that the highest impacts are generated by the exfoliation at 7 V followed by the exfoliation at 9 V while the smallest impacts are related to the exfoliations at 15 V. The only exception is the exfoliation performed with used electrodes that classifies as the third best process, but this batch cannot be strictly compared to the others due to the different state of the electrodes.

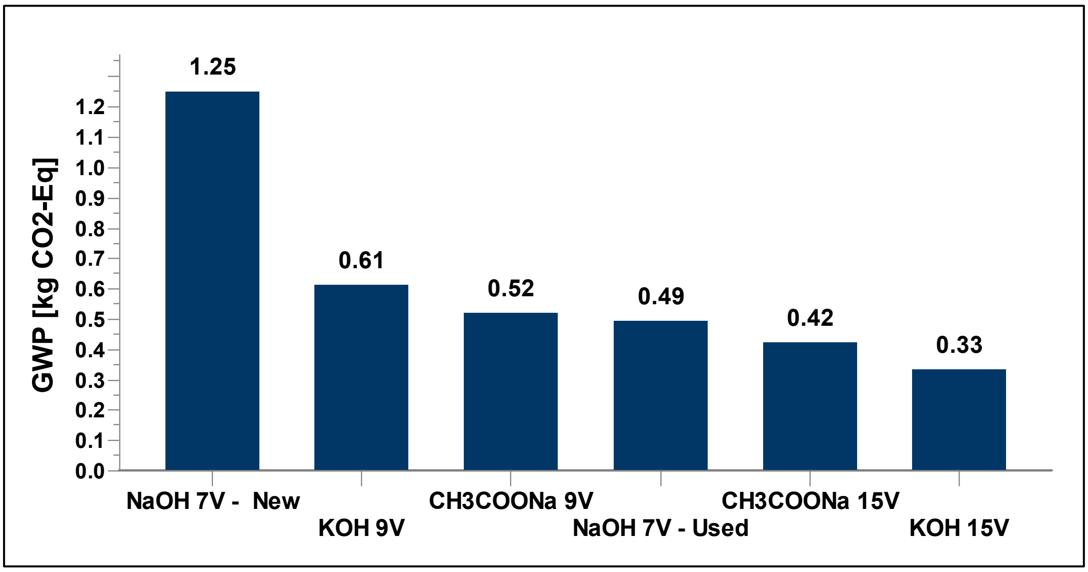
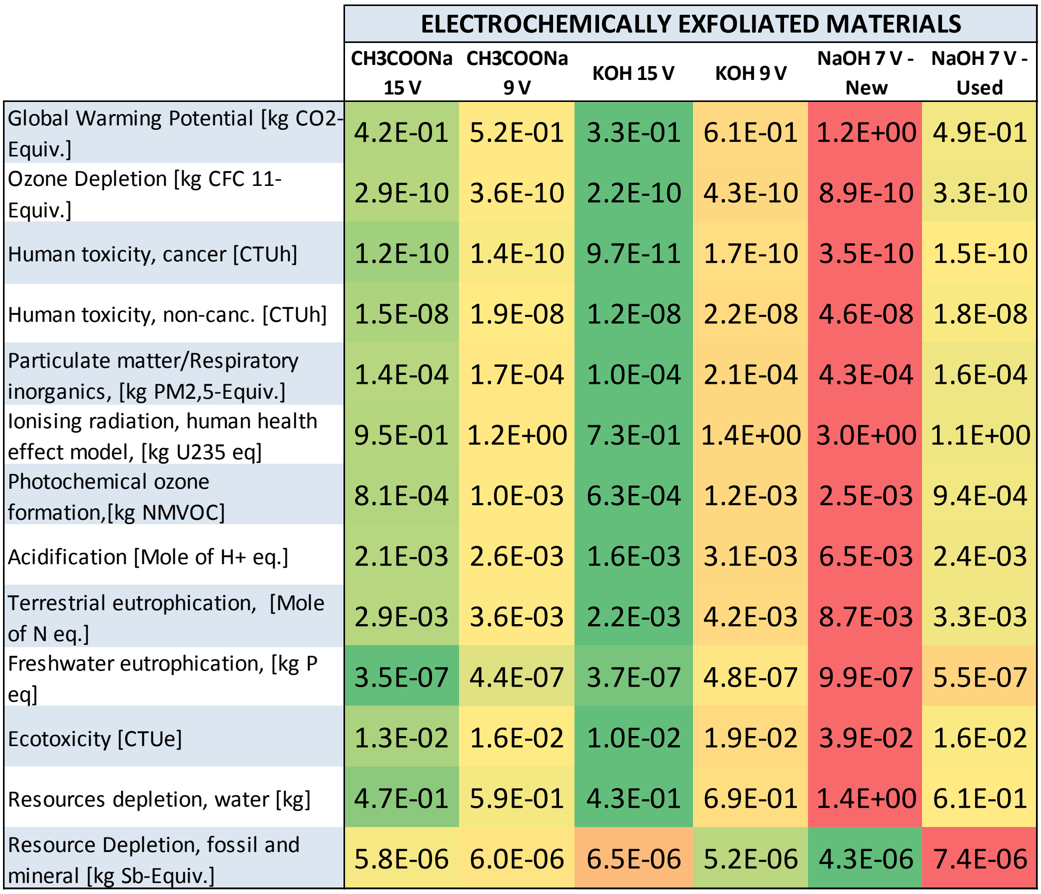


Figure 3.4 – Electrochemical exfoliation: global warming potential comparison. The processes are named after the electrolyte used and the voltage applied.

All other categories examined follow approximately the same pattern as shown in Table 3.2 where the KOH 15 V graphene is constantly the best material except for the water eutrophication and fossil and mineral resources depletion categories. In the latter, the best performing process is the one using NaOH at 7 V with new electrodes as this process is the best in terms of material conversion efficiency. Almost 50% of the graphite is turned into graphene, but it needs 50% more electricity compared to the twin process using used electrodes and this deteriorates its environmental performance in all other categories. For the same reasons the process using NaOH and old electrodes is the worst in the fossil and mineral resource depletion impact category as it consumes a lot of graphite.



	ELECTROCHEMICALLY EXFOLIATED MATERIALS					
	CH3COONa 15 V	CH3COONa 9 V	KOH 15 V	KOH 9 V	NaOH 7 V - New	NaOH 7 V - Used
Global Warming Potential [kg CO2-Equiv.]	4.2E-01	5.2E-01	3.3E-01	6.1E-01	1.2E+00	4.9E-01
Ozone Depletion [kg CFC 11-Equiv.]	2.9E-10	3.6E-10	2.2E-10	4.3E-10	8.9E-10	3.3E-10
Human toxicity, cancer [CTUh]	1.2E-10	1.4E-10	9.7E-11	1.7E-10	3.5E-10	1.5E-10
Human toxicity, non-canc. [CTUh]	1.5E-08	1.9E-08	1.2E-08	2.2E-08	4.6E-08	1.8E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.4E-04	1.7E-04	1.0E-04	2.1E-04	4.3E-04	1.6E-04
Ionising radiation, human health effect model, [kg U235 eq]	9.5E-01	1.2E+00	7.3E-01	1.4E+00	3.0E+00	1.1E+00
Photochemical ozone formation,[kg NMVOC]	8.1E-04	1.0E-03	6.3E-04	1.2E-03	2.5E-03	9.4E-04
Acidification [Mole of H+ eq.]	2.1E-03	2.6E-03	1.6E-03	3.1E-03	6.5E-03	2.4E-03
Terrestrial eutrophication, [Mole of N eq.]	2.9E-03	3.6E-03	2.2E-03	4.2E-03	8.7E-03	3.3E-03
Freshwater eutrophication, [kg P eq]	3.5E-07	4.4E-07	3.7E-07	4.8E-07	9.9E-07	5.5E-07
Ecotoxicity [CTUe]	1.3E-02	1.6E-02	1.0E-02	1.9E-02	3.9E-02	1.6E-02
Resources depletion, water [kg]	4.7E-01	5.9E-01	4.3E-01	6.9E-01	1.4E+00	6.1E-01
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	5.8E-06	6.0E-06	6.5E-06	5.2E-06	4.3E-06	7.4E-06

Table 3.2 – Electrochemical exfoliation: materials comparison for all impact categories. KOH 15 V is the least impacting material in 12 out of the 13 impact categories. Colours show the relative contribution per row from red (higher impact) to green (lower impact)

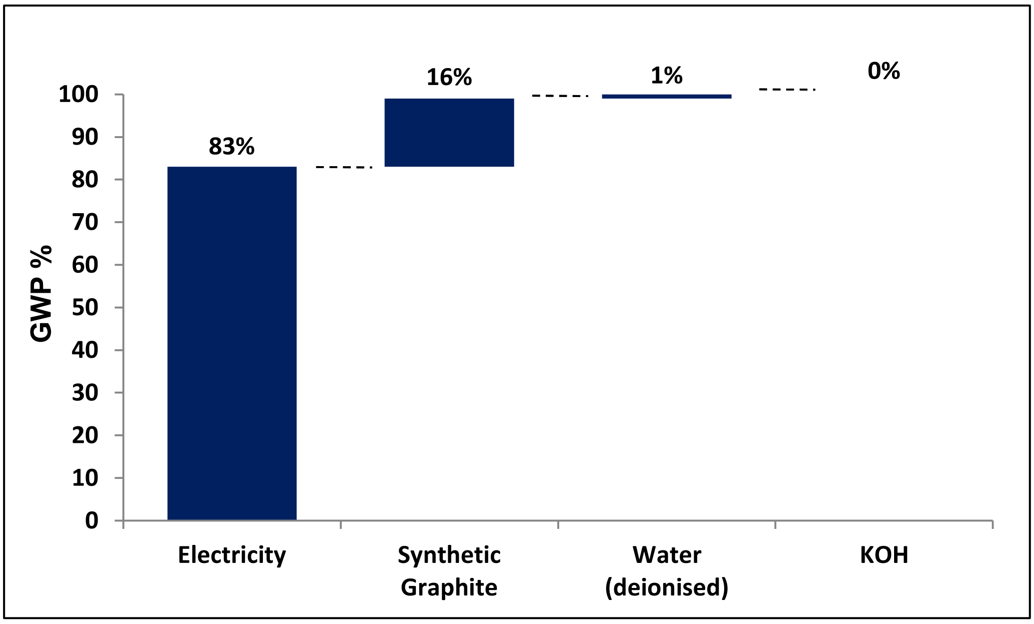


Figure 3.5 – Electrochemical exfoliation: KOH 15 V GWP impact breakdown in percentage of all material and energy inputs. Electricity consumption is the major concern.

It is understood that the resource depletion impact is driven by the production of synthetic graphite due to the use of fossil fuel energy in its manufacture as it requires a lot of heat [7]. However, it is not possible to be more precise as the industrial datasets provided by Thinkstep (GaBi software and database provider) come under non-disclosure agreement and this means that all data are aggregated in one unique process from raw material extraction to synthetic graphene production and that the detailed process breakdown is not shared.

In the fresh water eutrophication category the potassium hydroxide (KOH) 15 V performs slightly worse than the sodium acetate (CH_3COONa) 15 V process. KOH uses less electricity but it consumes more deionised water and this is what makes it more impacting in this category. However, due to data aggregation it is not possible to understand why the deionised water drives water eutrophication. When considering the overall water depletion, instead, the KOH 15 V is still the least impacting process showing that the larger part of water consumption is consumed during the electricity generation (hydropower accounts for 16% of the total electricity generated in EU [8]) and that the water consumed (Table 3.1) in the graphene synthesis is in comparison fairly small.

Investigating further the potassium hydroxide 15 V process it is possible to confirm that the electricity is the main driver of environmental impact in every category except for the fossil and mineral resource depletion driven by the use of graphite. From Figure 3.5 it is possible to appreciate how the electricity contributes for almost 85% to the overall global warming potential of the KOH 15 V material despite it being the one using the least amount of electricity.

The electrolyte is considered to be disposed of, but it can be potentially reused filtering out the graphene. This possibility was not investigated as the environmental burden of the electrolyte is very limited. (This is true even if including the neutralisation of NaOH or KOH with acids such as hydrochloric acid, nitric acid or sulphuric acid – see Appendix A paragraph A.1).

Even if it is possible to conclude that the potassium hydroxide (KOH) 15 V process is the best in terms of environmental performances, further investigation is recommended especially running the sodium hydroxide (NaOH) batch at 15 V to verify if a voltage increase would improve its environmental performances like in the other processes. Running a potassium hydroxide batch at 15 V in the larger set up is also recommended for evaluating the implication of using larger batches.

3.3 Chemical and thermal processes

The chemical processes performed at Danubia Nanotech can be summarised in five chemical oxidations of graphite powder and two types of subsequent reductions of graphite oxide, one chemical and one thermal (see Chapter 2 paragraph 2.3.3.2 for the process in detail). The graphene obtained using these methods can also be called reduced graphite oxide.

The five oxidations are achieved using the following methods:

- Modified Hummers (Fugetsu) – GO1
- Modified Hummers (Bangal) – GO2
- Modified Hummers (Jeong) – GO3
- Staundenmaier – GO4
- Brodie – GO5

Those five GOs are then reduced to obtain graphene in two ways:

- Chemically using Hydrazine – rGOxC
- Thermally in a flow of argon – rGOxT

During the oxidation process, several oxygen ions or groups intercalate inside the graphitic structure expanding it. The material obtained is oxidised graphite that weighs more than the original graphene due to the additional groups attached. During the subsequent reduction process, those groups are removed and what remains is a porous structure with randomly organised graphene nanoplatelets called reduced graphene oxide (rGO).

Figure 3.6 and Figure 3.7 show a summary of the processes. Between the oxidation and chemical reduction the GO is dispersed via sonication (Figure 3.6) while the sample entering the thermal reduction must be first dried (Figure 3.7).

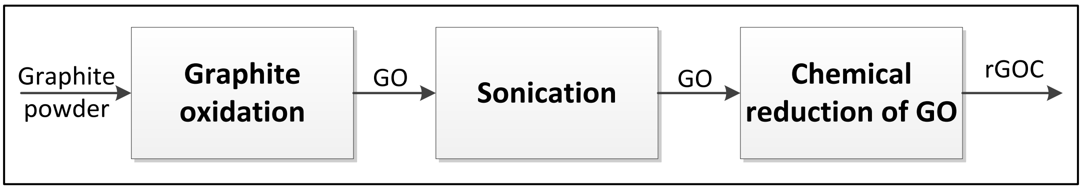


Figure 3.6 – Reduced graphite oxide with chemical reduction: graphite is first oxidised according to one of the 5 listed procedures, sonicated and finally reduced chemically

Figure 3.7 – Reduced graphite oxide with thermal reduction: graphite is first oxidised according to one of the 5 listed procedures, dried and finally thermally reduced

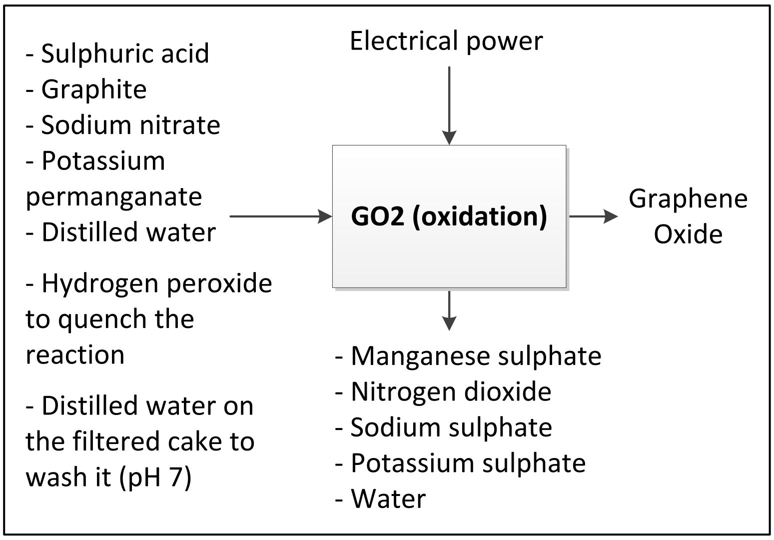


Figure 3.8 – Chemical Oxidation of graphite: Bangal method to produce the graphene oxide defined as GO2. All Inputs/outputs are listed.

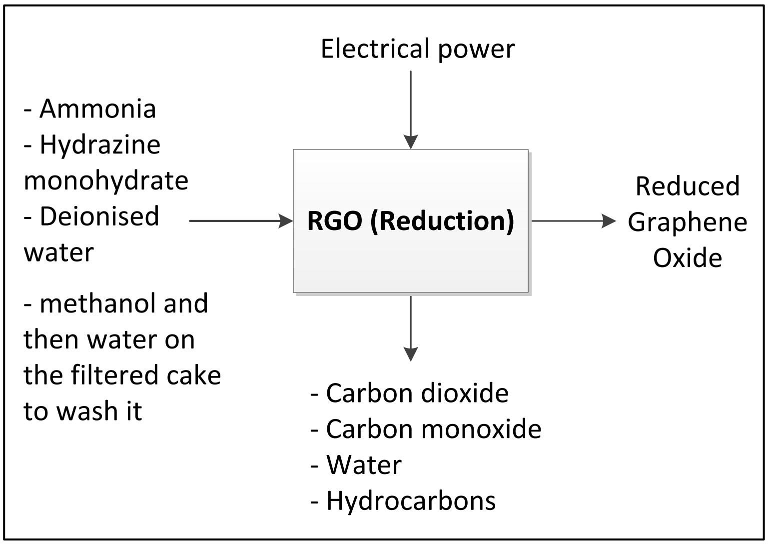


Figure 3.9 – Chemical reduction of graphite oxide: GOx is reduced using ammonia and hydrazine to obtain graphene (rGOC). All inputs/outputs are listed

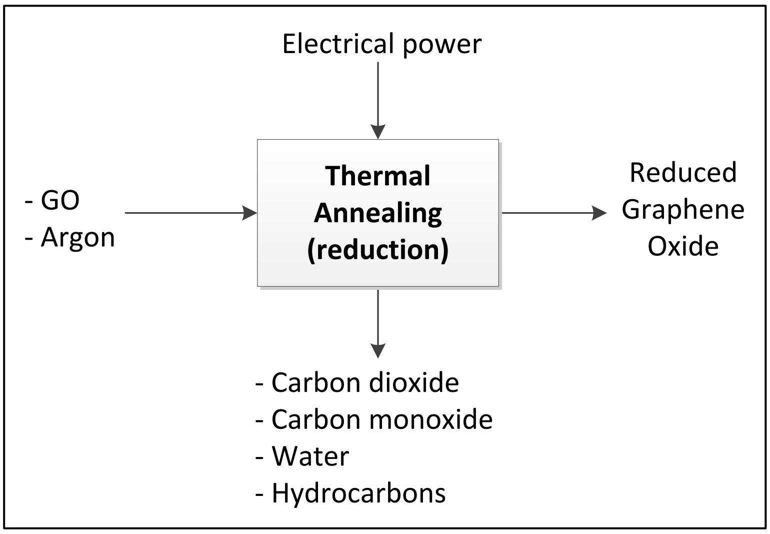


Figure 3.10 – Thermal reduction of graphite oxide: GOx is reduced using high temperature and argon to obtain graphene (rGOT). All inputs/outputs are listed

The procedures and methodologies for all the processes listed are available in detail in the literature review and only the GO2 (page 48) is reported here as example (Figure 3.8). The GO2 is obtained using 2 g of graphite powder and 1 g of sodium nitrate ($NaNO_3$) in 46 ml of sulphuric acid (H_2SO_4) stirred in ice bath. 6 g of potassium permanganate ($KMnO_4$) are added slowly in order to avoid excessive vigorous reactions and temperature increase higher than 20 °C. After 5 min the ice bath is removed and temperature increased to 35°C and stirred for 30 min. Next, 92 ml of distilled water are added slowly and the mixture is stirred for another 15 min. Then 80 ml of hot water at 60 °C and a hydrogen peroxide (H_2O_2) 3% aqueous solution are added to reduce the residual potassium permanganate until bubbling disappears [9]. The mixture is then filtered and washed until pH 7 is reached and dried at low temperature, around 50 °C, to avoid any thermal reduction.

The chemical reduction (Figure 3.9), instead, consists of mixing the GOx (1 g) – that can be GO1 to GO5 – with ammonia (1.5 ml) and 150 ml of deionised water. The mixture is stirred for 24 h at 85 °C. After cooling the content of the beaker is filtered and washed with 500 ml of deionised water and 50 ml of ethanol (or methanol) [10].

The thermal reduction (Figure 3.10) instead uses a vacuum furnace where the GOx is placed. In the procedure measured at Danubia, the sample is heated to 700 °C during almost 20 h with a precise heating rate: up to 140 °C the heating rate is 1.5 °C per minute and then the sample is kept at 140 °C for 30 min. The second ramp up is performed with a reduced heating rate of 0.3 °C per minute up to 350 °C and then the sample is kept at this temperature for 30 min. In the last stage, from 350 °C to 700 °C, the heating rate is again set at 1.5 °C per minute and the sample is kept at 700 °C for 2 h before turning off the furnace and let the sample cool down.

3.3.1 Process inventory and modelling

The processes measured are divided into two sections, the production of 1 g of graphite oxide and the production of 1 g of graphene (rGO). The reduction processes include sonication, for the chemical reduction, and drying in case of the thermal one. Electrical measurements were taken at the power socket as the conversion of electrical energy to thermal energy happens without other inefficiencies. All volumes and masses measurements were taken using laboratory scales and beakers that provided accurate data measurements.

The inventory for the first section, the graphite oxidation, is presented in Table 3.3. All the differences in electricity consumption presented are dependent on time and temperature of operation. For example, the GO4 material (Staudenmaier) is prepared at ambient temperature, but it takes several days, while the GO2

(Hummers – Bangal) needs a very limited heat input (requires 35 °C) but it is a very fast oxidation process that lasts about two hours. It must be noted that when the measurements were taken the room temperature was around 35 °C and therefore the heat input was even more limited especially after the short ramp up phase.

Graphite Oxide (1 g)	**GO1**	**GO2**	**GO3**	**GO4**	**GO5**	
Electricity	0.14	0.04	0.17	0.44	0.12	MJ
Graphite	0.71	0.71	0.77	0.73	0.80	g
Nitric acid (98%)	-	-	-	9.9	24.4	g
Sulphuric acid aq. (96%)	32.8	30.2	248	23.4	-	g
Water (deionised)	232	223	423	455	270	g
Potassium chlorate	-	-	-	8	-	g
Hydrogen peroxide (100%)	2.6	1.24	6.69	-	-	g
Sodium nitrate	0.36	0.36	0.39	-	-	g
Potassium permanganate	2.14	2.14	3.08	-	-	g
Hydrochloric acid	-	-	2.28	2.16	-	g
Sodium chlorate	-	-	-	-	6.80	g
Calcium hydroxide*	24.7	22.8	187	23.5	14.3	
* used for neutralising 100% of the acid(s) used						

Table 3.3 – Graphite oxidation: inventory of inputs for the production of 1 g of graphite oxide

To neutralise the acids used, calcium hydroxide has been selected as the least impacting neutralising agent among sodium hydroxide, soda and potassium hydroxide (see Appendix A paragraph A.2). The quantity presented in Table 3.5 is calculated based on the neutralisation of the totality of the acid(s) used. As there is no information on the quantity of acid consumed during the reaction a worst case scenario is proposed in which the 100% of acid is neutralised.

Reduced Graphite Oxide (1 g)	**rGO2C**	**rGO2T**	
Ammonia	0.34	-	g
Electricity	1.51	5.51	MJ
Graphite Oxide	1.25	1.67	g
Water (deionised)	163	-	g
Hydrazine	1.38	-	g
Methanol	10	-	g
Argon	-	14	g

Table 3.4 – Graphite oxide reduction: inventory of inputs for the chemical and thermal reduction of 1 g of GO2.

The second section, the reduction process, removes oxygen from the material, decreasing the initial mass of the GO. Therefore there is a need for more than a gram of GOx to obtain a gram of rGOx. Furthermore, as it is possible to understand from Table 3.4, the quantity of graphite oxide (GOx) needed in the thermal reduction is slightly bigger than that used in the chemical one. Therefore, the chemical reduction has a higher material conversion rate.

The chemical reduction process consumes less electricity than thermal reduction. However, 40% of the electricity used in the thermal reduction is for the drying process. In fact, the GOx must be dry when starting the thermal annealing and the water evaporation process runs for at least 24 h at 55 °C. When excluding the dying process, the thermal reduction consumes only 60% more than the chemical reduction (not 3.5 times more as shown in Table 3.4) even if it operates at temperatures 8 times higher (700 °C for 20 – 22 h vs. 85 °C for 24 h). This is due to a better thermal insulation of the tube furnace used in comparison to the zero insulation of the hot plate utilised for the chemical reduction.

3.3.2 Impact assessment – base lab scenario

3.3.2.1 Chemical oxidation of graphite

The global warming potential for the five oxidation processes analysed is shown in Figure 3.11. As it is possible to notice, the best performing oxidation in terms of environmental impacts per gram is the GO2 material followed by the GO1. GO5 uses almost the same amount of electricity as GO1, as shown in Table 3.3, but the larger use of nitric acid deteriorates its environmental performance in this category (most likely linked to the energy used during its production, but data aggregation prevents further speculation). All other materials use more electricity and more acids, which contribute to their greater global warming potential.

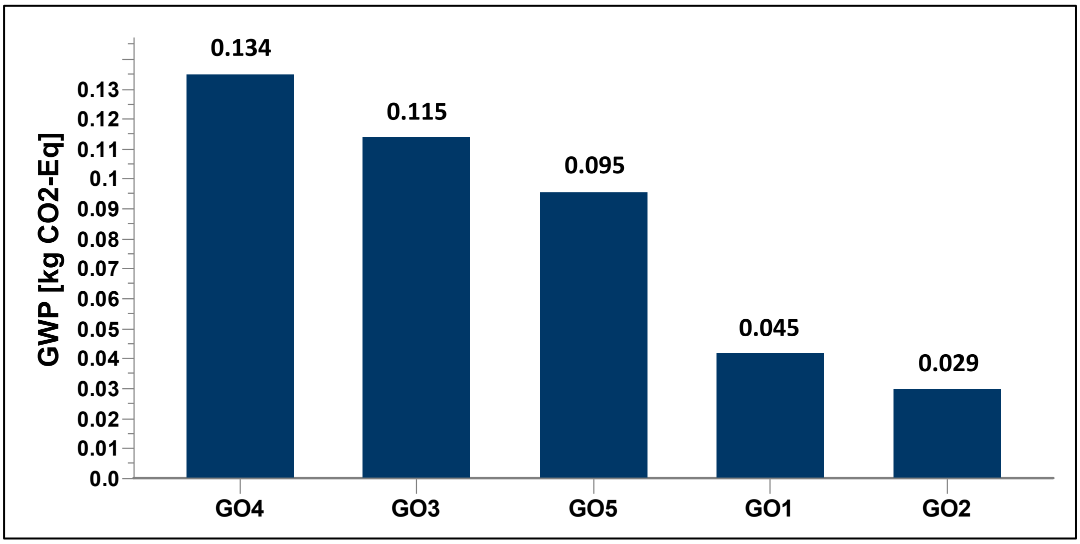


Figure 3.11 – Chemical oxidations: global warming potential comparison. GO2 (Hummers - Bangal) is the least impacting in the GWP impact category. Almost 35% less than GO1 and 80% than GO4

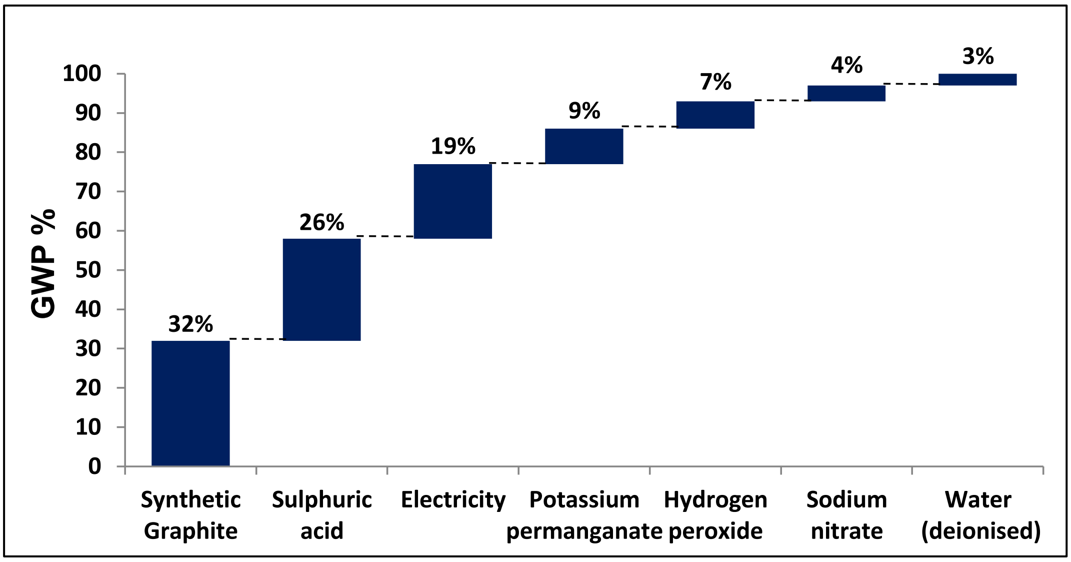


Figure 3.12 – Chemical oxidation: GO2 detailed breakdown in percentage of all material and energy inputs. The production of graphite, sulphuric acid and the use of electricity are the most impacting factors.

	GOx MATERIALS				
	GO1	GO2	GO3	GO4	GO5
Global Warming Potential [kg CO2-Equiv.]	4.5E-02	2.9E-02	1.1E-01	1.3E-01	9.5E-02
Ozone Depletion [kg CFC 11-Equiv.]	1.9E-11	1.0E-11	3.3E-11	1.4E-09	6.3E-10
Human toxicity, cancer [CTUh]	3.3E-11	2.2E-11	1.2E-10	2.8E-09	2.4E-09
Human toxicity, non-canc. [CTUh]	3.3E-09	2.1E-09	1.1E-08	1.4E-08	5.6E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	2.1E-05	1.6E-05	1.0E-04	5.8E-05	2.0E-05
Ionising radiation, human health effect model, [kg U235 eq]	6.5E-02	3.4E-02	1.2E-01	1.7E-01	6.3E-02
Photochemical ozone formation,[kg NMVOC]	1.0E-04	7.4E-05	3.8E-04	2.8E-04	1.3E-04
Acidification [Mole of H+ eq.]	4.0E-04	3.1E-04	2.1E-03	8.6E-04	2.7E-04
Terrestrial eutrophication, [Mole of N eq.]	3.0E-04	2.0E-04	8.0E-04	9.1E-04	4.9E-04
Freshwater eutrophication, [kg P eq]	1.0E-07	8.4E-08	3.2E-07	5.4E-06	2.6E-06
Ecotoxicity [CTUe]	4.3E-03	3.5E-03	2.4E-02	1.1E-01	5.7E-02
Resources depletion, water [kg]	5.5E-02	4.0E-02	1.0E-01	1.5E-01	8.0E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.2E-06	1.2E-06	1.3E-06	1.9E-06	1.4E-06

Table 3.5 – Chemical oxidation: summary of the analysed impact categories. GO2 is the least impacting material in 12 out of the 13 impact categories analysed.
Colours show the relative contribution per row from red (higher impact) to green (lower impact)

For the GO2 process (Figure 3.12) the use of synthetic graphite gives the main contribution to the global warming potential. The second largest contribution is given by the sulphuric acid as the reaction happens in excess of it to properly stir and disperse the graphite. Reducing its quantity might penalise the reaction quality making this a subject for further studies. If the chemical reaction cannot be improved (e.g.: yield, reaction conditions, reaction time, other), the impacts related with the GO2 production can be mitigated only by reducing the energy consumption (reduce heat losses) and by further optimising the production processes input materials especially synthetic graphite and sulphuric acid.

Taking into consideration all other categories (Table 3.5) it is possible to appreciate how the GO2 is overall the least impacting material. The GO1 and GO5 are respectively second and third while GO4 and GO3 are the most impacting. The only category where the GO2 is performing slightly worse than GO5 is the acidification potential (GO5 shows lower number and therefore a greener colour in the table) and it is due to its large use of sulphuric acid in comparison with the relatively less impacting nitric acid (opposite to what happens for the GWP). The electricity consumption is also a major contributor to this impact category.

3.3.2.2 Reduction of graphite oxide

Figure 3.13 shows the global warming potential for both reduction processes without including the GO production.

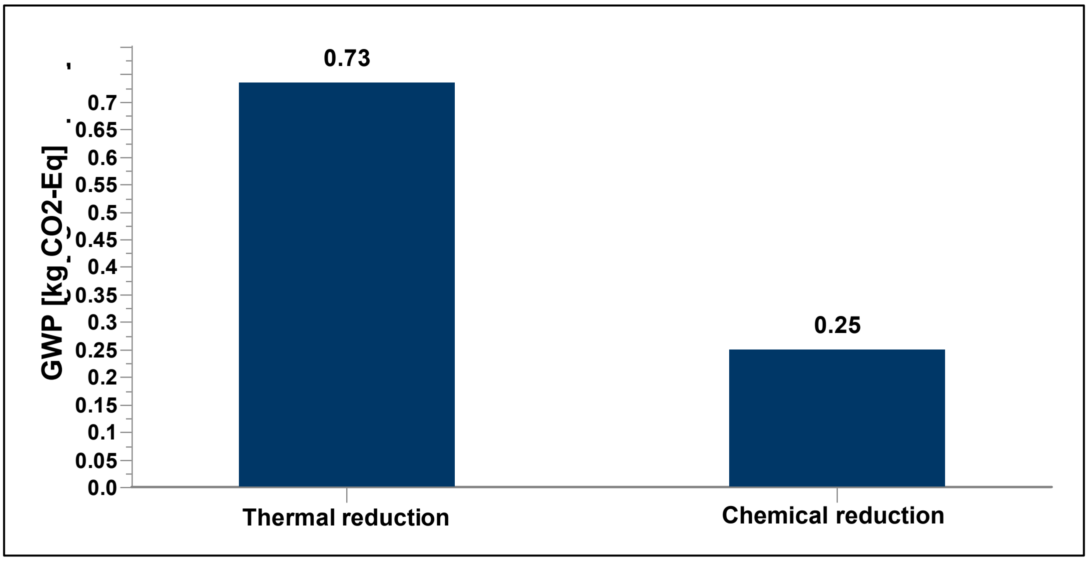


Figure 3.13 – Graphite oxide reductions: global warming potential. This chart does not include the impacts of the oxidation step but shows only the GWP of the reduction processes.

The reductions of graphite oxide consume most of the electricity used in the chemical/thermal routes for graphene synthesis because they run over several hours and at high temperature. The electricity consumption is thus the main driver for environmental impacts for all impact categories analysed and almost always in the same proportion as shown for global warming potential in Figure 3.13 (all categories for the reduction of GOx material in Appendix A paragraph A.3).

	GO2 REDUCED MATERIALS	
	rGO2C	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	0.29	0.78
Ozone Depletion [kg CFC 11-Equiv.]	1.6E-10	5.5E-10
Human toxicity, cancer [CTUh]	1.0E-10	2.4E-10
Human toxicity, non-canc. [CTUh]	1.1E-08	3.0E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	9.5E-05	2.8E-04
Ionising radiation, human health effect model, [kg U235 eq]	0.5	1.8
Photochemical ozone formation,[kg NMVOC]	5.6E-04	1.6E-03
Acidification [Mole of H+ eq.]	1.5E-03	4.4E-03
Terrestrial eutrophication, [Mole of N eq.]	1.9E-03	5.5E-03
Freshwater eutrophication, [kg P eq]	4.0E-07	6.2E-07
Ecotoxicity [CTUe]	1.4E-02	2.8E-02
Resources depletion, water [kg]	0.31	0.85
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.6E-06	2.3E-06

Table 3.6 – Comparison of chemically (rGO2C) and thermally (rGO2T) reduced GO2. This table includes also the oxidation of graphite. rGO2C is the least impacting (green) in all 13 categories.

When considering the impacts of graphite oxidation and subsequent reduction, the values of Table 3.5 can be summed to the values of the reductions presented in Appendix A as the two reduction processes are common for all GOs. Table 3.6, instead, shows the case of GO2 by comparing the chemical and thermal reductions performed to obtain rGO2C and rGO2T.

From Table 3.6 is clear that the chemical reduction is a less impacting process as it runs at lower temperature and it produces slightly more material (in weight) than the thermal reduction. Usually, during the thermal reduction there is a weight loss of about 35 – 40% [11] while in the chemical one it is just about 20 – 25% [12] and this means that the latter is a lower performing reduction process that does not remove as much oxygen from the graphite oxide as the thermal reduction does. In other words, the chemical reduction produces a graphene that contains more oxygen and consequentially it weighs more than the one obtained thermally. Therefore, to produce 1 gram of this reduced material there is a need for less graphite oxide.

For this reason, when including the GOx material in the impact analysis, the performances of the thermal reduction process deteriorate slightly more than those of the chemical one as it requires more graphite oxide (1.67 g Vs 1.25 g) to produce the same amount of rGOx.

3.3.3 Improved lab scenario

The improved lab scenario estimates the maximum output achievable in the laboratory using the same amount of energy and it is based assumptions provided by the laboratory personnel.

3.3.3.1 Chemical oxidation of graphene – improved lab scenario

In Danubia, with the equipment available it is possible to process 5 times the amount of GO1 GO2 GO4 and GO5 and 1.5 times the GO3 material as it uses much more sulphuric acid [11]. Therefore, to produce one gram of graphene, the inventory presented in Table 3.3 remains exactly the same (all inputs increase linearly), but the electricity consumption per gram decreases as shown in Table 3.7, because the MJ used are divided by a larger quantity of graphene. The input increase does not affect the energy consumption by an appreciable quantity because the heat supplied from the hot plate is mostly lost to the surrounding environment. The new results are compared with the old ones in Figure 3.14.

Material	Original MJ	Improved MJ	Reduction%
GO1	0.135	0.027	80%
GO2	0.043	0.009	79%
GO3	0.17	0.113	34%
GO4	0.44	0.088	80%
GO5	0.121	0.024	80%

Material	Original MJ	Improved MJ	Reduction%
GO1	0.135	0.027	80%
GO2	0.043	0.009	79%
GO3	0.17	0.113	34%
GO4	0.44	0.088	80%
GO5	0.121	0.024	80%

Table 3.7 – Chemical oxidation: improved electricity values. The original values are those reported in the inventory (Table 3.4) while the Improved MJ column shows data obtained maximising the laboratory production yield without increasing the heat input.

The quantity of material processed in this scenario is limited by the equipment in the laboratory but also by the quantity of energy available since increasing the volumes too much would increase excessively the heat capacity of the reacting batches and this would result in increased energy consumption.

In reality, without energy consumption constraint, the upscaling of the process in the laboratory is limited by the vigour of the reactions and therefore a maximum of 1 litre flask is used due to a lack of appropriate cooling.

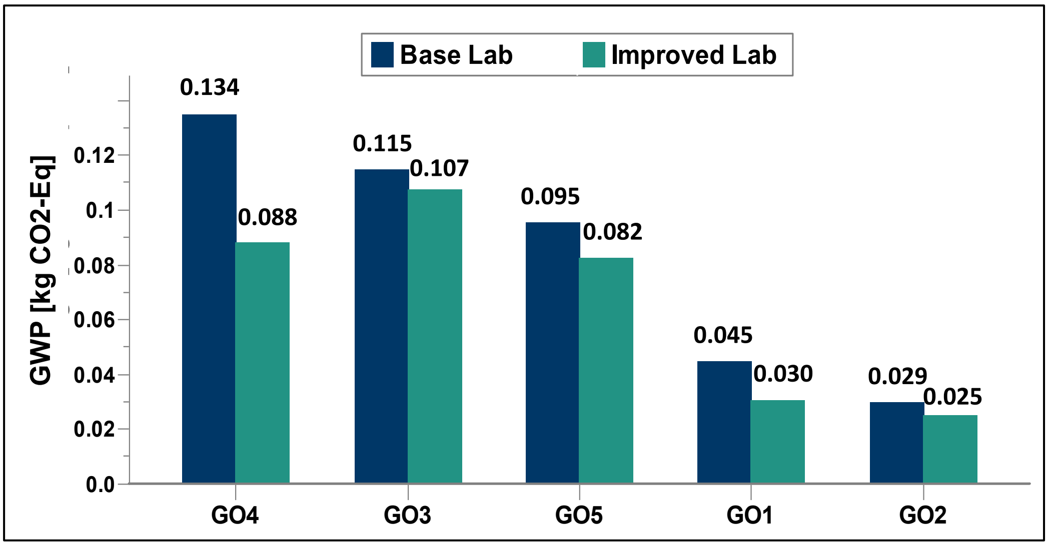


Figure 3.14 – Chemical oxidation: GWP of original scenario vs. maximised laboratory production scenario (Improved Lab)

	GOx MATERIALS - IMPROVED LAB SCENARIO				
	GO1	GO2	GO3	GO4	GO5
Global Warming Potential [kg CO2-Equiv.]	3.0E-02	2.5E-02	1.1E-01	8.8E-02	8.2E-02
Ozone Depletion [kg CFC 11-Equiv.]	8.7E-12	6.8E-12	2.8E-11	1.3E-09	6.2E-10
Human toxicity, cancer [CTUh]	2.9E-11	2.1E-11	1.2E-10	2.8E-09	2.4E-09
Human toxicity, non-canc. [CTUh]	2.8E-09	1.9E-09	1.1E-08	1.2E-08	5.1E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.6E-05	1.4E-05	1.0E-04	4.2E-05	1.5E-05
Ionising radiation, human health effect model, [kg U235 eq]	3.0E-02	2.3E-02	9.7E-02	5.7E-02	3.2E-02
Photochemical ozone formation,[kg NMVOC]	7.5E-05	6.4E-05	3.7E-04	1.9E-04	1.1E-04
Acidification [Mole of H+ eq.]	3.2E-04	2.8E-04	2.0E-03	6.2E-04	2.0E-04
Terrestrial eutrophication, [Mole of N eq.]	2.0E-04	1.7E-04	7.5E-04	5.8E-04	4.0E-04
Freshwater eutrophication, [kg P eq]	9.5E-08	8.1E-08	3.1E-07	5.3E-06	2.6E-06
Ecotoxicity [CTUe]	3.8E-03	3.4E-03	2.4E-02	1.0E-01	5.7E-02
Resources depletion, water [kg]	3.9E-02	3.5E-02	9.7E-02	1.0E-01	6.6E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.2E-06	1.2E-06	1.3E-06	1.9E-06	1.4E-06

Table 3.8 – Chemical oxidation: improved lab scenario comparison, all categories. (to be compared with Table 3.5) GO2 remains the least impacting material in 12 out of 13 categories

Figure 3.14 shows how this reduced consumption affects the global warming potential. It is clearly evident how GO3 and GO4 remain the most impacting materials in 7 categories out of 13. This new scenario benefits those materials having the energy consumption as main share of impact contribution. In this light is possible to deduct that GO4 is the material more affected by the energy consumption in the global warming potential category.

Overall, the GO2 remains the best performing material in terms of environmental impacts for 12 impact categories and actually improves compared to the base scenario in all categories except for the resource depletion that is mostly driven by the graphite usage that remains the same. In all other impact categories there is an improvement that goes from a 33% in the ionising radiation (driven by electricity usage) to the 4% of ecotoxicity. The improvement in the GWP impact category is around 16% The GO2 material remains weak in the acidification category due to the use of sulphuric acid (Table 3.8) that might be possible to partially reuse. This scenario analysis showed potential for further reduction in its environmental impacts when scaling it up.

3.3.3.2 Reduction of graphite oxide – improved lab scenario

Concerning the reduction process, it is possible to make the same type of reasoning and reduce the quantity of energy necessary to produce 1 g of reduced graphite oxide thus optimising the process outputs. Also in this case the processes are limited by the size of the equipment and the chemical reduction cannot process batches larger than one litre, while the thermal reduction is limited to the size of the tube furnace in the area where the heat is transferred homogeneously.

In the chemical reaction is possible to process up to 20 g of graphite oxide in a single batch stirred on the hot plate. For the thermal reduction it would be possible to accommodate around 100 g of GO material without modifying the energy demand [12].

It is possible to perform a simple calculation based on the Cp of graphite (710.8 J/kgK) to understand that during the almost 19h of operation the heat required to bring 100 g of graphite from 25 °C to 700 °C is only 0.05 MJ while the furnace consumes 9.8 MJ. Most of the heat is lost or used to heat the furnace rather than the graphite as the quantities are small.

Material	Base MJ	Improved MJ	Reduction %
rGOxC	1.51	0.38	75%
rGOxT	5.51	0.28	95%

Table 3.9 – GOs reduction: improved electricity values. The original values are those reported in the inventory (Table 3.5) while the Improved MJ column shows data obtained maximising the laboratory production yield without increasing the heat input.

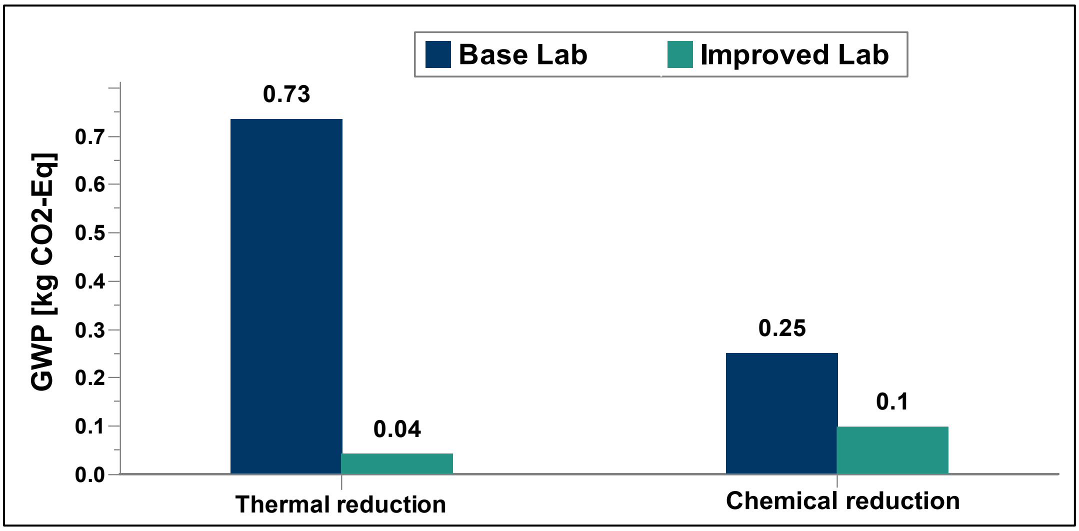


Figure 3.15 – GOs reduction: original scenario vs. maximised laboratory production yield (base scenario values from Figure 3.13). This chart does not include the oxidation process.

	GO2x REDUCED MATERIALS IMPROVED LAB SCENARIO	
	rGO2C	rGO2T
Global Warming Potential [kg CO2-Equiv.]	0.13	0.08
Ozone Depletion [kg CFC 11-Equiv.]	4.6E-11	3.8E-11
Human toxicity, cancer [CTUh]	6.2E-11	4.6E-11
Human toxicity, non-canc. [CTUh]	5.5E-09	4.7E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	4.1E-05	3.7E-05
Ionising radiation, human health effect model, [kg U235 eq]	0.2	0.1
Photochemical ozone formation,[kg NMVOC]	2.5E-04	2.0E-04
Acidification [Mole of H+ eq.]	7.2E-04	6.8E-04
Terrestrial eutrophication, [Mole of N eq.]	8.1E-04	5.6E-04
Freshwater eutrophication, [kg P eq]	3.0E-07	1.6E-07
Ecotoxicity [CTUe]	9.4E-03	6.9E-03
Resources depletion, water [kg]	0.14	0.10
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.5E-06	2.0E-06

Table 3.10 – rGO2T and rGO2C, improved lab scenario comparison. rGO2T becomes the least impacting material. This table includes the oxidation process (to be compared with Table 3.6).

Increasing the processed quantities will reduce the energy used per gram for both processes as shown in Table 3.9. For the thermal reduction though, a new heating profile is likely to be needed to heat the whole material homogeneously and maintain the same graphene quality [13]. Figure 3.15 includes only the reduction processes without including GOs and shows how the thermal reduction impacts less than the chemical one because it can processes more material per batch. This proves how impacts reduce when a process is more optimised (all categories in Appendix A paragraph A.3).

Summing the results for the oxidation and the reduction, the values become as shown in Table 3.10 (to be compared with Table 3.6). As the GO2 is the most oxidised material among those analysed [11] and the least impacting, it is the only one considered for the reduction. The values show a large reduction of the impacts for the thermal reduction from 73% of the fresh water eutrophication to 93% of the ionising radiation. For the chemical reduction the improvement is slightly lower since the share of the electricity in the overall impact is lower as it also involves chemicals. The reduction ranges from a 25% in the fresh water eutrophication to a 71% in the ozone depletion category. Only in the mineral and fossil resource depletion the reduction is minimal as this category is mostly driven by the graphite usage. With this scenario it is possible to see how an increase in the input volume favours the thermal reduction over the chemical one despite the latter producing on average 10 – 20% more material per gram of GO (as it is a lower performing reduction method - see Paragraph 3.3.2.2).

What this scenario modelling has shown is that the preparation of graphene could be made more efficiently already at laboratory stage, simply scaling it up to its full potential (detailed breakdown for GWP in Appendix A paragraph A.4) and that the throughput maximisation is important to reduce the environmental impacts. The next step would be to minimise the heat losses to further enhance the environmental performances of the processes requiring high temperatures.

3.4 Chemical vapour deposition (CVD)

This technique is studied both at the Trinity College Dublin (TCD) and at Danubia Nanotech in Slovakia. The type of graphene produced with this procedure is different compared to that produced with the two syntheses presented so far.

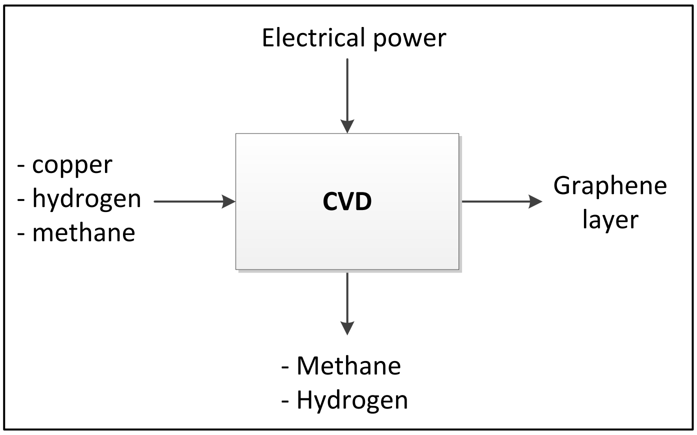


Figure 3.16 – Chemical Vapour Deposition performed at TCD: methane is released into a high temperature furnace swept with hydrogen and deposits on the surface of a copper substrate forming on single layer of graphene. All inputs/outputs are listed

The graphene obtained is not a dark thick layer made of several unorganised layers of graphene, but is a transparent single monoatomic layer of carbon deposited on a copper foil (see Chapter 2 paragraph 2.4.3.3 for details).

The procedures analysed in the two institutes are very similar. They both use a vacuum tube furnace with a copper sample inside used as substrate for the graphene growth. At Danubia:

- A mixture of argon and hydrogen flows inside the furnace
- Temperature increased to 960°C
- Conditions kept for 20min for removing oxides from copper and increase copper grain size
- Gases are stopped and hexane vapour is let flow for 5min
- The furnace is then turned off and the samples let cool off with the Ar/H_2 gas mixture flowing again for a couple of hours.

At TCD, instead, the procedure involves the following steps [14]:

- Pure hydrogen flows inside the furnace
- Temperature increased to 1035°C
- Conditions kept for 20min for removing oxides from copper and increase copper grain size
- Methane is released together with a reduced flow of hydrogen for 20min
- Furnace is turned off and the samples cool off with hydrogen flowing for 2h

3.4.1 Process inventory

As this type of graphene is in a form of monoatomic layer, its weight is extremely low. It is reported that one square meter of single-layer graphene weights 0.77 mg [15] therefore, the comparison with the previous graphene materials can be considered inappropriate. This graphene is not only different, but it is also used for other types of applications. However, for consistency reasons, the values reported in the inventory refer to the production of a gram of graphene.

CVD graphene (1 g)	Danubia	TCD	
Copper	203	203	kg
Electricity	831,944	1,282,508	MJ
Hydrogen	37	68	kg
Methane	-	12	kg
Argon	15896	-	kg
Hexane	2	-	kg

Table 3.11 – CVD graphene: inventory of inputs for the production of 1 g of graphene

In this case all measurements were taken directly in the laboratory and there is no need for assumptions. However, in order to calculate the energy requirements per gram of material produced the process output at laboratory stage was maximised. The surface of graphene generated in the tube furnace is assumed to fit exactly the whole tube circumference. The sample length is considered to be 15 cm to match the length of the tube where the temperature is uniform. This assumption generates a higher material production at Danubia as the diameter of their tube furnace is slightly bigger (4 cm vs 3.4 cm) than the one used at TCD.

The energy needed to produce one gram of graphene via CVD method (Table 3.11) is a million times bigger than that needed to operate the other methods. However, 1 gram of CVD monolayer graphene has a surface area of almost 1300 m^2 and, on the other hand, using the surface area as functional unit to compare the CVD with other routes would not make it a better comparison as the materials synthesised chemically or electrochemically considerably vary in thickness and weight.

3.4.2 Impact assessment

The impact assessment for the CVD graphene synthesis is in favour of the Danubia process as it consumes less energy due to its lower operational temperature and higher production rate. Figure 3.17 shows the difference in global warming potential between the two procedures, while from Figure 3.18 it is possible to understand the importance of electricity on the overall impact.

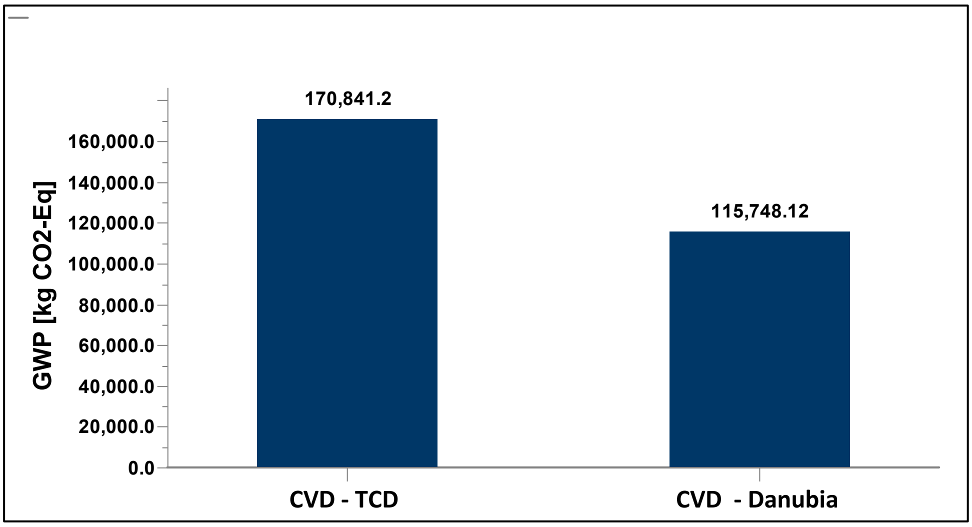


Figure 3.17 – CVD graphene: global warming potential comparison. The CVD process performed at Danubia is 32% less impacting

Table 3.12 illustrates the results for all impact categories analysed. It is clear how the process used in Danubia is less impacting. For all categories the situation is similar to the one depicted for the global warming potential. The electricity is the main environmental burden followed by the argon in case of Danubia. The fossil and mineral resources depletion category shows similar results for both processes because of similar use of copper, the main driver for this particular category.

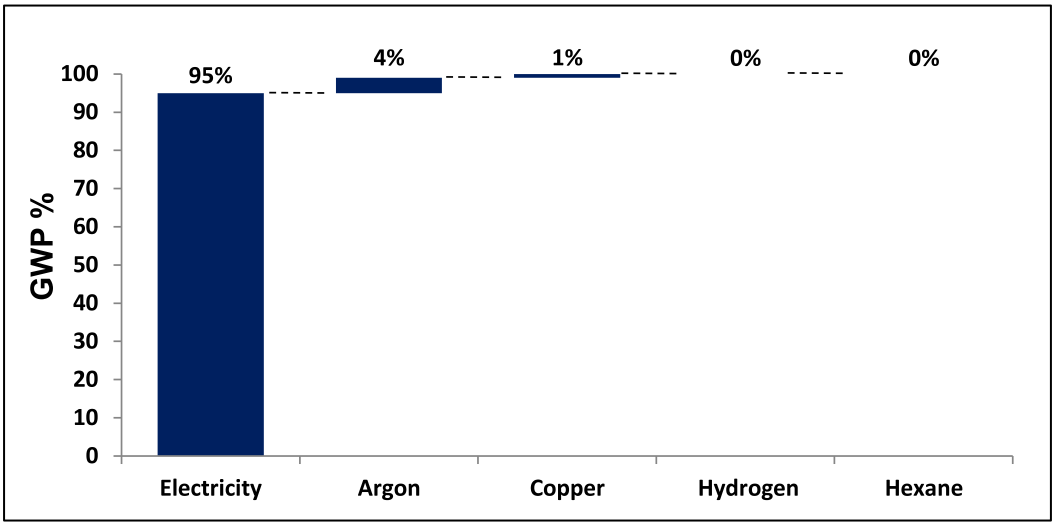


Figure 3.18 – CVD graphene: Danubia process detailed breakdown in percentage of all material and energy inputs. Electricity is the main cause of GWP.

	CVD comparison	
	Danubia	**TCD**
Global Warming Potential [kg CO2-Equiv.]	115748	170841
Ozone Depletion [kg CFC 11-Equiv.]	8.0E-05	1.2E-04
Human toxicity, cancer [CTUh]	3.3E-05	4.8E-05
Human toxicity, non-canc. [CTUh]	5.2E-03	7.2E-03
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	41	61
Ionising radiation, human health effect model, [kg U235 eq]	274954	411717
Photochemical ozone formation,[kg NMVOC]	228	341
Acidification [Mole of H+ eq.]	595	900
Terrestrial eutrophication, [Mole of N eq.]	804	1200
Freshwater eutrophication, [kg P eq]	0.08	0.11
Ecotoxicity [CTUe]	6356	8073
Resources depletion, water [kg]	123521	183830
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	6.33	6.38

Table 3.12 – CVD graphene comparison: all impact categories. The graphene synthesised at Danubia proves to be the least impacting (green) in all impact categories. It is less impacting from a 21% in the ecotoxicity to a 35% in the ozone depletion category. They are very similar in the fossil an mineral resource depletion.

Due to the completely different type of graphene produced, this type of production process will not be analysed and compared further as it will obviously result in the most impacting as the functional unit is mass related. However, it is important to notice that using furnaces that can work continuously in a well-insulated environment would considerably reduce the impacts related with energy consumption as most of the heat is now lost in heating the furnace and its surroundings. A positive aspect of this technology is that the time needed for the hydrocarbons to deposit on the copper substrate to form graphene is short and that is why, if developed differently, this method could become ecologically viable (e.g. roll to roll deposition - fast and continuous process).

Unfortunately, all technologies for commercial scale production of CVD graphene are patented by industry and no data on their consumption of energy and materials are publicly available; it is therefore not possible to quantify this improvement.

3.5 General comparison

The final aggregated results compare the least impacting graphene synthesis processes analysed using the production of 1 gram of graphene as functional unit. For the chemical route it is used the improved lab scenario only.

For the global warming potential case (Figure 3.19), it is the thermal reduction of GO2 that shows the best environmental performances. Looking at all categories (Table 3.13), it is possible to see how the trend is consistent, with the rGO2T being the least impacting in 12 of the 13 impact categories analysed and the rGO2C the second. The impacts of CVD graphene are hundreds of thousands of times larger making it the most impacting material.

The rGO2T material is less impacting than the first electrochemically exfoliated material (KOH 15 V) from a 33% in the ecotoxicity to a 82% in the ionising radiation, while the rGO2C is 8% better than the KOH 15 V exfoliated material in the ecotoxicity up to 80% in the ozone depletion category. From the resources depletion perspective, the best processes are the chemical ones and this is due to their better material conversion from graphite to graphene, as graphite production is the main cause of impact for this category. During the electrochemical exfoliation, in fact, some graphite is used as binder and it gets lost in the solution and as CO_2.

Looking at the potentials achievable when these processes will be scaled up, it is likely that the electrochemical processes will not benefit much from this type of activity. The small scale up performed in the lab to go from the small set up, used for potassium hydroxide (KOH) and sodium acetate ($CH_3COOHNa$), to the larger sodium hydroxide (NaOH) batch has not shown any significant improvement.

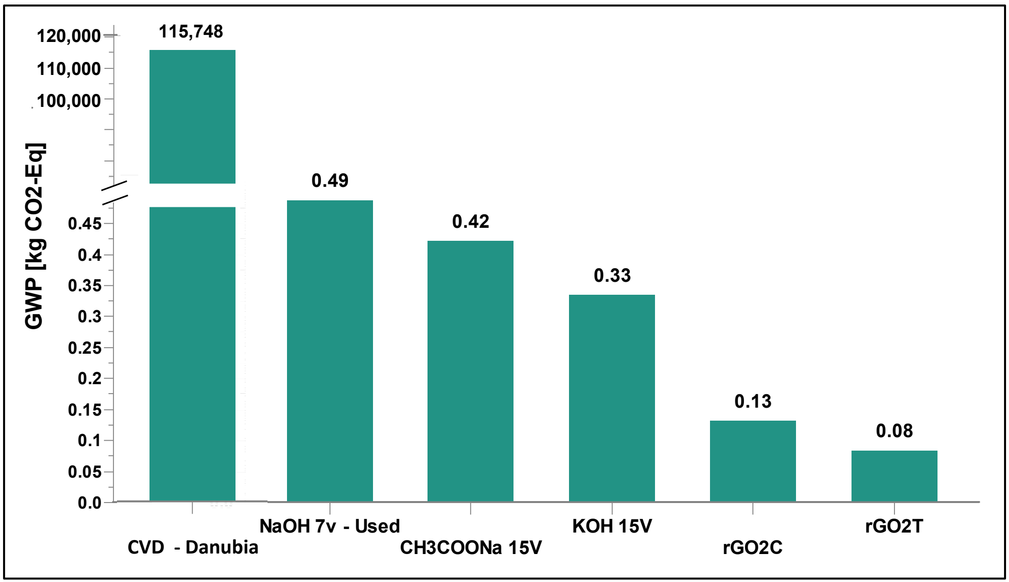


Figure 3.19 – Graphene production comparison: improved lab scenario, global warming potential. The chemical processes prove to be the least impacting in the GWP category

	GRAPHENE					
	CVD Danubia	NaOH 7V Used	CH3COONa 15V	KOH 15V	rGO2C	rGO2T
Global Warming Potential [kg CO2-Equiv.]	1.2E+05	4.9E-01	4.2E-01	3.3E-01	1.3E-01	8.3E-02
Ozone Depletion [kg CFC 11-Equiv.]	8.0E-05	3.3E-10	2.9E-10	2.2E-10	4.6E-11	3.8E-11
Human toxicity, cancer [CTUh]	3.3E-05	1.4E-10	1.2E-10	9.6E-11	6.2E-11	4.6E-11
Human toxicity, non-canc. [CTUh]	5.2E-03	1.8E-08	1.5E-08	1.2E-08	5.5E-09	4.7E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	4.1E+01	1.6E-04	1.4E-04	1.0E-04	4.1E-05	3.7E-05
Ionising radiation, human health effect model, [kg U235 eq]	2.7E+05	1.1E+00	9.5E-01	7.3E-01	1.7E-01	1.3E-01
Photochemical ozone formation,[kg NMVOC]	2.3E+02	9.3E-04	8.1E-04	6.3E-04	2.5E-04	2.0E-04
Acidification [Mole of H+ eq.]	5.9E+02	2.4E-03	2.1E-03	1.6E-03	7.2E-04	6.8E-04
Terrestrial eutrophication, [Mole of N eq.]	8.0E+02	3.3E-03	2.9E-03	2.2E-03	8.1E-04	5.6E-04
Freshwater eutrophication, [kg P eq]	8.0E-02	4.9E-07	3.5E-07	3.3E-07	3.0E-07	1.6E-07
Ecotoxicity [CTUe]	6.4E+03	1.5E-02	1.3E-02	1.0E-02	9.4E-03	6.9E-03
Resources depletion, water [kg]	1.2E+05	5.8E-01	4.7E-01	3.9E-01	1.4E-01	1.0E-01
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	6.3E+00	7.4E-06	5.8E-06	6.8E-06	1.5E-06	2.0E-06

Table 3.13 – Graphene production comparison: improved lab scenario, all categories. The chemical route produces the least impacting materials in all analysed categories (green)

Though it is not possible to derive any definite conclusion as the big batch was using different electrolyte and voltage, it is likely that the scale up of an electrolytic process will be obtained multiplying the number of electrolytic cells or enlarging its size without improving the efficiency. It might be possible to recover the hydrogen that is generated at the cathode and reuse it in a fuel cell to reduce the energy load, but this also depends on the commercial viability of the process. There might be room for improving the electrochemical processes analysed by optimising the distance between electrodes, their geometry and the electrolyte resistance, but these improvements are not directly related to a potential scale up of the current cell.

The chemical route, instead, shows improvements when scaled up as it can process more material per batch and, moreover, offers the possibility to further minimise its environmental burden by minimising the heat losses. Some other improvements might also be achieved in optimising the reaction rates and limit the excess of chemicals.

3.6 Conclusions

In conclusion it possible to say that the graphene production process is a very energy intensive process, with energy consumption values ranging from 1.28×10^6 MJ/g of CVD performed at TCD to 1.6 MJ/g of the chemical oxidation and reduction performed at Danubia laboratory. However, it offers a lot of potential for reducing its energy consumption (especially when considering the chemical/thermal processes that showed reductions of 77% for the rGO2C and 87% for the rGO2T), and this proved that a more optimised process is necessary to reduce significantly the environmental impacts of graphene.

After this preliminary analysis only three materials were selected to be further studied in more detail: the least impacting electrochemical exfoliation (KOH 15 V) and the least impacting chemical route (rGO2T) and the material that offers more potential in terms of heat losses minimisation (rGO2C).

The selected material are used to manufacture electrodes for supercapacitors and subsequently tested while an LCA is performed on the overall supercapacitor manufacturing activity. As the specific capacitance is a crucial parameter for supercapacitors, all materials were tested before the final selection and the rGO2C material showed the highest values of F/g.

The CVD method is discarded since it was proved not suitable for supercapacitor applications by the partners in the consortium and because the selected functional unit (1 g of graphene) makes this process way too impacting to be studied further.

3.7 References

1. Joint Research Centre (JRC - EU Commission), *ILCD handbook*2010: Institute for environment and sustainability European Commission Joint Researc Centre.
2. Huppes, G., et al., *Weighting environmental effects: Analytic survey with operational evaluation methods and a meta-method.* The International Journal of Life Cycle Assessment, 2012. **17**(7): p. 876-891.
3. Hankin, S. and S. Billet, *Electrograph final report (EU project FP7)*, 2014.
4. Siong, V., *Personal Communications*, 2012: Fraunhofer IPA Institute.
5. Shao, Y., et al., *Highly durable graphene nanoplatelets supported Pt nanocatalysts for oxygen reduction.* Journal of Power Sources, 2010. **195**(15): p. 4600-4605.
6. Siong, V., *Personal Communications*, 2013: Fraunhofer IPA Institute.
7. Cox, R.L., *18.1.4 Synthetic Graphite*, in *Engineered Tribological Composites - The Art of Friction Material Development*, SAE International. p. 358-359.
8. Eurostat. *Hydropower*. 2013 [cited 2016 03]; Available from: http://ec.europa.eu/eurostat/web/environmental-data-centre-on-natural-resources/natural-resources/energy-resources/hydropower.
9. Chen, W., L. Yan, and P.R. Bangal, *Preparation of graphene by the rapid and mild thermal reduction of graphene oxide induced by microwaves.* Carbon, 2010. **48**(4): p. 1146-1152.
10. Lobato, B., et al., *Reduced graphite oxide in supercapacitor electrodes.* Journal of Colloid and Interface Science, 2015. **446**(0): p. 203-207.
11. Kotrusz, P., *Personal Communications*, 2013: Danubia Nanotech.
12. Vretenar, V., *Personal Communications*, 2013: Danubia Nanotech.
13. Kotrusz, P., *Personal Communications*, 2014: Danubia Nanotech.
14. McEvoy, N., et al., *Functionalisation of graphene surfaces with downstream plasma treatments.* Carbon, 2013. **54**(0): p. 283-290.
15. *Scientific Background on the Nobel Prize in Physics 2010 GRAPHENE*. Class for Physics of the Royal Swedish Academy of Sciences 2010 10/2014; Available from: http://www.nobelprize.org/nobel_prizes/physics/laureates/2010/advanced-physicsprize2010.pdf.

CHAPTER 4: Case study: production of supercapacitors – a comparison

In this chapter a comparative LCA is performed involving several supercapacitors: a state of the art supercapacitor available on the market with electrode made with on activated carbon and three other supercapacitor prototypes having the graphene electrode material produced in the collaborating laboratories.

Comparing the mass produced activated carbon with the graphene production that is only available at lab scale would mean to compare a well refined industrial process with an inefficient one still in its development. For this reason it is necessary to simulate a commercial-scale graphene synthesis process.

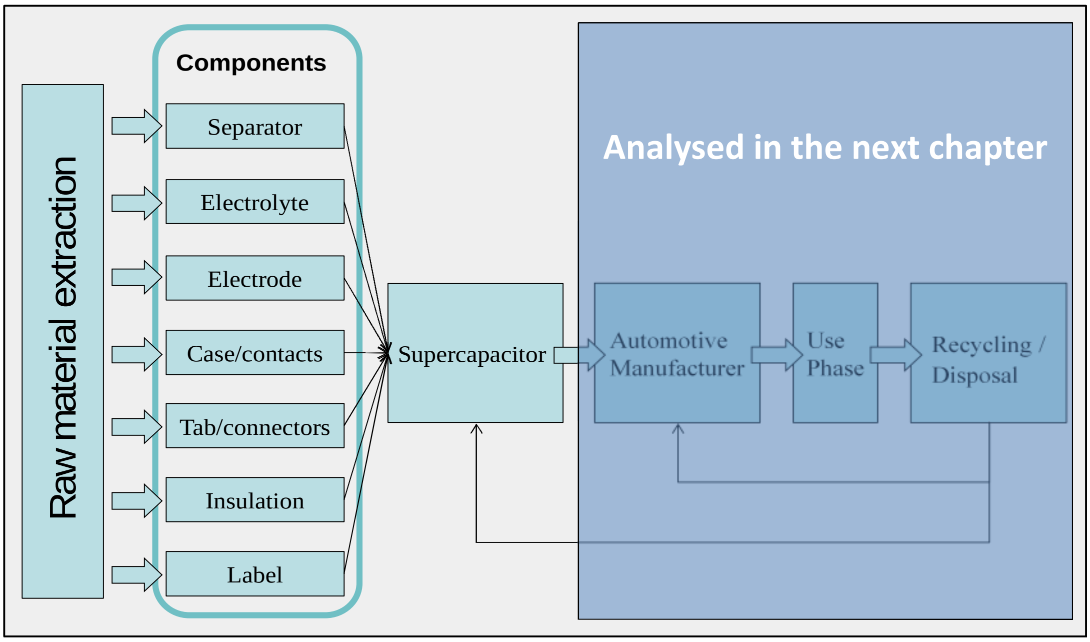


Figure 4.1 – Process overview: from raw material extraction to supercapacitor production (cradle-to-gate approach). All other phases are analysed in the next chapter

This chapter only focusses on the production phase of the supercapacitors as shown in Figure 4.1 while recycling and use phase are considered in the next one.

4.1 Methodology

This section is an overview and summary of the goal and scope of the comparative cradle to gate LCA focusing on the production process of the supercapacitors.

4.1.1 Life cycle assessment methodology

This is a comparative LCA between a state of the art supercapacitor mass produced by Maxwell Technologies Inc. and three prototypes that have the electrodes made with graphene.

The purpose of this chapter is to estimate the future potential of this new technology when compared to the current one in terms of environmental impacts and material performance. To do so, four supercapacitors are compared:

- One state of the art activated carbon based supercapacitor (5 F)
- Three graphene based prototypes (5 F) using three graphene types:
    - Electrochemical exfoliation with KOH at 15 V
    - Chemical oxidation and reduction (rGO2C)
    - Chemical oxidation and thermal reduction (rGO2T)

4.1.1.1 Function and functional unit

The supercapacitor is an energy storage device capable of delivering high power for a short period of time. It is fundamental that all supercapacitors are capable of performing the same function and for this reason they have to be modelled consistently. The capacitance of a supercapacitor is measured in Farads and for this type of comparison the functional unit is a capacitance of 5 F to correspond to the case study presented in Chapter 5.

4.1.1.2 System delimitation, boundaries, impact categories and data quality

This is an attributional comparison between supercapacitors that only depicts the situation without consequences of possible adoption of this technology. The LCA is a cradle to gate analysis from raw material extraction to the production of the supercapacitors as shown in Figure 4.1.

Since this is a comparative LCA, all transports are not included as they are assumed to be the same for both solutions. Moreover, on such small and light component and application, transport over distances of few hundreds kilometres were proven not to impact the environment significantly (see Chapter 5 paragraph 5.2.1).

The impact categories are the same as in the previous chapter and requested by the ILCD standard methodology. According to measurements performed by IOM (Institute of Occupational Medicine) in all laboratory or production facilities, no airborne particles were detected while assembling a supercapacitor [1].

The data are measured on site except for the supercapacitor manufacturing for which data are provided by Maxwell Technologies Inc.; data from GaBi 6 databases are used for all auxiliary processes and for all input materials production.

Assumptions are used during the process scale up and the data generated by the process simulator are applied to the LCA models.

4.1.2 Commercial-scale production of active material

The activated carbon production process was not disclosed and therefore, data for commercial-scale production of activated carbon are taken from GaBi database. However, since the data are protected by commercial agreements, it is not possible to investigate the process in detail as Thinkstep only provides aggregated values (one unique process including all sub-processes combined). Nevertheless, it is possible to deduct that the main inputs are coal, natural gas and electricity.

The graphene production must be scale up to commercial-scale and compared to the already mass produced activated carbon. Maxwell's current activated carbon production is around 3 tonnes per year [2] and the graphene simulated production process is modelled on the same numbers. For the chemical route the layout selected to reach the 3 ton/y production rate processes batches of 2kg (see Appendix B paragraph B.1) while the electrochemical exfoliation is considered a multiplication of the same electrolytic cell with multiple batches generating a continuous process. Stops will be necessary for some cells to substitute exhausted electrodes and change the electrolyte that might be saturated with carbon particles.

A process to mass produce graphene is under research in many universities, in this study, though, the upscaling assumes that the simulated industrial process follows the same procedures of the laboratory processes in the way they are performed today. This is also important because the quality of the materials analysed is defined on the base of the laboratory processes. Thermal efficiency is improved and volumes and cycle times optimised, in order to generate a best case scenario and compare it with the current supercapacitor production process.

Wastes and emissions values are estimated as it was not possible to measure them. Even so, they are taken into account as they are important to understand their magnitude if compared to the overall life cycle.

4.1.2.1 Electrochemical exfoliation (KOH 15 V)

This process consists in having two electrodes of graphite submerged in a solution of potassium hydroxide (KOH). When the circuit is closed and current flows through the electrodes, the anode electrode is exfoliated by intercalation of negative ions (O^{2-} and $(OH)^-$ in this case) producing graphene nanoplatelets (GNPs – More details in Chapter 2 paragraph 2.3.3.1).

For the scale up activity of this electrochemical process it was decided to use the best values achieved in the laboratory with different batches in terms of energy efficiency, material conversion efficiency and specific capacitance and combine them all together in order to generate a best case scenario. A more detailed upper theoretical limit of efficiency was not calculated or simulated in the view of the fact that the material produced with this process showed low specific capacitance.

The data used to simulate a commercial-scale process are (more details in Chapter 3 paragraph 3.2.1):

- Specific capacitance of the supercapacitor using this material is 7.5 F/g as the best result tested
- Material conversion efficiency 44% as achieved by the NaOH 7 V batch with new electrodes
- Energy per gram of graphene is 1.85 MJ as obtained with the KOH 15 V
- Voltage is 15 V as it is always performing faster exfoliations
- Electrical efficiency set at 90% allowing for a typical converter efficiency operating at the designated current and voltage.

About the last point, the electrical efficiency is introduced because all measurements were taken at the electrodes avoiding the inefficiency of the power converter that must be taken into consideration.

It was not possible to measure the emissions or to calculate them (the extent of the reaction is not clear). They are therefore estimated by Fraunhofer personnel and consist mostly of oxygen and hydrogen and a negligible quantity of CO_2. It is assumed that 50% of the O_2 intercalates while the remaining is emitted. Based on the energy consumption (1.85MJ) the H_2 release is calculated using the state-of-the-art electrolysers energy requirements. – 141,840 J/g(H_2) [3].

The electrolyte could be reused to produce further graphene once all carbon is filtered out, but the whole solution is considered disposed of as waste since the impact of the electrolyte is negligible if compared with the energy consumption and the graphite synthesis process (see Chapter 3). Some graphene oxide, too small to be filtered, remains in the solution and is considered waste [4].

It produces a graphene oxide with a low specific capacitance (at least with the electrolyte used) showing a value of only 7.5 F/g in the very best case, but with a much lower average set around 3 F/g (examples of measurements in Appendix B paragraph B.2). Maybe a reduction of this oxidised material would have increased those values but this possibility was not tested.

As comparison, Maxwell and INCAR measured the specific capacitance of the same commercial graphene to be 13 F/g (all measurements taken when the material is inside a supercapacitor) and therefore to build a 5 F supercapacitor with this material 0.43 g are needed. Though, this quantity must increase in the case of the electrochemically exfoliated material as its specific capacitance is lower.

4.1.2.2 Commercial-scale chemical and thermal processes (rGO2C and rGO2T)

Two materials are analysed and optimised, the rGO2T and rGO2C, with the help of a process simulation tool (SuperPro Designer v.9) to simulate commercial-scale production of graphene.

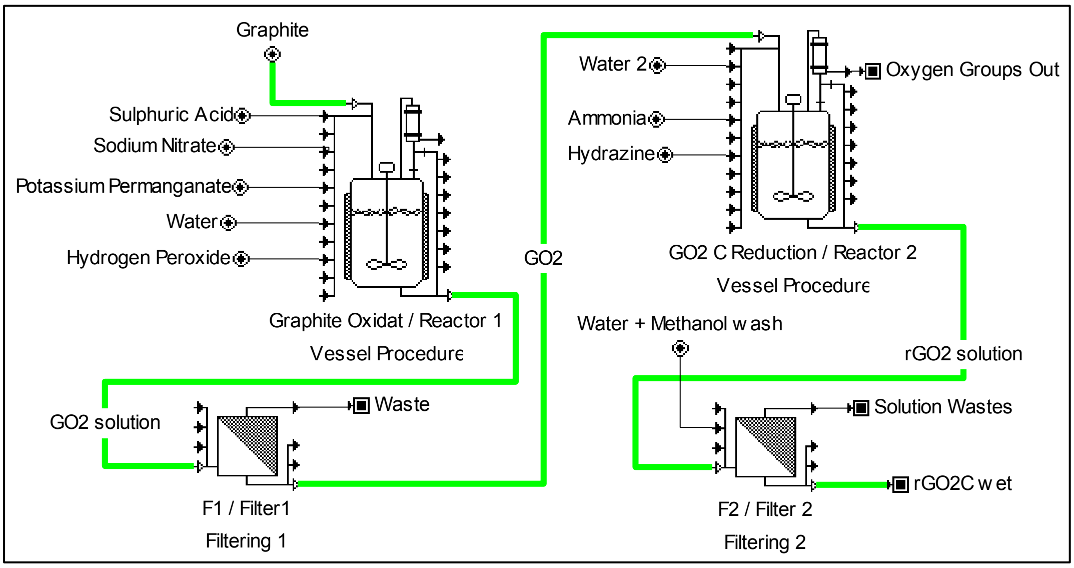


Figure 4.2 – Process simulation: rGO2C production

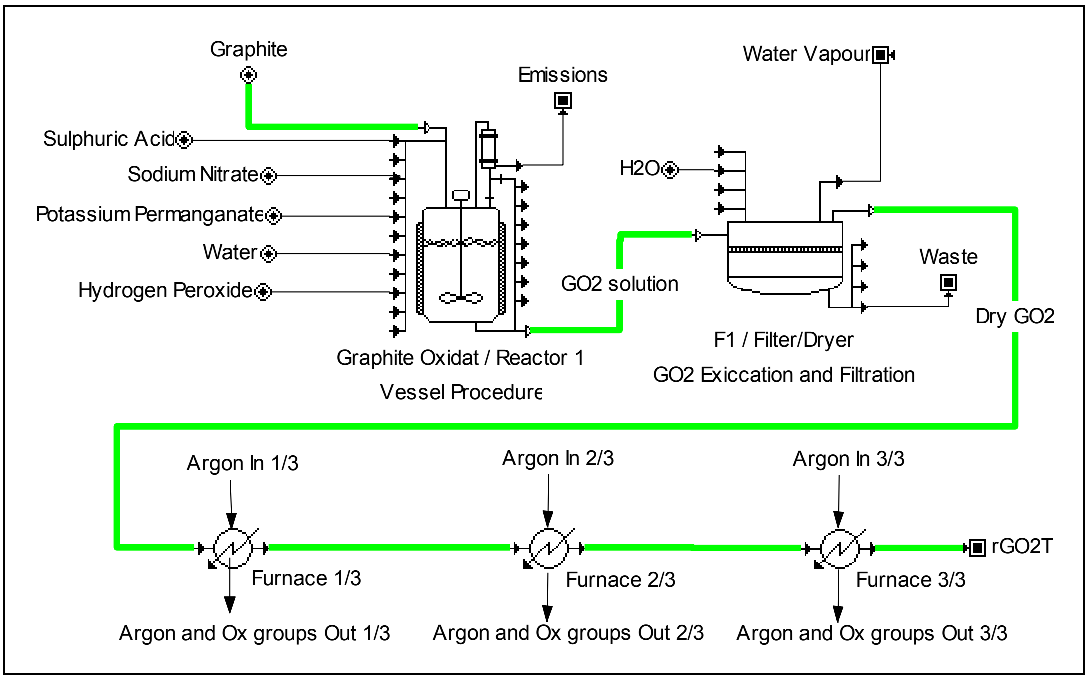


Figure 4.3 – Process simulation: rGO2T production

The graphene synthesis is upscaled but yields and efficiencies of reactions are kept constant. Heat inputs are minimised in order to exclude heat losses and therefore reduce the energy input.

Figure 4.2 show the chemical oxidation followed by the chemical reduction with hydrazine and ammonia, while Figure 4.3 shows the chemical oxidation followed by the thermal reduction. The thermal reduction is divided in three furnaces to show the three different stages of temperature and heating rate (140 °C at 1.5 °C/min – 350 °C at 0.3 °C /min – 700 °C at 1.5 °C/min) but it can be done in one unique furnace. This step can also be done in one unique step, depending on feasibility, cost, flexibility and production rate needs. For example, the second stage of heating is the longest. Having two or three furnaces operating in parallel with different timing will increase the throughput but will also increase the costs (see Appendix B paragraph B.4 for an example of optimised production layout).

4.1.2.2.1 Graphite oxidation

The first and common step for both rGO2s is the oxidation of graphite using the Hummers-Bangal method to obtain GO2. This method uses sulphuric acid and potassium permanganate at a temperature of about 35 °C for less than 2 hours (described in Chapter 2 section 2.3.3.2 and in Chapter 3 section 3.3). Figure 4.4 shows the GO2 production process and it replicates the procedures measured in the laboratory.

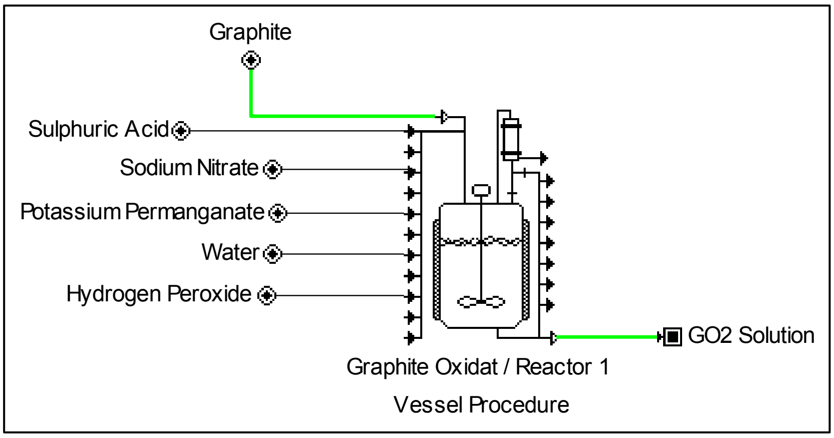


Figure 4.4 – GO2 production process – Oxidation process

To add the potassium permanganate in a faster way and shorten the time needed for this reaction to start, the vessel must be cooled. In fact, the heat released from the reaction is substantial (enthalpy of solution is -48 kJ/mol, enthalpy of reaction -28.7 kJ/mol when graphene to potassium permanganate ratio is 1 to 3 [5]) and this results in a need for 1.6 Wh per gram of graphite oxide produced. This energy is used for cooling the vessel to an initial temperature of around 0-5 °C, then to maintain it around 20 °C when $KMnO_4$ is added and finally for heating the vessel to 35°C and keeping the temperature constant until the end of the operation. When heating and cooling the heat transfer efficiency is set at 90%, the cooling has a coefficient of performance[1] of 4.5 and the reactors are considered adiabatic therefore no energy is required to maintain the temperature constant at 35 °C.

When adding the oxidative agent (potassium permanganate) the temperature must be kept between 0 °C and 20 °C. Instead of electricity, water can be used as refrigerant, but normal cool water, usually taken from rivers, wells or sea, is not cold enough (20 – 25 °C), thus chilled water (5 – 10 °C) should be used and it might already available at the plant as waste product generated by the air conditioning system [6]. Using it might contribute to the cooling of the reaction saving some energy and reducing environmental impacts. The last part of the reaction requires a limited amount of heat as the temperature has to go from 20 °C to 35 °C without heat losses and the mixture has to be stirred for 2 hours.

The heaters used in the laboratory were not very efficient and suffer from large heat losses; hence, the need to simulate adiabatic conditions to simulate commercial-scale processes generally operating with losses reduced to the minimum. This minimisation is also evaluated from environmental impacts point of views as the energy used to cool/heat the reactions is the main driver for environmental impacts for chemical graphene production. Thus, for the modelling, the heat requirements are calculated with the formula $Q=mCp\Delta T$ plus 10% as the electrical efficiency set at 90% (m = mass, Cp = heat capacity at constant pressure, ΔT = temperature variation).

Also in this case it was neither possible to measure the emission nor to precisely calculate them. In fact, the graphite oxidation and reduction reactions are not yet fully understood (see Chapter 2 paragraph 2.4.3.2) and the percentage of reacting material depends on many factors.

Nevertheless the emissions were roughly estimated by laboratory personnel and added to the model: in the chemical oxidation, the emissions are mostly carbon dioxide and monoxide, water and some hydrocarbons (methane, ethane, ethane, acetylene) and a smaller quantity of (poly)aromatic compounds (benzene, toluene, xylenes…) [7]. Some of those substances must be removed before fumes can be emitted in the atmosphere, but due to the high uncertainty on their quantity this activity is not considered in this LCA.

The wastes are estimated based on the fact that the reaction of $KMnO_4$ + $NaNO_3$ + H_2SO_4 will give approximately $MnSO_4$ + NO_2 + Na_2SO_4 + K_2SO_4 + H_2O. This reaction is non stoichiometric as the extent of the oxidation is unknown but it can be

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[1] The coefficient of performance is the ratio between the cooling provided and the energy consumed. A COP of 4.5 means that to provide 4.5kW cooling there is a need of 1kW of electricity (COP = Q_C/W where W is the work needed and Q_C is the heat taken from the cold reservoir at T_C. The work is equal to $Q_H - Q_C$ where Q_H is the heat given to the hot reservoir at T_H).

estimated using the difference in weight between the graphite and the graphite oxide. Assuming the reaction of $KMnO_4$ will be 100% shifted to the right (no oxidising agent left) and that the additional oxygen needed is given by the sulphuric acid, it is possible to give a rough estimation of waste quantity as a worst case scenario (no reuse possible) [8].

About the wastes, the main environmental concern is linked with the acid and the oxidant; potassium permanganate is totally dissolved at the end of the reaction with hydrogen peroxide, but sulphuric acid remains in a large quantity since only a minor portion takes part in the reaction, the rest is needed as solvent to facilitate the reaction. This acid must be neutralised and, since there is no knowledge about the extent of its depletion in the reaction, a worst case scenario is considered as if the whole quantity used had to be neutralised.

A set of alkaline materials (sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (Na_2CO_3) and calcium hydroxide ($Ca(OH)_2$)) are considered to determine which could achieve the lowest environmental impact. The remaining wastes are of a minor concern, except for the manganese, that, being a heavy metal, might need to be recovered from the neutralised material if the level exceeds the limit allowed by the legislation.

No further modelling was done of how manganese could be recovered or emissions stripped from hazardous components. This is because their composition is highly uncertain and, even more important, these processes are not yet efficient. For these reasons modelling abatement/recovery systems using highly uncertain values calculated on the base of highly inefficient processes might lead to totally wrong conclusions. In fact, even if it is true that, for chemical processes, larger batches are generally less efficient than smaller ones, it is also true that an industrial chemical process is generally much more optimised than those performed in the laboratories, especially at an early stage of research.

4.1.2.2.2 **Chemical reduction**

After the oxidative reaction, the graphite oxide can follow two routes: thermal and chemical.

The chemical reduction (Figure 4.5) is the simplest as it happens at lower temperature in a vessel full of hydrazine (N_2H_4) and ammonia (NH_3) and it is likely to be the cheapest route as it requires less energy and insulation (lower operational temperature) and as the two chemicals used are easily available.

For the selected application, this route shows good values of capacitance in a supercapacitor configuration at 20 F/g [9] showing the best results among the graphene material tested.

The reaction happens at 85 °C and even if the reaction is slightly exothermic, there is a need for more heating. In the case of the adiabatic reactor (90% heat transfer efficiency) this process consumes around 2 Wh per gram of graphene.

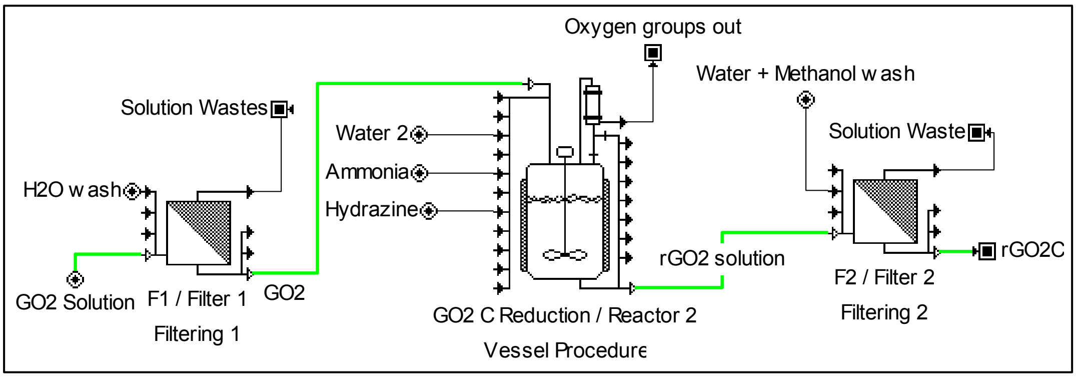

Figure 4.5 – rGO2C production process – Chemical reduction process

To neutralise the alkaline waste, some acid coming from the oxidation can be used, therefore no other substances are needed. Concerning the wastes and emissions, the same approach adopted for the oxidation was followed. This process releases mainly water and nitrogen but according to laboratory personnel, it releases negligible quantities of CO and CO_2 [7].

4.1.2.2.3 Thermal reduction

The material produced via thermal reduction (Figure 4.6 – in this figure the 3 temperature steps are grouped into one furnace for simplicity) should have similar characteristics as the one produced via chemical reduction. Unfortunately this material was never tested inside a supercapacitor but its characterisation highlighted a higher density (nanoplatelets restacking) and therefore a possible lack of storage space for electrons but an increased electrical conductivity [10].

Unfortunately, without proper measurements it is not possible to state whether the low internal resistance can compensate the low surface/volume ratio. For this analysis the specific capacitance of the material is kept equal to the one achieved with the chemical route

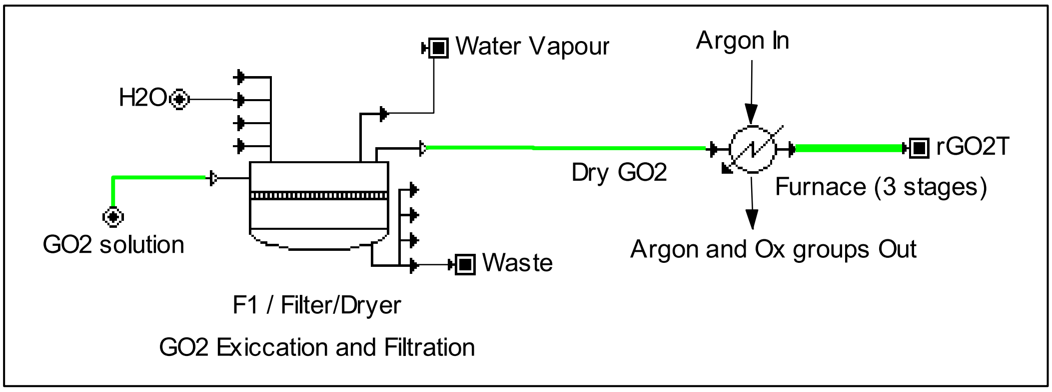

Figure 4.6 – rGO2T production process – Thermal reduction process (three heating stages aggregated in one)

According to laboratory personnel, the thermal reduction could be better achieved in an agitated or rotary drum where the filtered and dried powder can be better exposed to the heat and reduce faster. In fact, the lab drying process generates a foil of dry graphene oxide as the material is dried on a flat surface. This might also be the reason why this GO2 becomes denser and possibly reducing the space for storing electrons. The drying in a rotary drum might help maintaining a more random distribution of nanoplatelets and improve the specific capacitance of this material, but it might diminish its conductivity as well [10], thus further investigation is needed.

Compared to the chemical reduction, this process needs a higher temperature to be performed (peak 700 °C) and the reduction happens over 20 hours in an inert atmosphere (argon). It needs therefore more refined equipment and more insulation. The material needs to be filtered and dried before entering the furnace for the reduction and this is also an additional energy burden.

The drying process is slow as it happens at around 50 °C because higher temperatures can start the reduction process too early [8]. From experimental measurements, the wet cake of GO2 consists of 80% water and its evaporation requires an additional energy per gram of rGO2T produced (heat of vaporisation of water 2260 kJ/kg) making this process more energy demanding than the chemical reaction (in the case of an adiabatic system).

When the dry material enters the reduction process, oxygen is removed and with it some carbon as well. The weight loss was measured, but unfortunately the evolved gases were not, thus it was assumed that 50% of the weight lost was oxygen while the remaining 50% was a mix of other types of gaseous emissions consisting of 1/3 of CO_2, 1/3 CO, 1/6 hydrocarbons and 1/6 H_2O on the basis of discussions with Danubia [10].

4.1.3 Supercapacitor manufacture

The supercapacitors compared differ in shape (see chapter 2 paragraph 2.2.1) but they both use the same listed components (separator, electrolyte, electrodes, others) that differ in shape as well as they need to fit different structures: the commercial supercapacitor is rolled and therefore cylindrical while the prototype is flat. The flat capacitor does not have a rubber insulator.

For the rolled commercial supercapacitors, the general assembling process starts with rolling an electrode made of activated carbon on an aluminium substrate. Collectors are laser welded on the roll that is then sealed and laser welded into a cylindrical casing closed with a rubber and a welded lid. The supercapacitor is then vacuum-filled with electrolyte, hermetically sealed and tested.

The prototype is produced in a similar way but the electrodes are stacked and not rolled, collectors are then welded on the electrodes and placed inside the stainless steel casing that is then welded at the edges. The device is then vacuum-filled with electrolyte, sealed and tested. A more detailed breakdown of the essential step of the production of both the prototype and the supercapacitor is shown in Figure 4.7 and Figure 4.8.

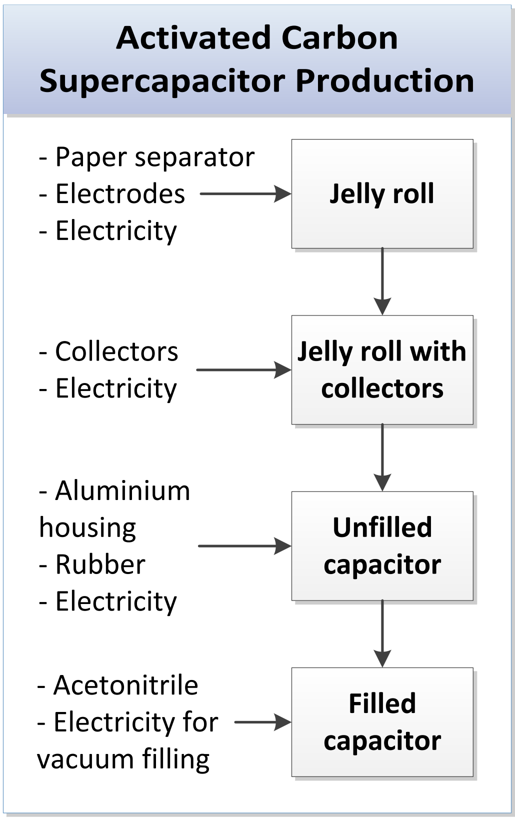

Figure 4.7 – Activated carbon supercapacitor production main steps

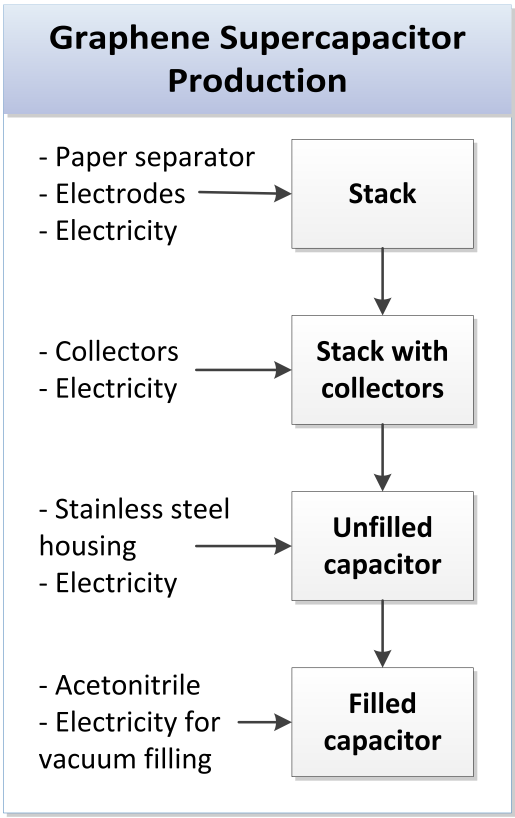

Figure 4.8 – Graphene supercapacitor production main steps

An important difference between the graphene supercapacitor and the standard supercapacitor, besides the shape, is that the prototype must have a casing in stainless steel to better withstand the internal pressure that can be generated by the evaporation of the electrolyte when the temperature increases. The prototype needs a more resistant casing because it has no safety valve and the flat shape was chosen as it is less complicated to manufacture. Both activated carbon and graphene supercapacitors are assembled at Maxwell Technologies Inc. therefore their assembling processes were measured and provided by Maxwell Technologies Inc. for both devices.

According to Maxwell Technologies, the tests performed on commercial graphene showed that the quantity of graphene needed to build a 5 F supercapacitor is 0.43 g [2]. This number, that includes an additional 10% margin, was double-checked at INCAR in Oviedo. INCAR tested directly the material (not inside a supercapacitor) and their results showed a specific capacitance of 52 F/g that when in a supercapacitor configuration becomes 13 F/g [9], a value that is in line with the tests performed at Maxwell.

This happens because, when the material is placed in a supercapacitor, the specific capacitance value measured for the material must be divided by 4 to obtain the theoretical value achievable by the supercapacitor. The reason is that, in a supercapacitor, the double layers formed in each electrode act like two supercapacitors in series. Therefore the overall capacitance (F) is half of the capacitance of each electrode. The electrode, though, has half of the mass of active material present in a supercapacitor and therefore its specific capacitance (F/g) is four times bigger than the specific capacitance of the whole device (see Appendix B paragraph B.3 for a mathematical explanation).

Material	Specific capacitance (F/g)	Graphene (g)
Commercial Graphene	13	0.43
KOH 15 V	7.5	0.71
rGO2C	20	0.27
rGO2T	20	0.27

Table 4.1 – Summary of material specific capacitance and graphene quantity in a supercapacitor

Table 4.1 summarises the specific capacitance of all materials tested and includes also the quantity of graphene needed to achieve the desired 5 F of the selected functional unit (the reference is the commercial graphene). The measurements are based on two different tests: the tests on supercapacitors performed at Maxwell with the procedure normally used for standard production and the tests performed at INCAR (see Appendix B paragraph B.2 for more details). The two measurements were showing consistency of results proving their reliability and therefore assuring that the supercapacitors can provide the same function.

The electrode production process for the activated carbon supercapacitors was not disclosed by Maxwell, but they could provide data for all material inputs and energy consumption needed to manufacture them. For commercial reasons, Maxwell could not disclose information about their binder. An alternative process for making the graphene based electrodes was not found by the collaborating laboratories; in fact, all electrodes tested showed poor adhesion of the material to the aluminium substrate. For this reason, the Maxwell electrode manufacturing process is used for both supercapacitors in the LCA models.

The electrolyte is a solution of acetonitrile with Et_4NBF_4 (Tetraethylammonium tetrafluoroborate / TEATFB – 1M per litre of solvent) [2] and is considered the same for all supercapacitors. It is the one used today on the market, it is low cost but no tests were performed to prove that it is the optimal choice for graphene. Different electrode materials work better when coupled with the properly matching electrolyte that has to be compatible with the porosity and wettability properties of the material (further details in Chapter 2 paragraph 2.3.2). For this reason several electrolytes should be tested to understand what the best match is for graphene, because if a more compatible electrolyte is found, it would improve the performance of the supercapacitor.

Ionic liquids were tested but did not show any positive result. It is likely that the vacuum-filling process used at Maxwell to fill supercapacitors (the same used for the acetonitrile) was not ideal for the ionic liquid tested and, as a result, the liquid did not wet enough active material. It is also possible that the ionic liquid chosen was not the right one and thus further research in this area is welcomed. Ionic liquids have a higher boiling point hence they can reach higher operational temperatures, they can have wider electrochemical windows thus operate at higher voltages, they are not flammable and they can be less or non-toxic.

Summarising, the supercapacitors were modelled as follows:

- Activated carbon supercapacitor: all data provided by Maxwell were relative to a 25 F supercapacitor therefore to calculate the quantities for a 5 F supercapacitor some assumptions were used. The total weight of a 5 F device was taken from Maxwell supercapacitors technical specifications publicly available online, the weight of the activated carbon was divided by five and the remaining weight was distributed on the remaining components based on their relative contribution to the overall weight. As no data were disclosed on the activated carbon production process due to commercial sensitiveness secondary specific data are used from another activated carbon production process available in the GaBi 6 database. For the electrolyte instead, only the acetonitrile is taken into account as no environmental data were found on the salt used.
- Graphene supercapacitors: all data are provided from Maxwell in detail for the type and mass of all material used and the energy consumption. Data on graphene specific capacitance are measured at INCAR and Maxwell and the weight of graphene needed to reach the required 5 F is calculated using the values measured for commercial graphene as reference. The electrolyte and electrode production process are the same as for the activated carbon supercapacitor. The graphene production is modelled according to a simulation of commercial-scale production. The simulations are based on experimental results presented in Chapter 3.

A break-even point is also calculated in order to evaluate the value of specific capacitance for the graphene supercapacitor to become better than the activated carbon technology in terms of environmental impacts.

4.1.4 Sensitivity analysis

In the modelling of chemical and thermal processes, the heat losses are not included and, in order to include them, sensitivity analysis is performed. In fact, in an industrial furnace there are some heat losses to the external environment and they must be compensated by some heat input.

The heat losses percentage values have been selected assuming to use very well insulated furnaces. They depend on temperature, as to higher temperatures correspond larger losses, and on the duration of the operation, as the heat is continuously lost to the surrounding environment during operations. The selected percentages refer to the original heat input values resulting from the adiabatic process modelling and they are:

- Chemical oxidation: 5% of heat loss every hour (T = 35 °C) that is 8% increase on the overall energy consumption as this process lasts slightly more than 1 hour.
- Chemical reduction: 10% of heat loss every hour (T = 85 °C) that is 240% increase on the overall energy consumption as this process lasts for 24 hours.
- Thermal reduction:
  - 10% of heat loss every hour (T = 25 °C -> 140 °C) is roughly 20% increase of the energy used for this first section of temperature increase lasting around 2 hours including 30 min holding.
  - 15% of heat loss every hour (T = 140 °C -> 350 °C) is a 185% increase of the energy used for this second section of temperature increase lasting slightly more than 12 hours including 30 min holding.
  - 20% of heat loss every hour (T = 350 °C -> 700 °C) is a 120% increase of the energy used for this third section of temperature increase lasting about 6 hours and 30 minutes including 2 hours holding.

  Summing the three phases results in a total of roughly 110% increase over the 3 stages (i.e. on the total energy consumption over 20 h of operation).

These values are assumed based on the fact that an industrial process usually limits heat losses to the minimum and a 20% of energy lost every hour seemed a reasonable upper limit. The other percentages are assumed scaling them with the temperature

Another crucial point is the quality of the material produced in terms of specific capacitance. According to the literature graphene could theoretically reach a specific capacitance of 550 F/g [11] while, according to INCAR, activated carbon could possibly reach around 200 F/g [9].

The specific capacitance value measured for Maxwell activated carbon material was averaging around 100 F/g while for graphene only the chemically produced material is taken into consideration due to the poor performance of the electrochemically exfoliated material. The specific capacitance of the chemically produced graphene was measured as 80 F/g in the case of the rGO2C material [9].

As previously explained (paragraph 4.1.3), when the material is placed in a supercapacitor, the capacitance value must be divided by 4 to obtain the theoretical value achievable with that device. Therefore, assuming that future developments of both technologies and electrolytes will progress towards the theoretical values of 550 F/g for graphene and 200 F/g for activated carbon, the theoretical achievable values for both the supercapacitors will be:

- activated carbon 50 F/g (100% more capacitance means 50% smaller electrodes)
- graphene 135 F/g (675% more capacitance means 85% smaller electrodes)

This means that the quantity of the material in a supercapacitor will be reduced resulting in a reduced environmental impact.

For the rGO2T material the sensitivity analysis assumes a performance deterioration of 35% in order to include laboratory personnel comment stating that this type of material, of which the specific capacitance was never measured, might not perform as well as the rGO2C (paragraph 4.1.2.2.3). A deterioration of the material specific capacitance of 35% means an increase in material quantity of roughly about 50%[2].

There is one important thing to notice however, when tested inside a prototype device (crafted with a more manual process) the activated carbon capacitance was 21 F/g, when tested as pure material it was 100 F/g (25 F/g if inside a theoretical supercapacitor with no losses) but in a rolled supercapacitor, according to Maxwell datasheets, there are 2.3 g of activated carbon in a 25 F supercapacitor. This indicates a large reduction of capacitance that might be due to a cost vs performance optimised production process. However, the standard production process used by Maxwell was not disclosed in detail and is not possible to speculate further. Thus, for the sensitivity analysis the basic material capacitance is used as reference.

The casing size is also evaluated as the device volume inherently scales with the electrode size variation. Higher capacitance means larger capability of storing

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[2] (Standard performance = 20F/g. Performance reduced by 35% = 13 F/g. Mass of graphene (20 F/g) in a 5 F supercapacitor = 0.27g. Mass of graphene (13 F/g) in a 5 F supercapacitor = 0.4 g that equals roughly 0.27 + 50%)

electrons and consequently a lower quantity of graphene is needed to achieve the desired performance. When the material quantity reduces, it is assumed that all other materials reduce with a linear relation (it was not possible to verify this assumption. It might as well be that a weight reduction corresponds to a density reduction to allow for more storage space). Therefore, the same sensitivity range tested for graphene and activated carbon is applied to the supercapacitor casing.

It is important to evaluate what happens if the casing would be made using aluminium, as in the commercial supercapacitors, since the stainless steel is a more problematic material for some impact categories. For instance, the ozone depletion category is not driven by the graphene production but by the stainless steel casing that has a much bigger environmental impact if compared to the aluminium casing. The stainless steel has a density that is on average 2.5 – 3 times higher than the aluminium [12], but the weight of the aluminium casing is calculated only as 2 times lighter than the stainless steel one in order to compensate for a likely thickness increase due a to a minor strength and stiffness of aluminium compared to stainless steel.

	Sensitivity		
AC	-50%	Quantity of Activated Carbon	0%
	-50%	Activated Carbon Casing Size	0%
rGO2C	-85%	Quantity of Graphene	0%
	-85%	Casing Size	0%
	0%	Electricity - Graphite Oxidation (per hour)	+8%
	0%	Electricity - Chemical Reduction	+240%
	-90%	Acid Use and Neutralisation	0%
rGO2C	0%	Quantity of Graphene	+50%
	0%	Casing Size	+ 50%
	0%	Electricity - Graphite Oxidation (GO2)	+8%
	0%	Electricity - Thermal Reduction	+110%
	-90%	Acid Use and Neutralisation	0%
	Aluminium casing (X/2 g) Vs stainless steel casing (X g) for rGO2x		

Table 4.2 – Summary of sensitivity analysis

Also the acid neutralisation for the graphite chemical oxidation phase is evaluated as, in the current process, all used acid must be neutralised. In this case, assuming an efficient industrial case, there will be a way of reusing the acid in order to reduce cost. According to the quantity of sulphuric acid involved and to the reaction performed ($KMnO_4 + NaNO_3 + H_2SO_4 \rightarrow MnSO_4 + NO_2 + Na_2SO_4 + K_2SO_4 + H_2O$), about 97% of the acid is used as solvent and does not take part in the reaction. However, the formula used does not take into account the graphite oxidation. Some SO_4^- ions might intercalate into the graphite layers consuming some of the 97% excess acid. Consequently, is reasonable to assume that a reduction of -90% in the acid consumption is possible.

No neutralisation is modelled for the chemical reduction, as it is of a minor concern and a very little portion of the acidic waste coming from the oxidation reaction could be used as neutralising agent. All the described variations that have been applied for the sensitivity analysis are summarised in Table 4.2

Additionally, a break-even point is calculated in order to evaluate the value of specific capacitance for the graphene supercapacitor to become better than the activated carbon technology in terms of environmental impacts for the case in which 90% of acid is reused and therefore 90% of the acid is also not neutralised.

4.1.5 Alternative scenarios

Two scenarios are evaluated. The first one stems from the analysis evaluating the swapping of the stainless steel with aluminium for the case of the prototype and it takes it one step further by evaluating what would happen if the graphene electrode would be placed inside a casing used for commercial supercapacitors. The whole package is therefore scaled linearly following the ratio between activated carbon and graphene weight. However, this scenario does not take into consideration the performance loss of the material inside a commercial supercapacitor (paragraph 4.1.4 page 82)

The second scenario, instead, is generated in order to evaluate what could happen in a hypothetical situation in which all possible improvements tested in the sensitivity analysis are met for the rGO2C material due to some future technological developments. The heat losses are included in this scenario. Concerning the rGO2T material, a downgrade of its specific capacitance is tested with exactly the same values used in the sensitivity analysis. This is done in accordance with the judgement of Danubia personnel that estimated a possible lower specific capacitance for this material.

Summarising:

- **Original scenario:** original values with the same quantity of graphene for both graphene based supercapacitors
- **Graphene with commercial casing scenario (AC package):** state of the art commercial package sized for graphene electrodes. The graphene specific capacitance is the one measured in laboratory and not modified.
- **Alternative scenario:** all values used for the sensitivity analysis presented in Table 4.2 are applied to the activated carbon and rGO2C and rGO2T materials.

4.2 Results

In this section the inventory of the life cycle for production (cradle to gate) is presented. All numbers are scaled to the selected functional unit that was selected to be a capacitance of 5 F.

4.2.1 Graphene production

For the best case scenario for the electrochemical exfoliation, the results are presented in Table 4.3. Further improvements to this process are possible (see Chapter 3 paragraph 3.2.2) but they were not explored.

Inputs for 1 g of graphene KOH 15V		
Electricity	2.04	MJ
Graphite	2.29	g
Potassium hydroxide	1.87	g
Water (deionised)	0.67	kg

Table 4.3 – Inputs for commercial-scale electrochemical exfoliation of graphite

For example, Table 4.4 shows that among the outputs of this process there are hydrogen and oxygen. These are valuable substances and could be stored and used in other processes, displacing new production or they could be used in a fuel cell in order to reduce the energy consumption of the graphene production. Those improvements could not be evaluated in this study as there was no possibility to measure the quantities released. It was also not possible to calculate those values as the reaction is not stoichiometric (part of the oxygen and hydroxyl groups present in the solution intercalates in the graphite rod for the exfoliation and the amount that intercalates is unknown).

Electrochemical exfoliation KOH 15V		
Outputs		
Graphene - Expanded Graphite (KOH)	0.71	g
Hydrogen [Inorganic emissions to air]	12	g
Oxygen [Inorganic emissions to air]	102	g
Potassium hydroxide [Inorganic emissions to fresh water]	1.33	g
Graphene oxide [Emissions to fresh water]	3.1	g

Table 4.4 – Outputs from the commercial-scale electrochemical exfoliation of graphite

For the chemical processes, instead, they both start with the chemical oxidation and differ for the reduction stage that can be chemical or thermal. Results of the inventory are presented in Table 4.5, Table 4.6 and Table 4.7 for the input materials. The inventory in Table 4.5 is exactly as the one presented in the previous chapter for the GO2, but differs due to a lower electricity requirement for a commercial-scale process.

Inputs for GO2 (1g)		
Electricity	0.006	MJ
Graphite	0.71	g
Sulphuric acid aq. (96%)	30.2	g
Water (deionised)	223	g
Hydrogen peroxide (100%)	1.24	g
Sodium nitrate	0.36	g
Potassium permanganate	2.14	g
Calcium hydroxide*	22.8	g
* used for neutralising 100% of the acid (s) used		

Table 4.5 – Inputs for commercial-scale GO2 production: chemical oxidation materials inventory

The sulphuric acid is neutralised using calcium hydroxide as this was found to be the least impacting after evaluating some common alkaline materials (see Appendix A paragraph A.2). The neutralisation of the sulphuric acid used in the chemical oxidation with calcium hydroxide produces gypsum $CaSO_4*2H_2O$ and it is listed in Table 4.9 together with all estimated outputs for the complete transformation of graphite into rGO2C at commercial-scale.

Inputs for rGO2C (1g)		
Electricity	0.008	MJ
Ammonia	0.34	g
Graphite Oxide	1.25	g
Water (deionised)	163	g
Hydrazine	1.38	g
Methanol	10	g

Table 4.6 – Commercial-scale rGO2C production: chemical reduction materials inventory

The chemical reduction is presented in Table 4.6 and also in this case it shows the same values presented in the previous chapter with a difference in the electricity consumption that is now related to an industrially produced reduced graphite oxide (here called rGO2C) in an adiabatic reactor. The difference with laboratory data is very large, from 1.51 MJ to less than 0,01 MJ, almost 200 times less as the process runs for 24 h and this illustrate that in the laboratory the heating process has a very low efficiency

Inputs for rGO2T (1g)		
Electricity	0.01	MJ
Graphite Oxide	1.67	g
Argon	14	g

Table 4.7 – Commercial-scale rGO2T production: Thermal reduction materials inventory

In the thermal reduction (Table 4.7) the decrease of the electricity consumption is the largest, from 5.5 MJ to 0.01 MJ, since also this process runs for long hours at high temperature. However, is to be noted that if it was not necessary to dry the material before entering the thermal reduction, this process would be the least energy consuming. The energy needed would be slightly less than 0.002 MJ (roughly 0.5 Wh) since there is less material to be heated (no added chemicals). However the drying process requires 0.009 MJ per gram of material produced making this process more energy demanding than the chemical reaction (in the case of an adiabatic system).

Material	Base MJ	Improved MJ	Commercial MJ
GO2	0.043	0.009	0.006
rGO2C	1.51	0.38	0.008
rGO2T	5.51	0.28	0.01

Table 4.8 – Comparison of electricity consumption among the base scenario, the improved lab scenario and the final commercial-scale simulation

However, those differences are not so big if compared with the improved lab scenario presented in the previous chapter, in which the laboratory process output is maximised keeping the same energy consumption. Table 4.8 shows that the chemical oxidation, for example, is already quite energy efficient as it happens over a short period of time with limited heat losses. The chemical and thermal reductions, instead, need longer time, and as result there are larger heat losses.

This also shows that for the chemical oxidation the environmental improvements should come from the optimisation of the chemical reaction since the electricity consumption is close to the value obtained simulating an adiabatic reactor.

Chemical Oxidation and Reduction			
Outputs	**GO2**	**rGO2C**	
Graphite Oxide 2 [Intermediate products]	0.34		g
Water (desalinated; deionised) [Operating materials]	33.8		g
Nitrogen dioxide [Inorganic emissions to fresh water]	0.18		g
Potassium [Inorganic emissions to fresh water]	0.51		g
Sulphate [Inorganic emissions to fresh water]	1.92		g
Gypsum (contaminated with 0.675g Mn)	14.4		g
Graphene - Reduced Graphite Oxide 2		0.27	g
Nitrogen [Inorganic emissions to fresh water]		0.58	g
Nitrogen (atmospheric) [Inorganic emissions to air]		0.58	g
Water vapour [Inorganic emissions to air]		0.77	g

Table 4.9 – Outputs from the commercial-scale rGO2C production: chemical oxidation and chemical reduction of graphite

Emissions and wastes (Table 4.9 and Table 4.10) are assumed to be released to the environment without treatment except for the neutralisation of sulphuric acid. This is not what would happen in a commercial-scale process, but this is a way to appreciate a worst case scenario. A real process, in fact, can only improve the results presented in this study.

Chemical oxidation and Thermal reduction			
Outputs	**GO2**	**rGO2T**	
Graphite Oxide 2 [Intermediate products]	0.45		g
Water (desalinated; deionised) [Operating materials]	45		g
Nitrogen dioxide [Inorganic emissions to fresh water]	0.24		g
Potassium [Inorganic emissions to fresh water]	0.68		g
Sodium sulphate [Inorganic emissions to fresh water]	0.29		g
Gypsum (contaminated with Mn)	19.14		g
Graphene - Reduced Graphite Oxide 2 (thermal)		0.27	g
Carbon dioxide [Inorganic emissions to air]		0.28	g
Carbon monoxide [Inorganic emissions to air]		0.18	g
Hydrocarbons (unspecified) [Organic emissions to air]		0.16	g
Polycyclic aromatic hydrocarbons [Group PAH to air]		0.32	g
Water vapour [Inorganic emissions to air]		0.06	g

Table 4.10 – Outputs from the commercial-scale rGO2T production: chemical oxidation and thermal reduction of graphite

From the nanomaterial particles release, measurements from IOM declared that no airborne particles were detected during the operations in the laboratory [1] and those operations are considered transferred to the industrial processes.

4.2.2 Supercapacitor manufacturing process

When combining the data of the commercial-scale graphene production with the data for the supercapacitor assembling, it is possible to evaluate which, among all processes, consumes more energy. Table 4.11 shows all data adjusted to the quantities needed for a 5 F supercapacitor. The data presented are those related to each part of the production process and they are not aggregated.

Looking at the data for the supercapacitors assembling, the main differences among supercapacitors are in the electrode weight, therefore in the quantity of active material used, and in the different materials used (e.g. stainless steel instead of aluminium for the casing). The MJ of electricity needed for the assembly of the prototype is slightly higher than for the model on the market; this is due to a different welding procedure that is not as efficient as the one used for the aluminium cylindrical casing.

When looking at the overall picture, it is important to notice that the electricity consumption for the graphene synthesis is quite significant for the electrochemical exfoliation, but it is quite small for the chemical routes.

Figure 4.9 shows the results of the cradle to gate LCA for the global warming potential. The activated carbon supercapacitor proves to be the least impacting technology but the graphene prototype shows interesting results that are comparable to those of the commercial state of the art supercapacitors.

Materials for a supercapacitor production	**Activated Carbon**	**KOH (15 V)**	**rGO2C**	**rGO2T**	
Supercapacitor Assembling					
Electrode (details below)	0.69	0.91	0.47	0.47	g
Case (aluminium)	0.52	-	-	-	g
Case (stainless steel)	-	1.5	1.5	1.5	g
Collectors (aluminium)	0.1	0.05	0.05	0.05	g
Electricity	0.07	0.1	0.1	0.1	MJ
Electrolyte	0.58	0.36	0.36	0.36	g
Paper Separator	0.1	0.02	0.02	0.02	g
Rubber	0.2	-	-	-	g
Lid (aluminium)	0.1	-	-	-	g
Electrode Production					
Activated carbon	0.52	-	-	-	g
Graphene (details below)	-	0.71	0.27	0.27	g
Aluminium foil	0.17	0.2	0.2	0.2	g
Electricity	0.01	0.01	0.01	0.01	MJ
Active Material Production					
Electricity	-	1.45	0.004	0.0055	MJ
Graphite	-	1.63	0.24	0.31	g
Potassium hydroxide	-	1.33	-	-	g
Water (desalinated; deionised)	-	0.48	0.12	0.09	kg
Ammonia	-	-	0.09	-	g
Hydrazine	-	-	0.37	-	g
Ethanol	-	-	2.7	-	g
Argon	-	-	-	3.87	g
Sulphuric acid aq. (96%)	-	-	10.2	13	g
Hydrogen peroxide (100%)	-	-	0.42	0.53	g
Sodium nitrate	-	-	0.12	0.15	g
Potassium permanganate	-	-	0.72	0.92	g
Calcium hydroxide	-	-	7.7	10.3	g

Table 4.11 – Material inventory for a 5 F supercapacitor commercial-scale production

Figure 4.10 and Figure 4.11 show the breakdown for the global warming potential of the rGO2C and rGO2T materials. They show how the rGO2T requires more GO2 material to synthesise the 0.27 g of graphene needed to achieve the 5 F capacitance, but also how the thermal reduction process has lower impact than the chemical one. What is important, though, it is that for both processes, when scaled up without heat losses, the most impacting activity is the supercapacitor manufacturing. This includes the electricity for the assembly plus all materials needed for a supercapacitor.

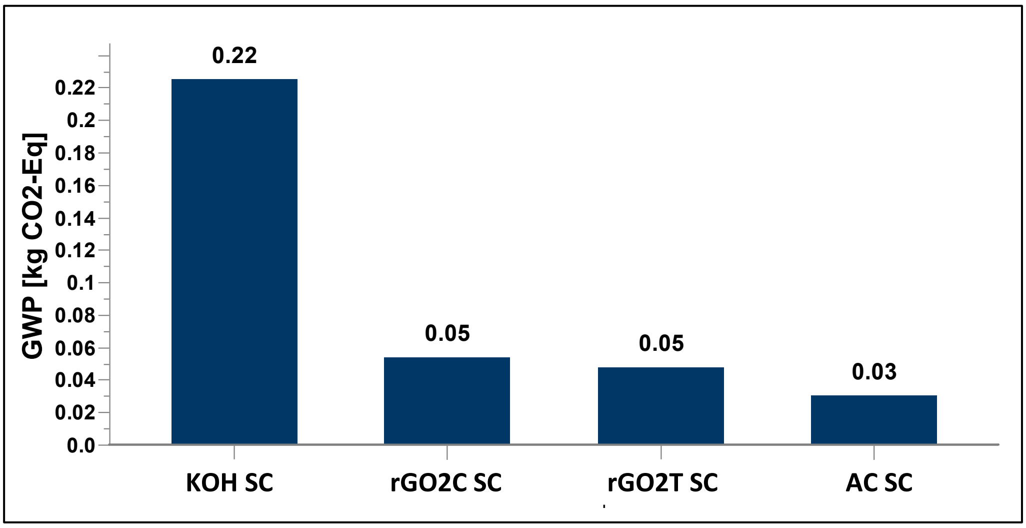

Figure 4.9 – Global warming potential: commercial-scale 5 F supercapacitor manufacturing. The activated carbon based supercapaictor is the least impacting (37% less than the rGO2T based, 44% less than the rGO2C based and 87% less than the KOH based)

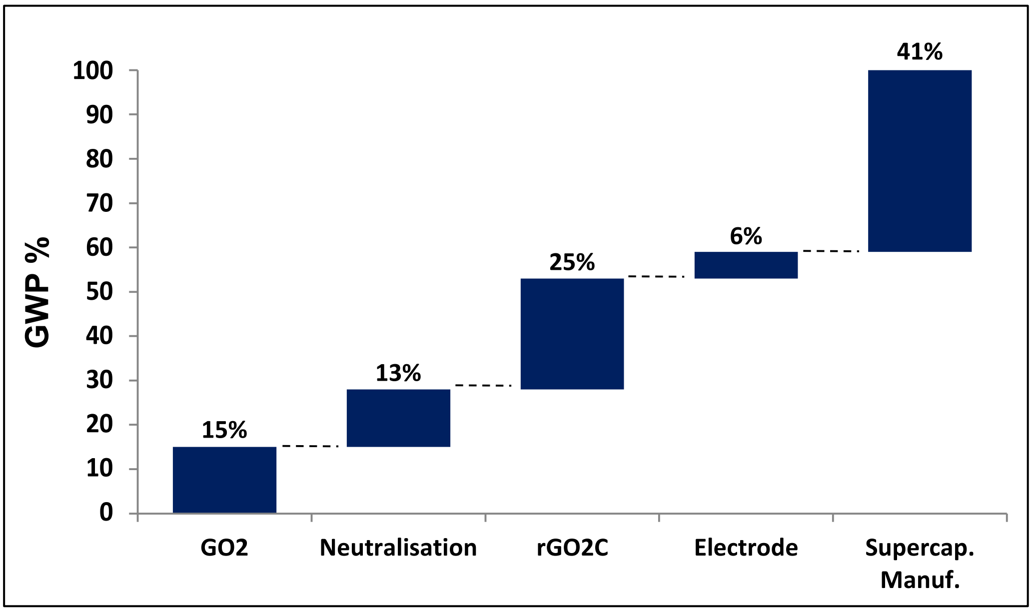

Figure 4.10 – Global warming potential: commercial-scale rGO2C based supercapacitor production breakdown in percentage of materials and energy inputs. The chemical reduction and the supercapacitor manufacturing are the most impacting activities.

The only difference between the two processes lies in the reduction step (broken down in Figure 4.12 and Figure 4.13). Even if the rGO2T consumes more electricity and requires more GO2, it is a less impacting reduction process as the use of hydrazine and ammonia makes the rGO2C slightly more harmful for the ecosystem. However, due to a very similar impact values between the two materials and the level of uncertainty in the study, it is not possible to clearly state which one of the two is least impacting. What is also to be noticed is that the impact related to emissions and wastes (grouped with water and labelled “rest” in Figure 4.12 and emissions in Figure 4.13) can be considered negligible.

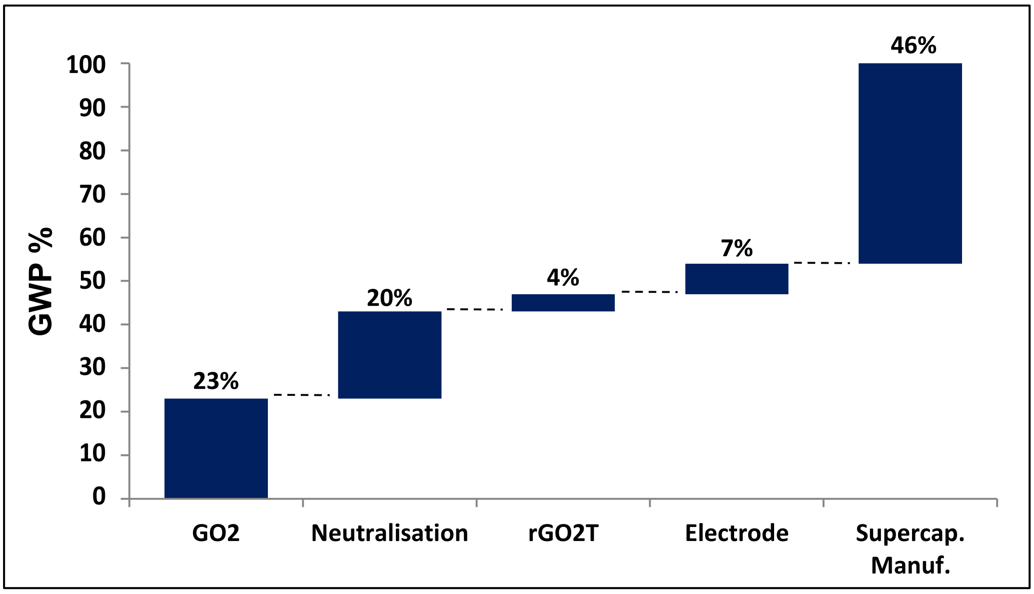

Figure 4.11 – Global warming potential: commercial-scale rGO2T based supercapacitor production breakdown in percentage of materials and energy inputs. The oxidation, the acid neutralisation and the supercapacitor manufacturing are the most impacting activities.

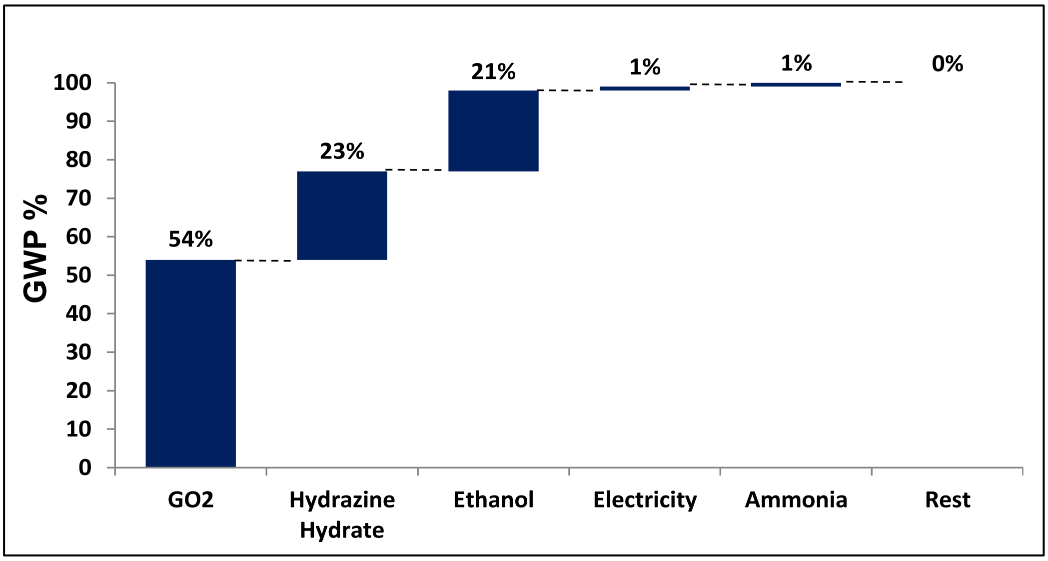

Figure 4.12 – Global warming potential: GO2 commercial-scale chemical reduction breakdown in percentage of materials and energy inputs. Hydrazine and ethanol make the chemical reduction more impacting than the thermal reduction.

Table 4.12 presents the results for all supercapacitor productions and for all impact categories. It is possible to see how the current activated carbon production is the best possible solution in terms of environmental impacts.

The two chemical processes are virtually identical, with a slight advantage towards the rGO2T in 7 out of 13 categories due to the use of hydrazine and ammonia in the rGO2C production process. In the remaining categories hydrazine and ammonia are not so problematic and therefore the rGO2C material becomes a favourable option (considering the same specific capacitance for both rGO2T and rGO2C graphene materials). The supercapacitor using graphene obtained via electrochemical exfoliation presents higher impacts due to the poor performance of the graphene.

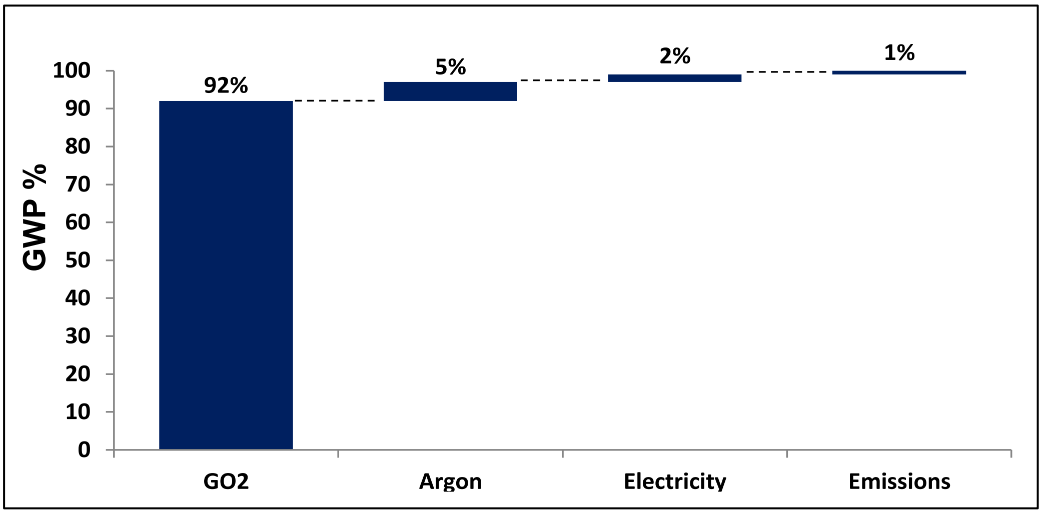

Figure 4.13 – Global warming potential: GO2 commercial-scale thermal reduction breakdown in percentage of materials and energy inputs. Very limited impacts are related to the thermal reduction as it only needs to heat some grams of graphene and no other chemicals

	COMPARISON OF SCALED UP SUPERCAPACITORS			
	KOH	**rGO2C**	**rGO2T**	**A. Carb**
Global Warming Potential [kg CO2-Equiv.]	2.25E-01	5.39E-02	4.75E-02	3.00E-02
Ozone Depletion [kg CFC 11-Equiv.]	5.07E-10	3.73E-10	3.74E-10	3.87E-11
Human toxicity, cancer [CTUh]	9.60E-11	5.36E-11	5.22E-11	1.33E-11
Human toxicity, non-canc. [CTUh]	1.19E-08	6.02E-09	6.14E-09	1.47E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	7.65E-05	1.85E-05	1.90E-05	1.55E-05
Ionising radiation, human health effect model, [kg U235 eq]	4.88E-01	5.03E-02	5.06E-02	4.12E-02
Photochemical ozone formation,[kg NMVOC]	4.49E-04	1.08E-04	1.06E-04	6.73E-05
Acidification [Mole of H+ eq.]	1.17E-03	3.08E-04	3.18E-04	1.53E-04
Terrestrial eutrophication, [Mole of N eq.]	1.58E-03	3.51E-04	3.16E-04	2.34E-04
Freshwater eutrophication, [kg P eq]	2.86E-07	1.36E-07	1.07E-07	2.31E-08
Ecotoxicity [CTUe]	1.48E-02	1.07E-02	1.01E-02	1.28E-03
Resources depletion, water [kg]	2.71E-01	4.43E-02	4.13E-02	2.93E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	3.30E-06	1.03E-06	1.15E-06	2.38E-07

Table 4.12 – Cradle to gate commercial-scale supercapacitors production comparison: all impact categories. The activated carbon based supercapacitor proves to be the least impacting solution for all 13 categories (green). It impacts from 18% less than the two chemical routes in the ionising ratiation to a 90% less the ozone depletion. It also impac around 80% less in the mineral and fossil resource depletion and 75% in human toxicity.

ACTIVATED CARBON SUPERCAPACITOR							
IMPACT CATEGORIES	**1st CONTRIBUTOR**	**%**	**2nd CONTRIBUTOR**	**%**	**3rd CONTRIBUTOR**	**%**	**Tot %**
Global Warming Potential [kg CO2-Equiv.]	Electriciy (Assembling)	33%	Housing (Aluminium)	28%	AC Electrode	18%	79%
Ozone Depletion [kg CFC 11-Equiv.]	AC Electrode	73%	Electriciy (Assembling)	18%	Housing (Aluminium)	6%	98%
Human toxicity, cancer [CTUh]	Housing (Aluminium)	42%	Electriciy (Assembling)	20%	AC Electrode	13%	76%
Human toxicity, non-canc. [CTUh]	Housing (Aluminium)	42%	Electriciy (Assembling)	24%	AC Electrode	14%	81%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	Housing (Aluminium)	42%	Electriciy (Assembling)	22%	AC Electrode	22%	86%
Ionising radiation, human health effect model, [kg U235 eq]	Electriciy (Assembling)	58%	Housing (Aluminium)	21%	AC Electrode	13%	92%
Photochemical ozone formation,[kg NMVOC]	Electriciy (Assembling)	29%	Housing (Aluminium)	28%	AC Electrode	17%	74%
Acidification [Mole of H+ eq.]	Electriciy (Assembling)	34%	Housing (Aluminium)	33%	AC Electrode	16%	83%
Terrestrial eutrophication, [Mole of N eq.]	Electriciy (Assembling)	29%	Housing (Aluminium)	27%	AC Electrode	16%	73%
Freshwater eutrophication, [kg P eq]	Electriciy (Assembling)	27%	Electrolyte (Acetonitrile)	25%	Insulator (Rubber)	13%	65%
Ecotoxicity [CTUe]	Housing (Aluminium)	27%	Electrolyte (Acetonitrile)	24%	Electriciy	23%	74%
Resources depletion, water [kg]	Housing (Aluminium)	42%	Electriciy (Assembling)	20%	AC Electrode	13%	76%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	Housing (Aluminium)	42%	Electriciy (Assembling)	24%	AC Electrode	14%	81%

Table 4.13 – Activated carbon supercapacitor manufacturing top contributors: the housing, the electricity for assembling and the electrode manufacturing are the main causes.

rGO2C GRAPHENE BASED SUPERCAPACITOR					
IMPACT CATEGORIES	**Supercapacitor Assembling**	**Electrode Assembling**	**rGO2C**	**Neutralisation**	**GO2**
Global Warming Potential [kg CO2-Equiv.]	41%	6%	25%	13%	15%
Ozone Depletion [kg CFC 11-Equiv.]	99%	0%	0%	0%	1%
Human toxicity, cancer [CTUh]	64%	3%	11%	9%	13%
Human toxicity, non-canc. [CTUh]	71%	3%	6%	10%	11%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	54%	11%	8%	2%	26%
Ionising radiation, human health effect model, [kg U235 eq]	66%	9%	10%	0%	15%
Photochemical ozone formation,[kg NMVOC]	53%	7%	18%	2%	20%
Acidification [Mole of H+ eq.]	53%	6%	9%	1%	31%
Terrestrial eutrophication, [Mole of N eq.]	56%	7%	19%	3%	16%
Freshwater eutrophication, [kg P eq]	49%	1%	29%	1%	20%
Ecotoxicity [CTUe]	78%	1%	9%	1%	11%
Resources depletion, water [kg]	46%	8%	19%	1%	26%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	58%	3%	1%	0%	39%

Table 4.14 – Commercial-scale rGO2C graphene based supercapacitor: exploded electrode production vs aggregated supercapacitor assembling. The assembling dominates as source of impacts followed by the graphite oxidation and reduction processes.

Table 4.13 shows that the top 3 contributors for the activated carbon supercapacitor manufacturing process account for more than 65% of its total impacts. It can be seen that the main contributors are generally electricity (for the assembling operation), the casing and the activated carbon electrode.

Concerning the graphene based supercapacitors, what is interesting is that for the commercial-scale chemical routes the supercapacitor assembling is more impacting than electrode manufacturing and the graphene synthesis for most of the analysed impact categories – excluding global warming potential, water eutrophication (only for rGO2C) and depletion (shown by Table 4.14, Table 4.15). For the electrode production, most of the impacts are related to the oxidation and reduction of graphite. This analysis shows that when the heat losses are optimised, the graphene electrode production contributes for less than half of the overall environmental impacts of the supercapacitor manufacturing.

Table 4.16 and Table 4.17 offer a different view: they are a breakdown of the three main environmental impacts contributors for the assembling phase of supercapacitors.

rGO2T GRAPHENE BASED SUPERCAPACITOR					
IMPACT CATEGORIES	Supercapacitor Assembling	Electrode Assembling	rGO2T	Neutralisation	GO2
Global Warming Potential [kg CO2-Equiv.]	46%	7%	4%	20%	23%
Ozone Depletion [kg CFC 11-Equiv.]	99%	0%	0%	0%	1%
Human toxicity, cancer [CTUh]	66%	3%	1%	12%	18%
Human toxicity, non-canc. [CTUh]	69%	3%	1%	13%	14%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	52%	10%	2%	2%	34%
Ionising radiation, human health effect model, [kg U235 eq]	65%	9%	6%	0%	19%
Photochemical ozone formation,[kg NMVOC]	53%	7%	10%	3%	27%
Acidification [Mole of H+ eq.]	52%	6%	1%	1%	40%
Terrestrial eutrophication, [Mole of N eq.]	62%	7%	3%	4%	24%
Freshwater eutrophication, [kg P eq]	62%	1%	2%	1%	34%
Ecotoxicity [CTUe]	82%	1%	0%	1%	15%
Resources depletion, water [kg]	49%	8%	3%	2%	37%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	62%	7%	3%	4%	24%

Table 4.15 – Commercial-scale rGO2T graphene based supercapacitor: exploded electrode production vs aggregated supercapacitor assembling. The assembling is the largest contributor but the electrode manufacturing, especially the graphite oxidation, is only slightly less impacting

rGO2C GRAPHENE BASED SUPERCAPACITOR							
IMPACT CATEGORIES	1st CONTRIBUTOR	%	2nd CONTRIBUTO	%	3rd CONTRIBUTO	%	Tot %
Global Warming Potential [kg CO2-Equiv.]	Graphene Electrode	59%	Electriciy (Assembling)	24%	Housing (s. steel)	12%	95%
Ozone Depletion [kg CFC 11-Equiv.]	Housing (s. steel)	96%	Electriciy (Assembling)	3%	Graphene Electrode	1%	100%
Human toxicity, cancer [CTUh]	Housing (s. steel)	56%	Graphene Electrode	36%	Electriciy (Assembling)	7%	98%
Human toxicity, non-canc. [CTUh]	Housing (s. steel)	61%	Graphene Electrode	29%	Electriciy (Assembling)	8%	98%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	Graphene Electrode	46%	Housing (s. steel)	26%	Electriciy (Assembling)	25%	97%
Ionising radiation, human health effect model, [kg U235 eq]	Electriciy (Assembling)	63%	Graphene Electrode	34%	Collectors	1%	98%
Photochemical ozone formation,[kg NMVOC]	Graphene Electrode	47%	Electriciy (Assembling)	24%	Housing (s. steel)	22%	93%
Acidification [Mole of H+ eq.]	Graphene Electrode	47%	Housing (s. steel)	28%	Electriciy (Assembling)	22%	97%
Terrestrial eutrophication, [Mole of N eq.]	Graphene Electrode	44%	Electriciy (Assembling)	26%	Housing (s. steel)	22%	92%
Freshwater eutrophication, [kg P eq]	Graphene Electrode	51%	Housing (s. steel)	40%	Electriciy (Assembling)	6%	97%
Ecotoxicity [CTUe]	Housing (s. steel)	73%	Graphene Electrode	22%	Electriciy (Assembling)	4%	98%
Resources depletion, water [kg]	Graphene Electrode	54%	Electriciy (Assembling)	32%	Housing (s. steel)	9%	94%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	Housing (s. steel)	56%	Graphene Electrode	42%	Collectors	1%	99%

Table 4.16 – rGO2C graphene based supercapacitor manufacturing top contributors. The exploded supercapacitor assembling process shows that the aggregated electrode manufacturing generates half of the impacts originating from the supercapacitor manufacturing process.

rGO2T GRAPHENE BASED SUPERCAPACITOR							
IMPACT CATEGORIES	1st CONTRIBUTOR	%	2nd CONTRIBUTO	%	3rd CONTRIBUTO	%	Tot %
Global Warming Potential [kg CO2-Equiv.]	Graphene Electrode	54%	Electriciy (Assembling)	27%	Housing (s. steel)	14%	95%
Ozone Depletion [kg CFC 11-Equiv.]	Housing (s. steel)	96%	Electriciy (Assembling)	3%	Graphene Electrode	1%	100%
Human toxicity, cancer [CTUh]	Housing (s. steel)	57%	Graphene Electrode	34%	Electriciy (Assembling)	7%	98%
Human toxicity, non-canc. [CTUh]	Housing (s. steel)	60%	Graphene Electrode	31%	Electriciy (Assembling)	8%	98%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	Graphene Electrode	48%	Housing (s. steel)	25%	Electriciy (Assembling)	24%	97%
Ionising radiation, human health effect model, [kg U235 eq]	Electriciy (Assembling)	62%	Graphene Electrode	35%	Collectors	1%	98%
Photochemical ozone formation,[kg NMVOC]	Graphene Electrode	47%	Electriciy (Assembling)	24%	Housing (s. steel)	22%	93%
Acidification [Mole of H+ eq.]	Graphene Electrode	48%	Housing (s. steel)	27%	Electriciy (Assembling)	22%	97%
Terrestrial eutrophication, [Mole of N eq.]	Graphene Electrode	38%	Electriciy (Assembling)	29%	Housing (s. steel)	24%	92%
Freshwater eutrophication, [kg P eq]	Housing (s. steel)	51%	Graphene Electrode	38%	Electriciy (Assembling)	8%	96%
Ecotoxicity [CTUe]	Housing (s. steel)	76%	Graphene Electrode	18%	Electriciy (Assembling)	4%	98%
Resources depletion, water [kg]	Graphene Electrode	51%	Electriciy (Assembling)	34%	Housing (s. steel)	9%	94%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	Housing (s. steel)	50%	Graphene Electrode	49%	Collectors	1%	99%

Table 4.17 – rGO2T graphene based supercapacitor top contributors. The exploded supercapacitor assembling process shows that the aggregated electrode manufacturing generates almost half of the impacts originating from the supercapacitor manufacturing process.

KOH GRAPHENE BASED SUPERCAPACITOR			
IMPACT CATEGORIES	Supercapacitor Assembling	Electrode Assembling	KOH Graphene
Global Warming Potential [kg CO2-Equiv.]	10%	1%	89%
Ozone Depletion [kg CFC 11-Equiv.]	73%	0%	27%
Human toxicity, cancer [CTUh]	36%	2%	62%
Human toxicity, non-canc. [CTUh]	36%	2%	63%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	13%	3%	84%
Ionising radiation, human health effect model, [kg U235 eq]	7%	1%	92%
Photochemical ozone formation,[kg NMVOC]	13%	2%	86%
Acidification [Mole of H+ eq.]	14%	2%	84%
Terrestrial eutrophication, [Mole of N eq.]	12%	1%	86%
Freshwater eutrophication, [kg P eq]	23%	0%	76%
Ecotoxicity [CTUe]	56%	1%	43%
Resources depletion, water [kg]	8%	1%	91%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	18%	1%	81%

Table 4.18 – Commercial-scale KOH graphene based supercapacitor: electrode production vs supercapacitor assembling. The exfoliation of graphite is the largest source of environmental impacts in all impact categories

This different breakdown shows that, within the supercapacitor manufacturing, the graphene electrode production is still one of the main contributors together with the stainless steel casing and the electricity consumption (of the manufacturing process only). It is also worth mentioning that the top 3 impact contributors account for more than 90% of the overall impact in each category.

For the exfoliated graphene (Table 4.18) the graphene production, and therefore the electricity consumption, is the main environmental burden. As the electrochemical exfoliation proved to be the most impacting and the least suitable for supercapacitor applications, it is not analysed any further.

Table 4.19 shows the break-even point values of specific capacitance per each category beyond which the graphene supercapacitors (rGO2C and rGO2T) have a lower impact than the activated carbon supercapacitor. It shows that the rGO2C material could become better than activated carbon only in four categories, while the rGO2T only in five (provided it has the same specific capacitance of rGO2C). This is quite important because it means that improving only the material performance is not enough to make the graphene supercapacitor the least impacting (even when reaching its upper theoretical limit of specific capacitance of

135 F/g is a supercapacitor configuration). More should be done therefore to improve the graphene synthesis in order to make it less impacting than activated carbon per gram of material produced (current situation depicted in Table 4.20). Though, these results do not take into consideration the variation in the casing as consequence of a reduced graphene quantity requirement.

	Global Warming Potential [kg CO2-Equiv.]	Ozone Depletion [kg CFC 11-Equiv.]	Human toxicity, cancer [CTUh]	Human toxicity, non-canc. [CTUh]	Particulate matter / Respiratory inorganics, [kg PM2,5-Equiv.]	Ionising radiation, human health effect model, [kg U235 eq]	Photochemical ozone formation,[kg NMVOC]	Acidification [Mole of H+ eq.]	Terrestrial eutrophication, [Mole of N eq.]	Freshwater eutrophication, [kg P eq]	Ecotoxicity [CTUe]	Resources depletion, water [kg]	Resource Depletion, fossil and mineral [kg Sb-Equiv.]
	Specific Capacitance [F/g] to achieve for graphene to impact less than activated carbon												
rGO2C	125	Never	Never	Never	36	74	Never	Never	Never	Never	Never	77	Never
rGO2T	97	Never	Never	Never	43	76	Never	Never	128	Never	Never	66	Never

Table 4.19 – Specific capacitance to achieve for graphene to impact less than activated carbon

	Impact per gram of material		
	AC	**rGO2C**	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	4.98E-03	1.06E-01	8.27E-02
Ozone Depletion [kg CFC 11-Equiv.]	5.24E-11	1.00E-11	1.23E-11
Human toxicity, cancer [CTUh]	6.31E-13	6.46E-11	5.95E-11
Human toxicity, non-canc. [CTUh]	7.04E-11	5.84E-09	6.30E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	3.15E-06	2.43E-05	2.64E-05
Ionising radiation, human health effect model, [kg U235 eq]	2.18E-03	4.64E-02	4.76E-02
Photochemical ozone formation,[kg NMVOC]	9.92E-06	1.63E-04	1.57E-04
Acidification [Mole of H+ eq.]	1.58E-05	4.65E-04	5.02E-04
Terrestrial eutrophication, [Mole of N eq.]	3.34E-05	4.91E-04	3.60E-04
Freshwater eutrophication, [kg P eq]	2.73E-09	2.52E-07	1.45E-07
Ecotoxicity [CTUe]	5.59E-05	8.08E-03	6.14E-03
Resources depletion, water [kg]	1.24E-03	7.63E-02	6.51E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.11E-07	1.51E-06	1.98E-06

Table 4.20 – Impacts per gram of active material

4.2.3 Sensitivity analysis

The most important result of the sensitivity analysis for the global warming potential impact category, presented in Table 4.21, is that for all technologies a large impact is connected with the active material. For the activated carbon, a reduction in the required mass of 50% translates into 9% less emissions, while, for the graphene technology, a reduction of 85% in mass reduces the emissions of about 50% for the rGO2C and 45% for the rGO2T. In this last case, an increase of 50% in mass of graphene is causing an increase of emissions of about 27%. This proves how the graphene production is the phase where most of the focus should be put in order to reduce its global warming potential.

Connected with the active material quantity variation is the size of the supercapacitor casing. For the activated carbon based supercapacitor, the case size reduction results in the largest impact. For the rGO2C graphene based supercapacitor, the impact related to the reduction of this parameter is larger than it is for the activate carbon one, but the largest impact is connected with the quantity of graphene. Summing the global warming potential (GWP) reductions obtained by reducing the active material quantity and the casing size, the results show a reduction of about 20% for the activated carbon supercapacitor and more than 60% for the rGO2C based one.

Given the almost identical impacts of the rGO2T based supercapacitor and the rGO2C based one, it is possible to say that a similar reduction of rGO2T quantity would give almost identical results as those presented for the rGO2C, but for this material an increase of 50% in quantity is tested and the result shows a GWP increase of more than 35% when including the casing size.

	Global Warming Potential [kg CO2-Equiv.]						
	Impact reduction		**Sensitivity Variation**	**Sensitivity Results Production**	**Sensitivity Variation**	**Impact increase**	
	Final Value	**%**				**%**	**Final Value**
AC	2.73E-02	-9.0%	-50%	Quantity of Activated Carbon	0%	0.0%	3.00E-02
	2.66E-02	-11.1%	-50%	Casing Size	0%	0.0%	3.00E-02
rGO2C	2.69E-02	-50.1%	-85%	Quantity of Graphene	0%	0.0%	5.39E-02
	4.71E-02	-12.6%	-85%	Casing Size	0%	7.8%	5.81E-02
	5.39E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	5.39E-02
	5.39E-02	0.0%	0%	Electricity - Chemical Reduction	+240%	4.3%	5.63E-02
	4.62E-02	-14.3%	-90%	Acid Use and Neutralisation	0%	0.0%	5.39E-02
rGO2T	4.75E-02	0.0%	0%	Quantity of Graphene	+50%	26.7%	6.02E-02
	4.75E-02	0.0%	0%	Casing Size	+ 50%	8.9%	5.18E-02
	4.75E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	4.76E-02
	4.75E-02	0.0%	0%	Electricity - Thermal Reduction	+110%	0.8%	4.79E-02
	3.73E-02	-21.6%	-90%	Acid Use and Neutralisation	0%	0.0%	4.75E-02

Table 4.21 – Sensitivity analysis results for global warming potential.

It is also interesting to notice how, even if the electricity consumption is largely increased, the variation on the GWP is minimal. This shows that a well-insulated furnace is necessary limit the impacts generated by the electricity usage and to obtain an environmental friendly graphene.

For the graphene prototypes, an important parameter is the sulphuric acid usage and neutralisation that when is reduced by 90% results in a considerable abatement of the global warming potential showing values ranging from around 15% of the rGO2C to more than 20% of the rGO2T. The latter benefits more from this reduction as it requires more GO2 to obtain the same quantity of graphene (sulphuric acid is used for GO production).

For most of the impact categories, the sensitivity analysis shows similar trends to those presented for the global warming potential (with different percentages). For the activated carbon, therefore, the casing size is the parameter generating larger variations in all impact categories except for the fresh water eutrophication in which it is linked with active material quantity. For graphene, the largest impact variations are originated by the graphene quantity, the casing size and acid use and neutralisation, in this order of importance. However, even for categories in which the parameter causing the largest impact variation is the stainless steel casing size (i.e. ozone depletion, human toxicity (cancer and non-cancer) ecotoxicity and resources depletion), the graphene quantity variation is still the most important parameter since the casing size variation is directly connected to it. The acid use/neutralisation is the third area to focus on for all impact categories (see all sensitivity tables in Appendix B paragraph B.5).

It is worth highlighting that, the electricity plays essentially an irrelevant role for all the 13 measured impact categories. This again confirms that well insulated thermal processes are necessary to minimise the environmental impacts of graphene production (as shown in Figure 4.12 and Figure 4.13).

Graphene supercapacitor casing material shift from stainless steel to aluminium

Table 4.22 shows the impacts variation obtained when changing the stainless steel material into aluminium. It shows that in some cases, the stainless steel performs better than the aluminium as in the case of the global warming potential and other 3 categories (water resource depletion +18% increase, ionising radiation and particulate matter +23%). In all other categories the benefits are more towards the aluminium casing with impact improvements ranging from 2% of the terrestrial eutrophication to 95% of the ozone depletion. The substitution seems slightly beneficial since more categories benefits from lower impacts; however, nothing is certain as it is not clear which category is more important than others.

Aluminium Case Impact Variation	**rGO2C**	**rGO2T**	**Aluminium Case Impact Variation**	**rGO2C**	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	+7%	+8%	Photochemical ozone formation,[kg NMVOC]	-2%	-2%
Ozone Depletion [kg CFC 11-Equiv.]	-95%	-95%	Acidification [Mole of H+ eq.]	-6%	-6%
Human toxicity, cancer [CTUh]	-42%	-43%	Terrestrial eutrophication, [Mole of N eq.]	-2%	-2%
Human toxicity, non-canc. [CTUh]	-47%	-46%	Freshwater eutrophication, [kg P eq]	-40%	-51%
Particulate matter/Respiratory	+24%	+23%	Ecotoxicity [CTUe]	-70%	-73%
Ionising radiation, human health effect model, [kg U235	+23%	+23%	Resources depletion, water [kg]	+17%	+18%
			Resource Depletion, fossil and mineral [kg Sb-Equiv.]	-40%	-36%

Table 4.22 – Impact variation due to casing material change from stainless steel to aluminium

	Specific Capacitance [F/g] needed for graphene to impact less than activated carbon												
	Global Warming Potential [kg CO2-Equiv.]	Ozone Depletion [kg CFC 11-Equiv.]	Human toxicity, cancer [CTUh]	Human toxicity, non-canc. [CTUh]	Particulate matter / Respiratory inorganics, [kg PM2,5-Equiv.]	Ionising radiation, human health effect model, [kg U235 eq]	Photochemical ozone formation,[kg NMVOC]	Acidification [Mole of H+ eq.]	Terrestrial eutrophication, [Mole of N eq.]	Freshwater eutrophication, [kg P eq]	Ecotoxicity [CTUe]	Resources depletion, water [kg]	Resource Depletion, fossil and mineral [kg Sb-Equiv.]
	Specific Capacitance [F/g] to achieve for graphene to impact less than activated carbon												
rGO2C	125	Never	Never	Never	36	74	Never	Never	Never	Never	Never	77	Never
rGO2T	97	Never	Never	Never	43	76	Never	Never	128	Never	Never	66	Never
	Specific Capacitance [F/g] to achieve for graphene to impact less than activated carbon 90% acid reused												
rGO2C	87	Never	Never	Never	17	66	Never	Never	Never	Never	Never	70	Never
rGO2T	46	Never	Never	Never	14	63	Never	Never	83	Never	Never	58	Never

Table 4.23 – Break-even points for specific capacitance to achieve for graphene to impact less than activated carbon including base results and with 90% acid reuse

The sensitivity analysis proved that the specific capacitance is an important factor as it reduces the quantity of graphene inside a supercapacitor and therefore its environmental impacts. Table 4.23 shows the break-even point for the specific capacitance beyond which the 5 F graphene based supercapacitor becomes better than the activated carbon based one for all impact categories. It includes the base case already presented in the previous paragraph (Table 4.19) and a scenario in which 90% of acid can be reused (therefore not neutralised) that shows some improvements; however, in the categories where the graphene production and the acid use (and neutralisation) do not impact as much, the activated carbon supercapacitor have the least impact. Although these results do not take into consideration the variation in the casing as consequence of a reduced graphene quantity requirement, they confirm that improving the material specific capacitance would not be enough to make the graphene based supercapacitor the least impacting solution and this includes the case in which 90% of the acid is recycled. In fact, like for the base case, in most categories the results will never be better than those for the activated carbon based device.

Nevertheless, some categories benefit from the acid recycling showing a lower break-even point and those are the categories in which the use of sulphuric acid has a large share on the final impacts. This proves that to further reduce impacts of graphene on the environment it is necessary to optimise the chemical reactions.

4.2.4 Alternative scenarios

In this section two different scenarios are evaluated. The first scenario presented is the "AC Package" scenario in which the graphene based electrode is placed inside the commercial supercapacitor package produced by Maxwell Technologies.

Figure 4.14 shows the result for global warming potential of this scenario modelling compared with the original values. It shows how a reduction in the casing size due to the smaller graphene electrode compared with the activated carbon electrode slightly improves the results for the graphene based supercapacitors, but not for a considerable amount.

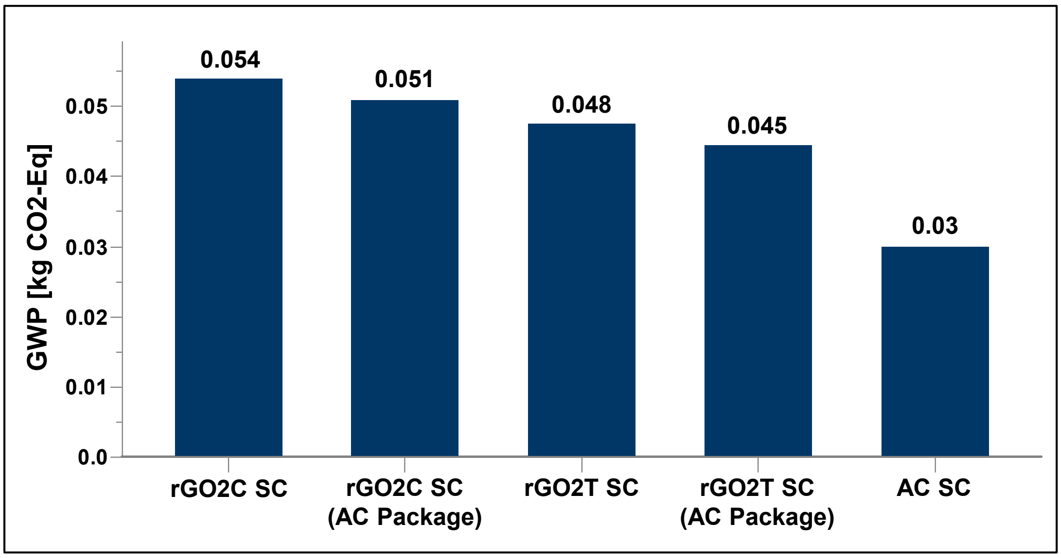

Figure 4.14 – Global warming potential scenario comparison: original vs. AC package. Activated carbon remains the least impacting technologies also when the graphene is placed in the same commercial package used for the activated carbon based supercapacitor

Table 4.24 shows the results of this comparison for all categories together with the original values of Table 4.12 and it is easy to see that the improvements derived from the change of supercapacitor casing and structure are quite small. In fact, the activated carbon commercial solution remains the least impacting in all categories excluding ozone depletion. In the latter, the stainless steel is by far the largest contributor making the original values for the graphene supercapacitors the most impacting. Moreover, in this category, the activated carbon production is the main impact driver for the supercapacitor based on activated carbon.

	SUPERCAPACITORS: ORIGINAL Vs AC PACKAGE SCENARIOS				
	rGO2C	rGO2T	rGO2C (AC Package)	rGO2T (AC Package)	Activated Carbon
Global Warming Potential [kg CO2-Equiv.]	5.39E-02	4.75E-02	5.08E-02	4.45E-02	3.00E-02
Ozone Depletion [kg CFC 11-Equiv.]	3.73E-10	3.74E-10	1.32E-11	1.38E-11	3.87E-11
Human toxicity, cancer [CTUh]	5.36E-11	5.22E-11	2.72E-11	2.59E-11	1.33E-11
Human toxicity, non-canc. [CTUh]	6.02E-09	6.14E-09	2.69E-09	2.81E-09	1.47E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.85E-05	1.90E-05	1.73E-05	1.79E-05	1.55E-05
Ionising radiation, human health effect model, [kg U235 eq]	5.03E-02	5.06E-02	4.84E-02	4.87E-02	4.12E-02
Photochemical ozone formation,[kg NMVOC]	1.08E-04	1.06E-04	9.32E-05	9.17E-05	6.73E-05
Acidification [Mole of H+ eq.]	3.08E-04	3.18E-04	2.43E-04	2.53E-04	1.53E-04
Terrestrial eutrophication, [Mole of N eq.]	3.51E-04	3.16E-04	3.04E-04	2.69E-04	2.34E-04
Freshwater eutrophication, [kg P eq]	1.36E-07	1.07E-07	8.46E-08	5.58E-08	2.31E-08
Ecotoxicity [CTUe]	1.07E-02	1.01E-02	3.13E-03	2.61E-03	1.28E-03
Resources depletion, water [kg]	4.43E-02	4.13E-02	4.39E-02	4.09E-02	2.93E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.03E-06	1.15E-06	5.33E-07	6.62E-07	2.38E-07

Table 4.24 – Original vs. AC package scenario supercapacitor comparison all categories. The activated carbon remains the least impacting technologies for 12 out of 13 categories (green).

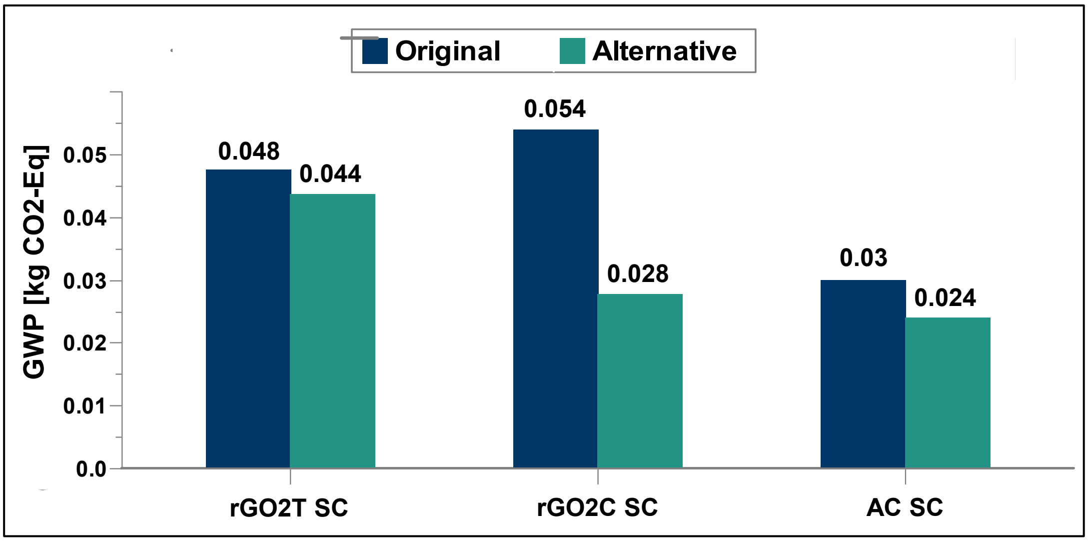

Figure 4.15 – Global warming potential: alternative scenario comparison. Activated carbon is the least impacting but the graphene technology becomes better than the current state-of-the-art supercapacitors on the market today
AC = activated carbon SC = supercapacitor

The graphene based solution with aluminium case therefore benefits from the lack of both stainless steel and activated carbon and this makes it the least impacting technology for the ozone depletion category.

In general, though, eliminating the stainless steel from the graphene based supercapacitor would not make a big difference even in those categories where the main impact driver is the stainless steel casing. This implies once again that the graphene production must be improved to reduce the environmental burdens of the graphene based supercapacitor.

This scenario also proved that the commercial casing is better than the prototyped one and better also than the prototyped solution with a case made of aluminium, however, this first scenario is not analysed further because, based on real data (see paragraph 4.1.4 page 82), when the active material is placed inside a commercial casing its specific capacitance seems to downgrade by 65% and this would completely overturn the results.

	ORIGINAL			**ALTERNATIVE SCENARIO**		
	Activated carbon	**rGO2C**	**rGO2T**	**Activated carbon**	**rGO2C**	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	3.00E-02	5.39E-02	4.75E-02	2.39E-02	2.77E-02	4.38E-02
Ozone Depletion [kg CFC 11-Equiv.]	3.87E-11	3.73E-10	3.74E-10	2.36E-11	8.51E-11	5.72E-10
Human toxicity, cancer [CTUh]	1.33E-11	5.36E-11	5.22E-11	1.01E-11	1.67E-11	6.27E-11
Human toxicity, non-canc. [CTUh]	1.47E-09	6.02E-09	6.14E-09	1.12E-09	1.91E-09	7.47E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.55E-05	1.85E-05	1.90E-05	1.12E-05	1.11E-05	1.94E-05
Ionising radiation, human health effect model, [kg U235 eq]	4.12E-02	5.03E-02	5.06E-02	3.51E-02	4.54E-02	5.20E-02
Photochemical ozone formation,[kg NMVOC]	6.73E-05	1.08E-04	1.06E-04	5.40E-05	5.80E-05	1.16E-04
Acidification [Mole of H+ eq.]	1.53E-04	3.08E-04	3.18E-04	1.21E-04	1.51E-04	3.26E-04
Terrestrial eutrophication, [Mole of N eq.]	2.34E-04	3.51E-04	3.16E-04	1.89E-04	1.96E-04	3.55E-04
Freshwater eutrophication, [kg P eq]	2.31E-08	1.36E-07	1.07E-07	2.10E-08	4.19E-08	1.40E-07
Ecotoxicity [CTUe]	1.28E-03	1.07E-02	1.01E-02	1.07E-03	2.73E-03	1.40E-02
Resources depletion, water [kg]	2.93E-02	4.43E-02	4.13E-02	2.38E-02	2.82E-02	4.56E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	2.38E-07	1.03E-06	1.15E-06	1.52E-07	3.02E-07	1.55E-06

Table 4.25 – Original vs. Alternative scenario all categories. Activated carbon remains the least impacting in 12 out of 13 categories (green) while the impacts generated by graphene based prototype become comparable to those originated by the current activated carbon technology

The second scenario, the “alternative scenario”, investigates the effect of applying all variations tested in the sensitivity analysis to the original data. The results for the global warming potential are presented in Figure 4.15 together with a comparison with the original data. It is possible to see improvements for both activated carbon and rGO2C supercapacitors but a larger improvement for the latter. In fact, for the global warming potential impact category, the rGO2C supercapacitor becomes 7% less impacting than the current activated carbon supercapacitor (original scenario).

Always comparing the original results for activated carbon supercapacitor with the alternative scenario for the rGO2C supercapacitor (see Table 4.25) it is possible to see that in some categories the latter become better than the activated solution on the market (besides GWP, 28% lower impact for particulate matter, 14% less in photochemical ozone creation, 1% less in acidification, 16% in terrestrial eutrophication and 4% in water depletion) and in the other categories the order of magnitude of the impacts becomes comparable. When comparing the alternative scenario results for both supercapacitors, instead it is possible to see that the activated carbon supercapacitor impacts least but also that the rGO2C based one shows encouraging comparable results.

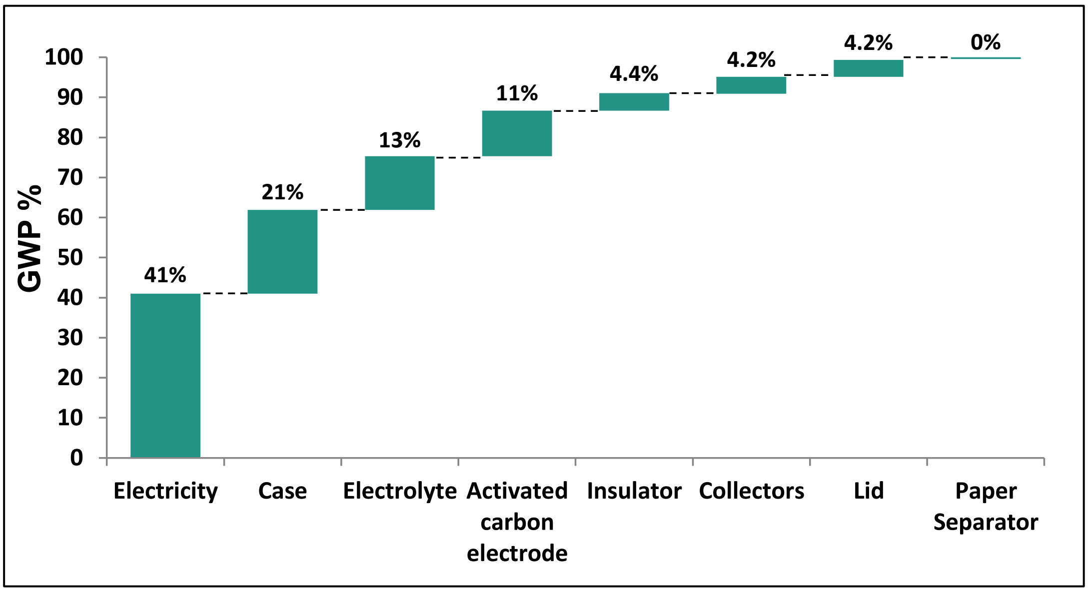

Figure 4.16 – Activated carbon supercapacitor alternative scenario breakdown GWP. The electricity used for the assembling is the main cause of global warming potential

For the rGO2T, instead, the results are similar to the original results due to deterioration of its specific capacitance that is the cause of 50% increase of graphene quantity. The minor improvement shown is due to the acid usage and neutralisation reduced by 90%.

A confirmation that the graphene production process is the area where improvements are needed in order to cover the gap with the activated carbon is given by the breakdown of the alternative scenario for the activated carbon (Figure 4.16) and rGO2C (Figure 4.17) supercapacitors. The activated carbon production is a much less impacting process if compared with the graphene production process (0.002 Vs 0.013 CO_2eq) even though much less graphene is used in the supercapacitor.

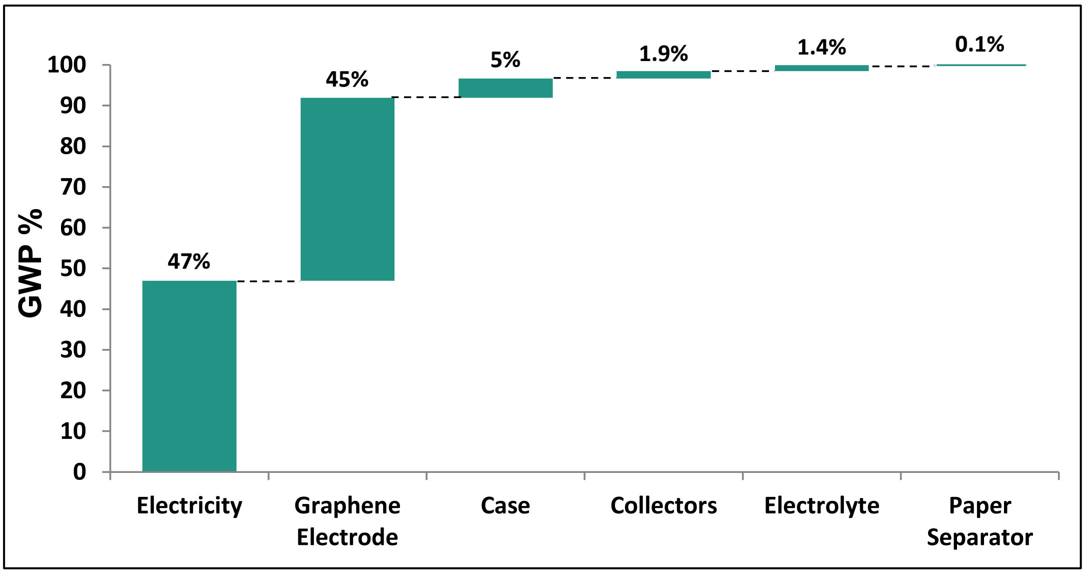

Figure 4.17 – rGO2C supercapacitor alternative scenario breakdown GWP. The electricity for the assembling and the electrode manufacturing (i.e.: the graphene production) are the main source of CO_2 emissions and therefore global warming potential

It is important, though, to stress the fact that the yields used for graphene synthesis in this study are those measured in the laboratories, and they might improve as the research moves forward. An optimised graphene production process that increases the yield of the reactions and reduces wastes and reaction time (less heat losses) will definitely benefit the environmental performances of this new material. However, at this stage of development there is not much research focus on process efficiency for graphene synthesis, but more on improving the material properties. Process efficiency comes generally at a later stage in the technological development, when cost-down initiatives become necessary to boost the material market penetration.

4.3 Conclusions

In this chapter it is shown that the production process of the activated supercapacitor has lower impact on the environment, for all categories compared, than the production process of the graphene prototype and that this is true also and when using the current commercial package used by Maxwell Technologies Inc. with graphene electrodes.

A break-even point for specific capacitance beyond which the graphene prototype would become the least impacting technology is also presented. It showed that in 8 categories, regardless to the specific capacitance achieved, the activated carbon supercapacitor will always impact less than the competing technology proving that a more efficient graphene synthesis is necessary.

A scenario including possible improvement in the graphene supercapacitor production is presented. It included an increase of the material specific capacitance to its theoretical limits, a consequential reduction of the casing size, a minimisation of the heat losses during production and a reduction of 90% of acid used and the neutralising agent. The results showed the graphene supercapacitor production impact to be comparable with that of the current activated carbon supercapacitor on the market and even better in 6 impact categories. However, when the same improvements are applied to the activated carbon technology, the latter performs better than the graphene based in 12 out of 13 impact categories with percentages ranging from 4% for terrestrial eutrophication, 7% for photochemical ozone formation and 14% for global warming potential to 72% of ozone depletion 60% for ecotoxicity and 50% for fresh water eutrophication.

Nevertheless, it is also important to point out that even if the activated carbon based supercapacitor remains the least impacting device, the values of the impacts are of the same order of magnitude and therefore comparable. This is also a very encouraging result. For this scenario to become reality, though, research is needed to increase the specific capacitance of the graphene close to its theoretical value, to improve its conversion efficiency (increase the percentage of graphene against graphite for the same unit of volume) and to adjust the orientation of the nanoplatelets in a way that offers more storage volume per surface area.

To further reduce the graphene synthesis impacts, further research could focus on increasing production yields while diminishing the reaction times, as this would also reduce the energy spent in heating and the heating losses. It would also be important to focus on reducing the excess of chemicals in the reactions, and therefore the waste, by optimising their quantities without compromising the material properties. Reuse or recycle of part of the chemicals in excess could be an important activity to investigate.

All those points must be addressed before it is possible to reach either the values shown proposed in the “alternative” scenario or even better ones; however it can be said that the material offers great potential, and so does its synthesis process, for improving both its technological and environmental performance.

Concerning the LCA side of this study, a deeper analysis and more measurements should be carried on wastes and emissions in order for the life cycle analysis to provide more detailed and precise results. More studies are also necessary to understand the chemistry of the reactions for the graphene synthesis since this would allow a more precise and standardised calculation of the reaction equilibrium and therefore of the wastes and emissions composition.

4.4 References

1. Hankin, S. and S. Billet, *Electrograph final report (EU project FP7)*, 2014.
2. Gisler, L. and M. Angeloz, *Personal communications*, 2013: Maxwell Technologies Inc.
3. Bertuccioli, L., et al. *Development of water electrolysis in the European Union*. Lausanne, Switzerland: Fuel Cells and Hydrogen Joint Undertaking 2014; Available from: http://www.fch.europa.eu/sites/default/files/study%20electrolyser_0-Logos_0_0.pdf.
4. Siong, V., *Personal Communications*, 2012: Fraunhofer IPA Institute.
5. Lee, S., et al., *Large-scale production of high-quality reduced graphene oxide.* Chemical Engineering Journal, 2013. **233**(0): p. 297-304.
6. Foo, D.C.Y., *Process symulation workshop*, 2014: University of Nottingham.
7. Kotrusz, P., *Personal Communications*, 2014: Danubia Nanotech.
8. Kotrusz, P., *Personal Communications*, 2013: Danubia Nanotech.
9. Lobato, B. and T. Centeno, *Personal communications*, 2013: Instuto nacional del carbon - CSIC.
10. Vretenar, V., *Personal Communications*, 2013: Danubia Nanotech.
11. Zhao, Y., et al., *A Versatile, Ultralight, Nitrogen-Doped Graphene Framework.* Angewandte Chemie, 2012. **124**(45): p. 11533-11537.
12. Davis, J.R., *Concise Metals Engineering Data Book*, ASM International. p. Tab. 8.1.

CHAPTER 5: Case study: use-phase and end-of-life of supercapacitors – a comparison

This chapter focuses on finalising the comparative LCA presented in the previous chapter adding the use-phase of the supercapacitors and their recycling at the end of their life. It extends the analysis to the entire process shown in Figure 5.1.

The recycling processes are simulated for both activated carbon and graphene supercapacitors in order to estimate their energy consumption when processing large volumes.

An application for the supercapacitor is selected in order to present a real case example and perform a cradle to grave comparative LCA. The application is a door mirror of a car where the supercapacitor is powering the motor to adjust the mirror position. The recycling possibilities, instead, were investigated at the University of Nottingham and involve some thermal treatments and separation.

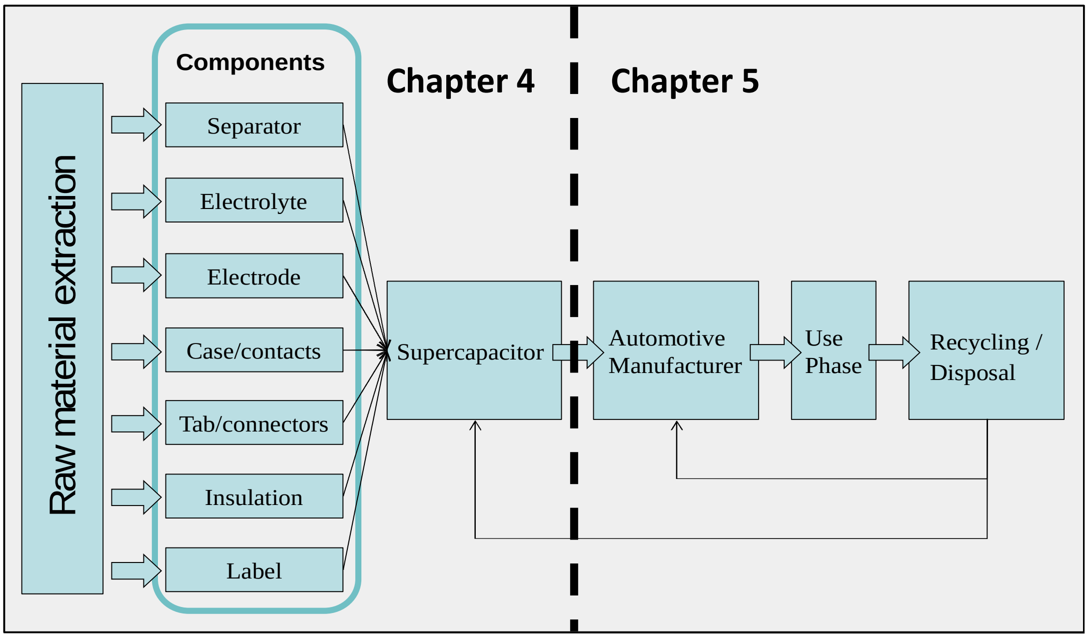

Figure 5.1 – Process overview

Sensitivity analysis is also presented in order to simulate some heat losses and the impact of different supercapacitor weight on the use-phase, but also the different quantities of material recycling extending the sensitivity analysis presented in the previous chapter to the life cycle phases added.

On top of this, normalisation and weighting of impact categories is applied to rank them in order of importance and to re-evaluate the results obtained on the base of this ranking. Finally, some indications are given of the possible improvement in terms of eco-design for future supercapacitors.

5.1 Methodology

This section summarises the goal and scope of this LCA and includes a case study that expands the analysis of the supercapacitor production, presented in the previous chapter, including the use-phase and end-of-life phase making this study a cradle-to-grave LCA.

5.1.1 The cradle-to-grave life cycle assessment methodology

This section includes a comparison of the whole life cycle of three of the four supercapacitors presented in the previous chapter:

- Activated carbon based supercapacitor (AC)
- Graphene based supercapacitor using:
    - rGO2C chemically oxidised and chemically reduced material
    - rGO2T chemically oxidised and thermally reduced material

A fourth supercapacitor using graphene obtained with the electrochemical exfoliation was evaluated in Chapter 4. This supercapacitor is not included in the current analysis due to its relatively large environmental impact and the material's low specific capacitance compared to the other graphene-based supercapacitors. Only the devices showing comparable values of performances (technological and environmental) to those of the activated carbon supercapacitor are considered.

The data used for the supercapacitors production are taken directly from Chapter 4 while the use-phase and the end-of-life are modelled consistently for all devices. This consistency is also eased by the fact that the car application is the same for all supercapacitors and that the recycling procedure is very similar for all devices.

5.1.1.1 Function and functional unit

The supercapacitors are to be placed in a car door mirror that becomes a self-powered unit completely detached from the battery. The unit is charged via a flexible solar panel placed on the mirror casing surface, facing forward and commanded via Wi-Fi. No design modifications are allowed as the aerodynamic coefficient of the car must remain the same because it impacts considerably on the fuel consumption increasing the drag. The mirror used as demonstrator is a door mirror already on the market and installed by FIAT in one of their vehicles.

The door mirror was selected because the power delivered by a graphene based supercapacitor prototype was small. On the other hand, the limitations of this type of application are quite evident, above all the need to be exposed to direct sunlight to recharge the supercapacitors.

For this application the supercapacitor(s) must guarantee four mirror movements of five seconds each. The unit is controlled via Wi-Fi as there are no cables going through to the car chassis and the power consumption of the electronics can be considered negligible [1]. Hence, the operational parameters and technological specifications required for the supercapacitor(s) are set by the motors to be powered.

The motors could be replaced by more optimised motors that would require less energy for the task, but it was decided to use the ones currently used in the chosen mirror. The supercapacitor(s) must therefore fit in the mirror currently used by FIAT and must be able to deliver enough energy over 20 sec (4 movements of 5 sec each) at the rated voltage. To match the performance requested by the function selected, a rack of five 5 F commercial supercapacitors connected in series was tested by CRF (Centro Ricerche FIAT) and proved to be enough to deliver the energy needed. The selected functional unit is therefore a rack of five 5 F supercapacitors. Details are summarised in Table 5.1.

Specification	Symbol	Formula	Unit	Requirements
Current (Motor - Peak)	I	I	A	0.25
Voltage (Motor - DC)	U	V	V	14
Required power output	P	V·I	W	3.5
Single actuation time	t	t	s	5
Number of actuations	n	n	n	4
Total actuation time	t	t	s	20
Required Energy	E	P·t	J	70
			Wh	0.02
Required Charge	Q	I·t	C	5
Required Capacitance	C	Q/V	F	0.36

Table 5.1 – Detailed list of requirements for the selected application

Five supercapacitors are required because the electrolyte used cannot withstand voltage higher than 2.7 V while the motors run at 14 V. In a rack of five 5 F supercapacitors in series, the overall capacitance will be reduced to 1F (for supercapacitors in series $V_{\text{tot}}=\sum_{i=1}^{n} V_i$ and $C_{\text{tot}}=\sum_{i=1}^{n}(1/C_i)$) but it is still more than twice the capacitance needed (Table 5.1).

The motors operating voltage range is between 9 and 16 V and this means that not all the energy stored in the supercapacitors can be delivered as below 9V the motor will stop running; however, the calculations allow for a big margin and tests performed at CRF have shown that with this configuration, the motors can be powered for more than a minute and recharged in five through the solar panel [1].

5.1.1.2 System delimitation, boundaries, impact categories and data quality

The system boundaries are now extended to obtain a cradle-to-grave LCA that starts with the raw material extraction and finishes at the end of the life of the devices. This section therefore includes a comparison of the use-phase that takes into account the differences among the three supercapacitors studied when inserted in a car door mirror to power the motors. It does not include how this solution impacts the car structure (e.g.: fewer cables, smaller cables and others) as this prototype was never meant to go on the market [1] and thus no further studies were carried out at FIAT. The system boundaries are therefore limited to the mirror and how its weight modification affects the fuel consumption of a class C vehicle. All data are provided by CRT (FIAT research centre) and based on the prototype they built in their Italian facility.

The section also includes the recycling of both activated carbon and graphene. The study does not take into consideration the collection and transportation of supercapacitors as there are no recycling facilities at the moment and a simulated industrial footprint would be purely based on assumptions. Excluding these activities is expected to have a minor impact on the overall impacts generated by the supercapacitors.

The recycling in this LCA is modelled by substitution, meaning that the recovered material displaces the production of the same pristine material. The quantity displaced depends on the quality of the material recovered compared with the pristine material. It is important to highlight that when the recovered material displaces the production of pristine material, it generates a negative impact in the results that is credited to the device and thus reducing its environmental burden.

The impact categories are the same used in the previous chapters and requested by the ILCD standard methodology. IOM (Institute of Occupational Medicine) performed tests at the University of Nottingham and showed that no airborne particles were detected while recycling supercapacitors [2].

5.1.2 Use-phase

The modelling of the use-phase is done considering the impact of a supercapacitor weight and its implications for fuel consumptions. According to FIAT measurements, the standard segment C car consumes around 3% more when its weight increases by 100 kg (is 5% for Chrysler brand and heavier vehicles) [1]. This shows that even a light component like a supercapacitor can make the difference over a lifetime of the vehicle as the standard lifetime used in FIAT is 150,000 km for a petrol engine and 300,000 km for a diesel engine. For this modelling only the 150,000 km range using petrol is used.

The weight of the supercapacitors included in the door mirror affects the performance of the car and therefore the fuel consumption and the related environmental impacts. The consumption used to model the use-phase is from GaBi database and is for an engine up to 1.4l and the driving cycle involves 30% motorway, 31% city roads and 39% outside of towns for the whole life of the car (150,000 km).

The lifetime of the supercapacitors is assumed to be the same or longer than that of the vehicle. No solution would be accepted if it would require a replacement of a supercapacitor (if not of the whole mirror) during a car lifetime. For these reasons only the difference in weight between the supercapacitors is driving the difference in the use-phase.

The adoption of this technology would change the wirings of the car, for example there would not be a cable passing from the mirror through the car chassis to the battery and this would eliminate the hole on the door but also would reduce the cabling safety specifications (less protections needed) as the risk of water getting in contact with them would be very limited. The mirror would become a plug and play device that can be produced externally, maybe together with the whole door. The motors not connected to the battery would mean that less energy is drawn from the battery itself extending its lifetime [1].

Many other modifications might occur, however, this would apply to all types of supercapacitors and therefore none of this modelling has been taken into account as a comparative LCA common parts can be neglected as they would just add the same impact to all solutions.

Another reason why this type of consequential analysis was not conducted is because FIAT declared that this type of solution is not suitable for the automotive market yet. It would not add any real benefit but it might introduce problems in a simple, reliable and well-established technology. Moreover, it has several limitations: it would not work overnight, it might have problems with multiple users over a short period of time, it has not enough power (yet) to operate the bigger motor that folds mirrors inwards when the car turns off and it cannot (yet) de-ice the mirror in cold temperatures. Those functions require much more power and thus a much bigger supercapacitor rack that will not fit the mirror inner space. Reducing the mirror functionality also reduces the quality perception on the market. It is also, nowadays, much more expensive than the current solutions [1].

Nonetheless the automotive trend is to delocalise the power supply units that feed all motors and lights and for this reason the automotive sector is investigating supercapacitors and graphene and their possible applications. In fact, when the graphene based supercapacitor technology will be mature it should achieve higher energy density and therefore reduce the supercapacitor rack size.

5.1.3 End-of-life

For recycling all data are primary data measured in the laboratory at the University of Nottingham and used to simulate a commercial-scale process with SuperPro Designer. Both supercapacitors are recycled following the same route and, therefore, the scale up methodology is consistent. All other processes belonging to the background system (i.e.: rubber and paper incineration and aluminium or stainless steel recycling) are modelled using secondary generic datasets available inside GaBi 6 databases.

The recycling process [3] requires first cutting the supercapacitor in order to extract the electrodes. Cutting can be done either manually or with an automated process depending on the volumes. All remaining materials are easily separated and collected either manually or with a set of cyclones and filters and then recycled or incinerated separately. The electrodes, instead, undergo a pyrolysis process in order to detach the active material from the aluminium substrate. The binder is the same for both supercapacitors as the process to make electrodes is considered the same. After pyrolysis the electrodes are shredded in water and the shredded suspension is then filtered in order to separate the aluminium from the active material. As the filtering and shredding processes are exactly the same, only the heating process is taken into account. The heat input is different as there is a different quantity and mix of material to be heated between the activated carbon and graphene based supercapacitors.

The pyrolysis process for electrodes starts with placing the electrodes in a nitrogen swept reactor heated at 200 °C in order to evaporate and recover the acetonitrile by distillation. When the process is completed after approximately 15 min, the temperature is increased to 350 °C and maintained for about one hour. This second heating step could be also performed at 600 °C for 5 min.

Without a temperature increase, at 200 °C, the binder is not decomposed and the carbon recovered from the aluminium substrate is only 40%. In this way, instead, it is possible to recover 95% of the activated carbon with a surface area per gram that is 95% of the original. The 600 °C alternative decomposes all the binder allowing the recovery of 100% of the material but it also collapses some micro pores in the activated carbon structure halving the value of the surface per gram measured [3]. For this reason this option is not modelled in this LCA.

To test the quality of the graphene material recovered the measurements were performed differently. The material was used to reinforce a polymer and tests were made directly on the moulded polymer to verify its enhanced mechanical properties. The results showed similar values to those found in literature for pristine graphene used as reinforcement for polymers.

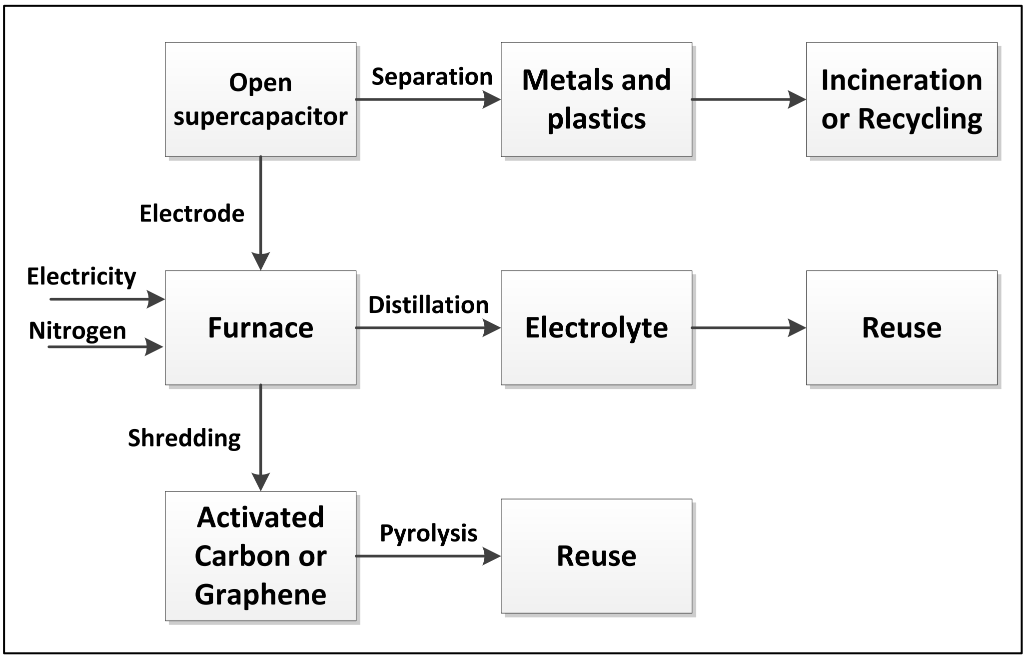

Figure 5.2 – General process for supercapacitor recycling

In detail, if the pyrolysis is run at 200 °C, the reinforcement increases by 8% the tensile strength of the polymer, while when using graphene that underwent the 5 min pyrolysis at 600 °C the results matched those found in literature and obtained using pristine graphene (+12% tensile strength increase) [4]. This last option is the one modelled for this LCA.

This also shows that the binder has some deteriorating effect in the reinforcing properties of graphene, but that its removal is not so crucial. In fact, the recycling process can happen also at 200 °C without reducing the reinforcing properties of graphene properties too much.

All materials in a supercapacitor can be theoretically 100% recovered, except for the electrolyte. Nevertheless, 10% process inefficiency is considered, therefore the recovery rate is set to 90%. The recovered paper and rubber are considered incinerated, while aluminium and stainless steel are considered recycled.

The recycling of active material is modelled for substitution so the active material recovered is set to replace pristine one. However, in the case of activated carbon, there is a 5% quality degradation to consider and so it has a displacement ratio of 95% that, including the 90% efficiency, brings the overall recovery down to about 85%. This means that the recovered activated carbon displaces 85% of its mass of pristine material production. The avoided production generates a negative impact in the result that diminishes the overall environmental burden. The graphene instead is recovered to its 100% potential and allowing for 10% process inefficiency is set to replace 90% of new graphene production. The acetonitrile recovered, instead, was generally around 40%. It is considered reusable and therefore displacing new production as in the case of the active materials.

Comparison of supercapacitor assembling phase	**Activated Carbon**	**KOH (15 V)**	**rGO2C**	**rGO2T**	
Electrode (details below)	0.69	0.91	0.47	0.47	g
Casing (aluminium)	0.52	-	-	-	g
Casing (stainless steel)	-	1.5	1.5	1.5	g
Collectors (aluminium)	0.1	0.05	0.05	0.05	g
Electricity	0.07	0.1	0.1	0.1	MJ
Electrolyte	0.58	0.36	0.36	0.36	g
Paper Separator	0.1	0.02	0.02	0.02	g
Rubber	0.2	-	-	-	g
Lid (aluminium)	0.1	-	-	-	g
Comparison of the electrode production					
Activated carbon	0.52	-	-	-	g
Graphene (commercial-scale)	-	0.71	0.27	0.27	g
Aluminium foil	0.17	0.2	0.2	0.2	g
Electricity	0.01	0.01	0.01	0.01	MJ

Table 5.2 – Supercapacitor manufacture inventory summary

Table 5.2 shows the table already presented in Chapter 4 (section 4.2.1) showing all material used in a supercapacitor. It is clear that the more the production is energy intensive, the more the credit given by the recycling through avoided production is substantial and positively impacting the overall results.

The emissions, as in the previous chapter, were not measured and are therefore estimated.

5.1.3.1 Recycling process simulation

The scale up is done in the same way it was done for the graphene production processes using Super Pro Designer v9.

For the recycling process, there is no limit set for a yearly production as it depends on the quantity that would be available to process on the market. However, for this example, the same quantity produced is recycled, excluding any other player on the market, and therefore 3 tonnes a year is the total volume to be processed.

The main energy consuming component is the furnace while the cutting and the separating activities are very small contributors to the overall energy consumption according to the measurements done. The second most consuming device is the pump (for the nitrogen circulation) that consumes a hundred times less than the furnace and is therefore a minor concern.

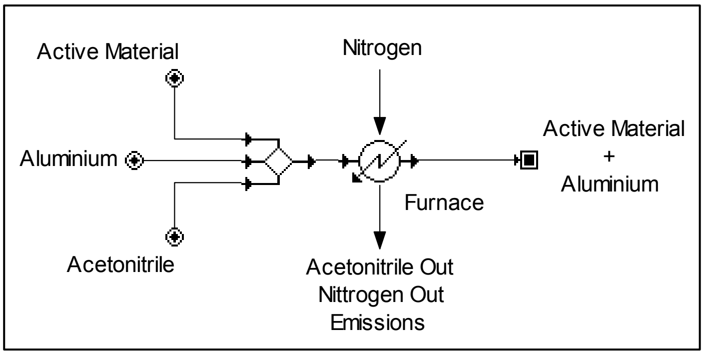

Figure 5.3 – General recycling process for electrodes via pyrolysis.

For this reason the furnace is the only process step that is scaled up to a commercial-scale to reduce its energy consumption using an adiabatic model with a 90% thermal efficiency. For the other steps, the electricity consumption is kept as measured in the laboratory as the pump used could easily handle batches of 2 or 3 kilograms of active material and the cutting and separation consume a small amount of energy. Figure 5.3 shows the pyrolysis process as modelled in SPD.

The biggest uncertainty about this scale up is linked to the emissions. Once again there is no way to understand the types of emissions generated. According to laboratory personnel, the most problematic is the PTFE binder (Teflon) that breaks into gaseous TFE [4]. Depending on their level, these emissions might not be permitted and therefore the gases must be cleaned and Teflon could be recycled.

Unfortunately it was not possible to model the mitigation of Teflon-related emissions or Teflon recovery due to a lack of reliable measurements on emissions; however, it is not an expensive and problematic process from an environmental standpoint. Once the material has been pyrolysed at 600 °C (the temperature is crucial to obtain the right types of fluoric compounds and yields), the gases must pass through some hot cyclones or electrostatic precipitators to remove impurities (e.g. soot) and then condensed to obtain TFE to be reused [5]. However, in this study the binder is the same, and in the same quantity, for both supercapacitors and therefore neglecting the Teflon recycling process would not impact the environmental performance comparison of the supercapacitors.

5.1.4 Sensitivity analysis

In this section the same sensitivity seen in the previous chapter is carried over and applied to the use-phase and to recycling activity to understand how these variations affects the use-phase and recycling, first, and subsequently final results. For the use-phase, is important to test what happens when the weight of the five supercapacitor rack changes. For the recycling, instead, it is more important to test what happens when the quantity of active material recycled varies and when heat losses are applied to the simulated adiabatic process.

5.1.4.1 Use-phase sensitivity analysis

For the use-phase a variation in weight for the supercapacitors is evaluated; the sensitivity analysis is based on the values applied in the sensitivity analysis for production phase. This means that, as seen in Chapter 4, when an increase of the specific capacitance of the active material occurs, the dimension and weight of the supercapacitor decrease and vice versa.

The sensitivity applied in the production phase is based on the specific capacitance variation of +50% for the activated carbon, of +85% for the rGO2C and of -35% for the rGO2T. The variation of the specific capacitance implies a variation in the size of the supercapacitor and thus in its weight.

	Sensitivity to Use-phase	
-43%	AC Supercapacitor weight	0%
-74%	rGO2C supercapacitor weight	0%
0%	rGO2T supercapacitor weight	+46%

Table 5.3 – Use-phase sensitivity analysis values

The reduction (or the increase) in the size of the components of the supercapacitor contribute to the weight variation as shown in Table 5.3.

5.1.4.2 End-of-life sensitivity analysis

The recycling process is modelled according to adiabatic reactions and some sensitivity analysis must be performed. The pyrolysis allows the sensitivity analysis only on heat losses. However, as the time spent at high temperature is fairly low they are foreseen to be quite low. The heat losses are calculated in percentage of the heat input of the adiabatic process. The same percentages applied in the previous chapter for similar temperatures are used:

- Activated carbon supercapacitor recycling:
    - 10% heat lost every hour at 200 °C equals to 3% heat loss for this step as the time of operation is 15 min.
    - 15% heat lost every hour at 350 °C equals 15% heat loss for this step as the time of operation is 60 min.
- Graphene based supercapacitor prototype recycling:
    - 10% heat lost every hour at 200 °C equals to 3% heat loss for this step as the time of operation is 15 min.
    - 20% heat lost every hour at 600 °C equals 7% heat loss heat loss for this step as the time of operation is 20 min (5 min at 600 °C + 15 min ramp up)

Summing the heat losses for activated carbon they contribute to an additional 8% heat input (above adiabatic), while in the case of graphene they are only adding 6% more on the adiabatic value because the process is much faster.

	Sensitivity to Recycling		
AC	0%	Electricity	+8%
	-50%	Activated Carbon Recycling	0%
	-50%	Acetonitrile Recycling	0%
	-50%	Nitrogen	0%
	-50%	Aluminium Recycling	0%
rGO2C	0%	Electricity	+6%
	-85%	Graphene Recycling	0%
	-85%	Acetonitrile Recycling	0%
	-85%	Nitrogen	0%
	-85%	Stainless steel Recycling	0%
rGO2T	0%	Electricity	+6%
	0%	Graphene Recycling	+50%
	0%	Acetonitrile Recycling	+50%
	0%	Nitrogen	+50%
	0%	Stainless steel Recycling	+50%

Table 5.4 – End-of-life sensitivity analysis values

On top of this, when applying to the recycling activity the variation of specific capacitance presented in the previous chapter for the production sensitivity analysis, this affects also the quantity of material recovered and recycled. In fact, if the size and weight of the supercapacitor components diminish due to an increase in specific capacitance of graphene, there will be less material available to process. In general, the quantity of recycled material could diminish for many reasons and it is therefore important to understand its impact on the recycling phase. The process efficiency and the quality degradation for the activated carbon are kept the same as in the original recycling process. Table 5.4 summarises all variation applied to this process.

5.1.5 Alternative scenario

The limit of the sensitivity analysis is that this type of analysis looks at the variation of the results when varying a single parameter. This approach is not applicable to the whole life cycle because when reducing one parameter, this variation does not affect the others. In other words, if the sensitivity tests what happens when the graphene production is decreased by 85%, the recycling phase is still recycling the original amount of material. This was chosen to investigate the impacts of the sensitivity on the single phases and evaluate the overall performance with the scenario analysis.

		Sensitivity to Production	
AC	-50%	Quantity of Activated Carbon	0%
	-50%	Casing Size	0%
rGO2C	-85%	Quantity of Graphene	0%
	-85%	Casing Size	0%
	0%	Electricity - Graphite Oxidation (GO2)	+8%
	0%	Electricity - Chemical Reduction	+240%
	-90%	Acid Use and Neutralisation	0%
rGO2T	0%	Quantity of Graphene	+50%
	0%	Housing Size	+ 50%
	0%	Electricity - Graphite Oxidation (GO2)	+8%
	0%	Electricity - Thermal Reduction	+110%
	-90%	Acid Use and Neutralisation	0%
		Sensitivity to Use Phase	
	-43%	AC Supercapacitor weight	0%
	-74%	rGO2C supercapacitor weight	0%
	0%	rGO2T supercapacitor weight	+46%
		Sensitivity to Recycling	
AC	0%	Electricity	+8%
	-50%	Activated Carbon Recycling	0%
	-50%	Acetonitrile Recycling	0%
	-50%	Nitrogen	0%
	-50%	Aluminium Recycling	0%
rGO2C	0%	Electricity	+6%
	-85%	Graphene Recycling	0%
	-85%	Acetonitrile Recycling	0%
	-85%	Nitrogen	0%
	-85%	Stainless steel Recycling	0%
rGO2T	0%	Electricity	+6%
	0%	Graphene Recycling	+50%
	0%	Acetonitrile Recycling	+50%
	0%	Nitrogen	+50%
	0%	Stainless steel Recycling	+50%

Table 5.5 – Summary of variation applied in the alternative scenario. All variation are derived from the sensitivity applied to the production process. When the specific capacitance is increased, less material is needed to achieve 5 F and therefore the casing is smaller, the weight reduced and the quantity of material recovered diminished.

An alternative scenario is thus generated in which all phases are taken into account and it is assumed that all the variations applied in the sensitivity analysis of the three phases are met.

The values from the alternative scenario presented in Chapter 4 are repeated. The rGO2T graphene specific capacitance is downgraded by 35% (Chapter 4 paragraph 4.1.4) while an increase of 85% of specific capacitance is considered for rGO2C in order to reach its theoretical maximum.

This variation impacts both the use-phase, as there would be less weight to carry for the car and, therefore less fuel consumption, and the recycling phase, as the heat needed from the furnace (adiabatic) would be less as there would be less material to heat. However, the heat losses, calculated as stated in the previous paragraph, still apply and they are added to the new value. Table 5.5 summarises the variations applied with respect to the original measured values.

5.1.6 Normalisation and weighting

To further analyse the results obtained in the alternative scenario, it is possible to normalise them according to the latest European guidelines. Normalisation is technique used to understand the magnitude of the impacts of a product/system in relation to the average European emissions per person per year. It results in a dimensionless number for each impact category showing the relative contribution of the product/system to the yearly EU emissions. The normalisation for the ILCD recommended categories (the one analysed in this comparative LCA) is still under development and it is therefore subjected to modification in the future. However a preliminary draft is being tested and it is therefore applied to this study [6].

Normalisation is normally coupled with weighting. This means that each category is given a weight in order to set priorities among impact categories. Weightings are generally decided by policy makers and institutional bodies. For the ILCD methodology, the weighting for the EU27 is now set to 1:1:1 and it means that all categories have the same weight.

Weighting, though, can be considered subjective and therefore several bodies issue their own weighting sets and in this study three weighting sets are applied: the first set is obtained averaging the values presented in [7], a paper summarising some studies done at the JRC of the EU Commission, while the second set is the one proposed by Thinkstep (formerly PE international) resulting from a survey submitted to about 500 experts and available in the last release of the PEF Kit (Product Environmental Footprint) upon request. This weighting set is carried until the end of the analysis because it was considered more reliable due the large number of experts involved in its creation. The third set is created for this analysis by merging standard TRACI 2.1 and ReCiPe weighting sets picking the values matching the unit of measure of each impact category considered in this study.

5.2 Results

The results are presented in this section include the results presented in Chapter 4, however they do not refer to one single supercapacitor but they are presented for the rack of 5 supercapacitors as requested by the functional unit selected for the cradle to grave LCA.

5.2.1 Use-phase

The result of this analysis shows that even for a small weight increase (5 activate carbon supercapacitors rack 11.45 g and 5 graphene supercapacitors rack 12.7 g) leads to considerable fuel consumption increase. In fact, the additional fuel needed is 23.4 g for the activated carbon rack and 26g for the graphene rack. An increase in weight that is larger than both racks weights.

This happens because the consumption difference is calculated over 150,000 kilometres, but this also shows that the transport of these components between the different manufacturing facilities can be neglected.

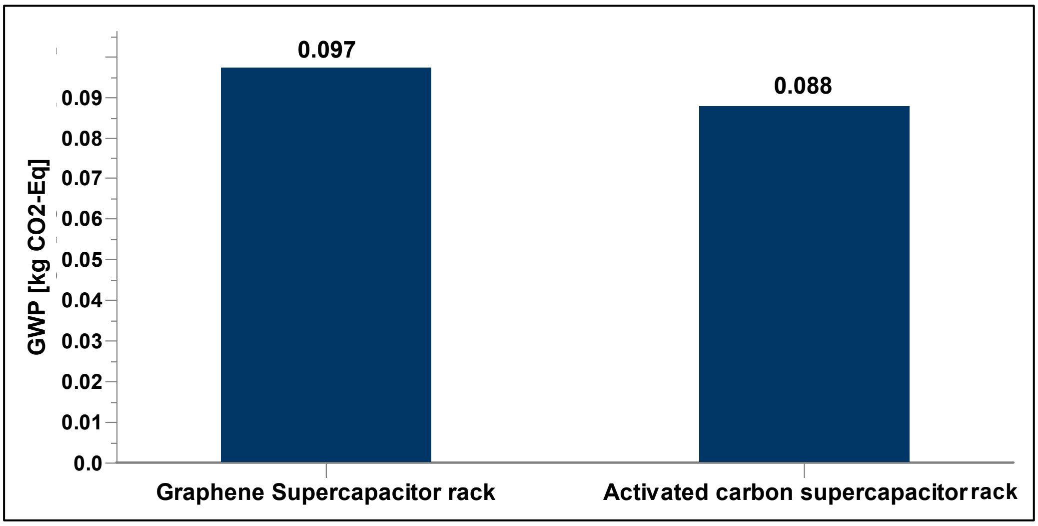

Figure 5.4 – Global warming potential: use-phase. As a result of its lower weight, the activated carbon supercapacitor shows a less impacting use-phase

Figure 5.4 shows the results for the use-phase of a rack of 5 supercapacitors. The two graphene supercapacitors have practically the same weight and therefore their use-phase is almost identical. The activated carbon rack is slightly less impacting in terms of global warming potential, but this is mostly due to the lighter aluminium case. If the graphene prototype used aluminium instead of stainless steel for the case, its final weight would be reduced by 30% and therefore also the environmental impacts connected with the use-phase would be reduced accordingly due to lower fuel consumption. However the aluminium production impacts the GWP category more than the production of stainless steel and therefore it might be a worse solution overall.

As the only factor impacting the use-phase is the weight of the components, it is also possible to say that this trend is replicated to all impact categories and it is thus possible to say that, with the current technology status, the use-phase of the activated carbon rack proves to be the least impacting for the environment.

5.2.2 End-of-life

Table 5.6 shows the energy requirements for the recycling processes for both activated carbon and graphene electrodes. The only recycling route of graphene analysed in this LCA is the one with binder removal happening at 600 °C that recovers graphene having properties that match those of pristine graphene.

When looking at this comparison, it is noticeable how recycling the graphene electrode is slightly less energy consuming (higher temperature but less material to heat), but when recycling the same amount of material (i.e.: 1 g) recycling the graphene electrodes is more energy intensive because in the graphene electrode there is more aluminium in percentage than there is in the activated carbon electrode and the specific heat capacitance (Cp) of aluminium is higher than that of carbon (Carbon Cp ≈ 8.5 J/[Kmol K] Aluminium Cp ≈ 31.5 J/[Kmol K]). Table 5.6 also includes the energy consumption for the graphene recycling at a temperature of 350 °C, the same as activated carbon. This is only an exercise to show that when using the same process and temperatures, the recycling of graphene is more energy intensive per gram of material but not per single electrode.

Pyrolysis of active materials	1 gram	1 electrode	
Activated Carbon (350°C)	0.0021	0.0011	MJ
Graphene (600°C)	0.0038	0.0010	MJ
Graphene (200°C)	0.0019	0.0005	MJ
Graphene (350°C)	0.0025	0.0007	MJ

Table 5.6 – Energy needed for the recycling of supercapacitors. The graphene based electrode is made of less material and therefore requires less energy to be heated in an adiabatic reaction. However, in a gram of electrode material the percentage of aluminium (higher Cp) is larger in the case of graphene, therefore the heat required per gram favours the activated carbon device.

The results for the rack of 5 supercapacitors presented in Figure 5.5 show how the activated carbon supercapacitor does not gain a lot of credit for the displaced production of pristine activated carbon, showing that the material recovered is not a very valuable material. Graphene, on the contrary, is a material with a lot of embedded energy and displacing the production of new graphene is beneficial for the environment. Recycling the rGO2T is slightly less beneficial as the production of this type of graphene is less energy intensive if compared to the rGO2C.

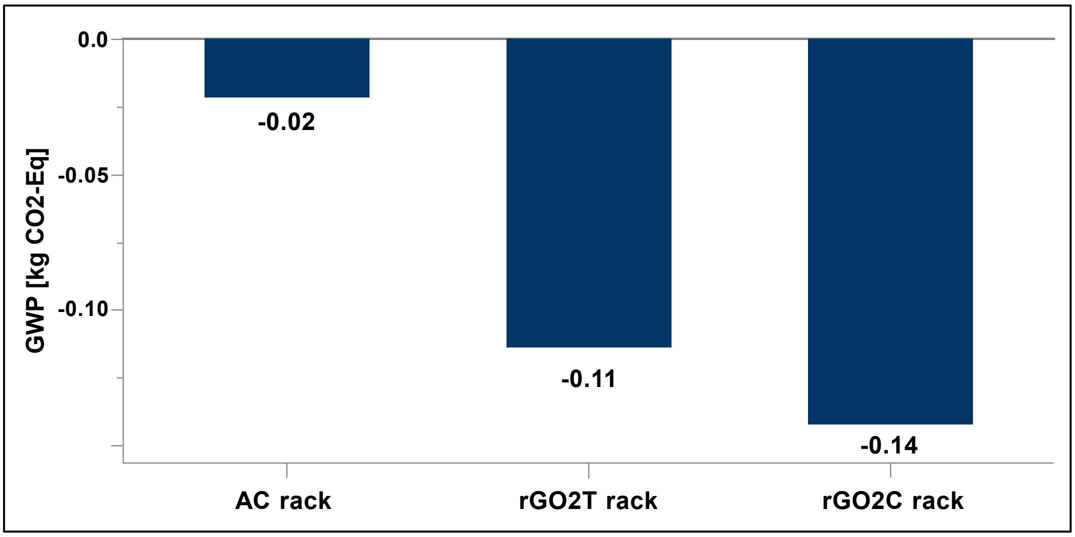

Figure 5.5 – Global warming potential: end-of-life. The activated carbon proves not very use-phasevaluable while the graphene materials generated large environmental credits

Breaking down the end-of-life phase (Figure 5.6) of the rGO2C supercapacitor, it is important to notice that the main credit is coming from the graphene recycling, while the main burden for this activity is the nitrogen consumption. To reduce the nitrogen impact it might be possible to recycle it or at least reduce the quantity used. However, to verify this possibility it is necessary to perform a more detailed analysis of the gaseous emissions as varying the nitrogen flow might modify the quality of the material recovered, since it is needed to maintain the furnace oxygen free and to clean it of the binder gasification.

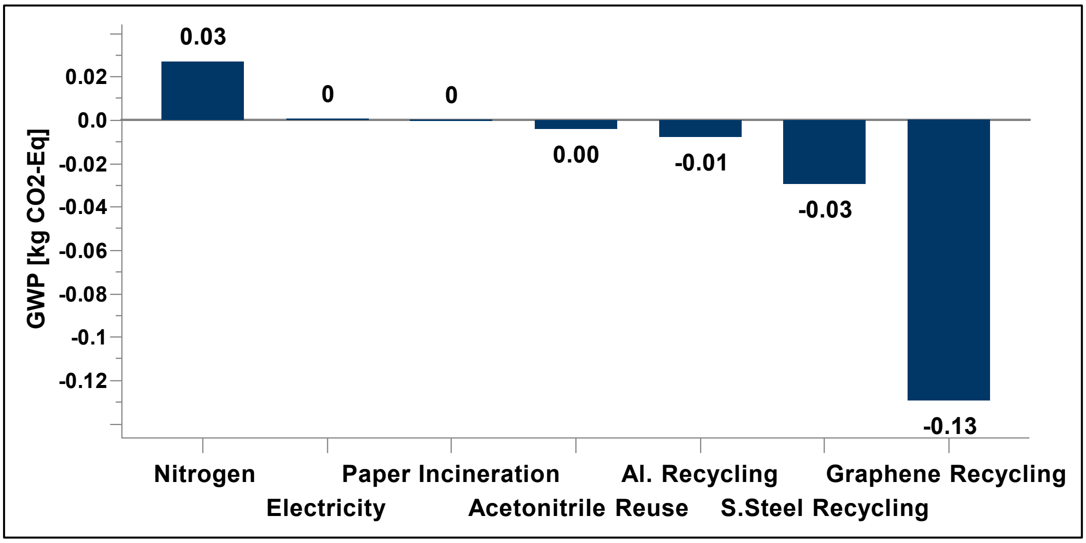

Figure 5.6 – Global warming potential: rGO2C end-of-life breakdown. GWP is generated mostly by the use of nitrogen while the credits are largely generated by the graphene recycling.

The graphene recycling offers also the possibility of a more energy efficient material recycling at 200 °C, without binder removal, but the material recovered offers lower performance as polymer reinforcement. However, it offers a competitive advantage for industry as it can produce the same quantity of material using half of the energy (Table 5.6). For a saving of 50% in electricity consumption, there is a decrease in mechanical performance of the graphene reinforced polymer of around 30-35%, from 12% increase in strength to 8% (see paragraph **Error! Reference source not found.**).

	Activated Carbon		Graphene		
	Initial	**Recovered**	**Initial**	**Recovered**	
Active material	0.52	0.44	0.27	0.24	g
Aluminium	0.72	0.65	0.25	0.23	g
Stainless Steel	0.58	0.23	1.50	1.35	g
Electrolyte	0.58	0.23	0.36	0.14	g
Paper	0.10	Incineration	0.10	Incineration	g
Rubber	0.20	Incineration			

Table 5.7 – List of materials in a supercapacitor and quantity recovered

Table 5.7 summarises the quantities of different materials in a supercapacitor and the quantity recovered according to the rate of recovery measured in the laboratory and presented in paragraph **Error! Reference source not found.**. These values show a very high rate of recovery making this recycling process promising. However, it does not take into consideration the logistics of the collection of the supercapacitors from the door mirrors when a car will reach the end of its life and that could make the whole process unfeasible. Nevertheless, it is not a concern for this LCA since it is an issue equally affecting both devices and thus neglected.

More important is the value analysis of the products that are recovered for recycling or for reusing. The most valuable materials inside the supercapacitors are graphene and activated carbon as they can be reused, and therefore compared with pristine materials, while aluminium and stainless steel are considered scrap for recycling. The scrap prices for aluminium and stainless steel range from 0.35 to 2.30 $/kg [8] while the pristine activate materials are much more expensive with a price of 15$/kg for activated carbon and a long term predicted price for graphene ranging from 4 to 40$/kg [9]. The recovery of these materials is therefore what should drive the supercapacitor recycling business, besides environmental policies.

5.2.3 Total Cradle-to-grave LCA results

The impacts presented here include all phases of the life cycle, production, use-phase and end-of-life for the three types of supercapacitor. As the functional unit selected requires five supercapacitors, all three phases are set for five supercapacitors. For this reason, all numbers related to the production of the supercapacitors are here five times bigger than in the previous chapter.

Figure 5.7 shows that for the case of the global warming potential, the two technologies are very similar. The chart follows a Pareto order from the most impacting on the left to the least on the right. The activated carbon is still the least impacting but the difference is minimal. The recycling of the graphene proves to be a promising possibility as it allows the recovery of a high quality material.

Figure 5.7 shows also the contribution of each phase to the overall global warming potential. This is the final result of the analysis that combines the whole life cycle of the product. When comparing the three phases, the production process is the main contributor, but the impact share of the use-phase is quite substantial if compared with the overall production impacts of these small and light devices. This proves that even a small variation in weight can contribute considerably to the impacts of a car over its life time. The environmental credit generated by recycling of graphene is shown to be fundamental to make the new prototypes, with simulated commercial-scale production and recycling, environmentally comparable to the current state of the art supercapacitors. It can be said that in this type of application, the recycling contribution offsets the use-phase impact and that the production causes the largest environmental burden.

When looking at the detailed breakdown of the rGO2C supercapacitor (Figure 5.8) it is important to highlight that the graphene electrode production is the main source of impact, however, the use-phase is the second (0.1 CO_2Equiv.) and the electricity for the assembly the third. The nitrogen use is also a substantial contribution that is comparable to the one generated by the stainless steel case, but it is only the fifth in order of importance.

Table 5.8 shows an overall of all categories for the three supercapacitors broken down into production, use-phase and End-of-life (EoL). From this table is possible to conclude that for all three technologies the production is the main environmental burden for all thirteen categories. The only two exceptions are, for the activated carbon, the eutrophication of fresh water, where the use-phase impact is slightly bigger than production and ecotoxicity.

For the graphene supercapacitors the production phase is always the most problematic aspect even when simulated with no heat losses. This highlights once more that the production is where research should focus to increase/optimise the yields of reactions and reduce the excess of chemicals (see details in Chapter 4 paragraph 4.3) in order to improve the throughput per unit of time and reduce wastes and consequentially the environmental burden.

In the use-phase, the main environmental burden is the petrol consumption that is driven by the weight of the device to be carried by the car. Considering a breakdown like the one in Figure 5.8 for all impact categories, the use-phase is generally quite substantial and ranks as second cause of impacts for the global warming potential, fresh water consumption and terrestrial eutrophication. It is the third cause of impacts for the fresh water eutrophication and human toxicity (both cancer and non-cancer). It is the fourth cause for all remaining categories excluding the ozone depletion for which it is the seventh cause of impact.

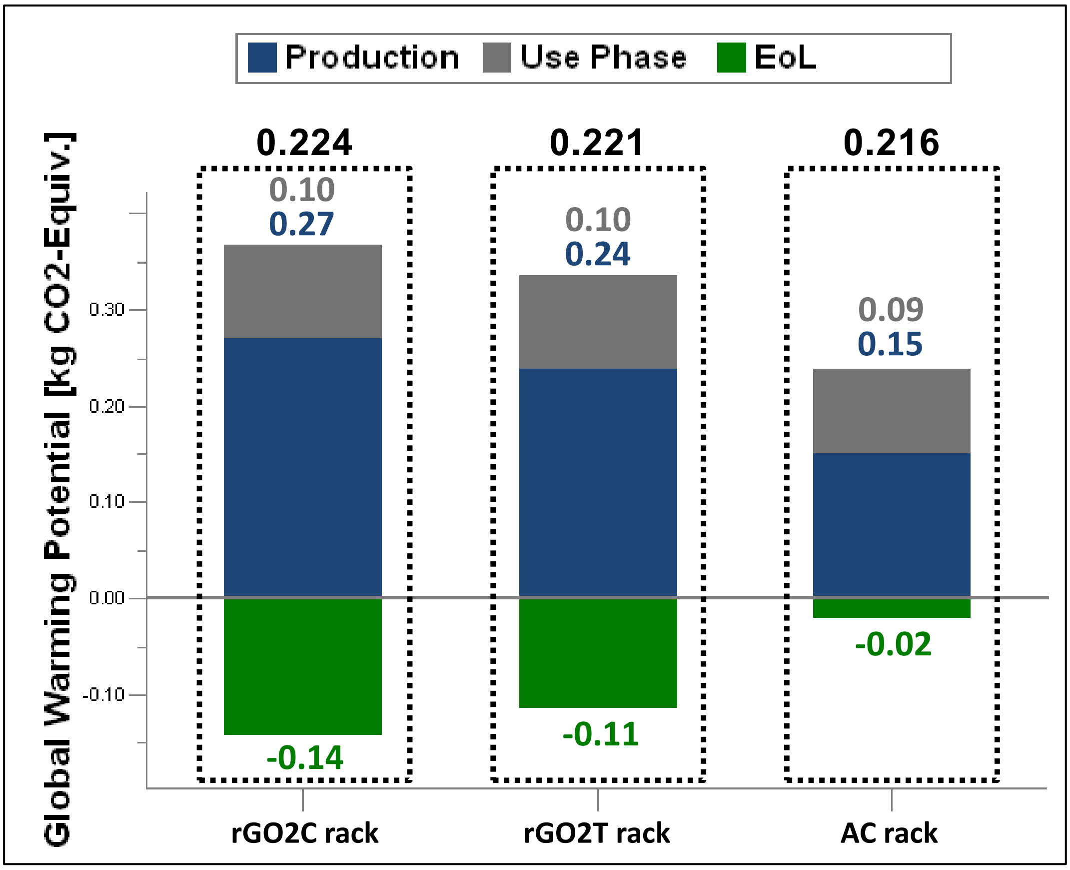

Figure 5.7 – Global warming potential: overall LCA results split in 3 phases. The activated carbon supercapacitor results in being the least problematic, however the supercapacitors show very similar impacts. (Numbers are rounded, for more details see Table 5.8).

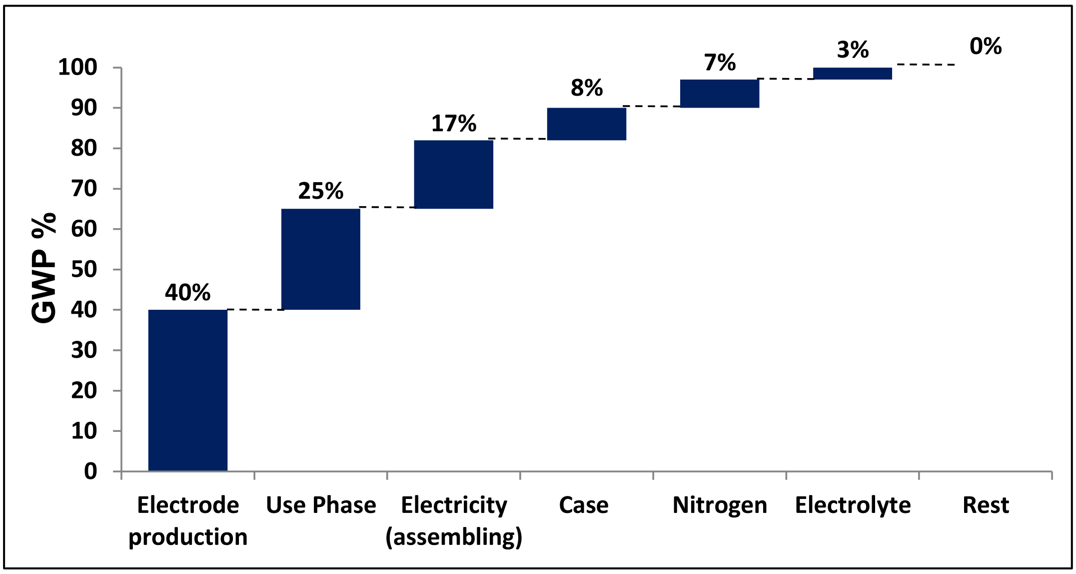

Figure 5.8 – Global warming potential: rGO2C rack 3 phases breakdown. The electrode production (i.e.: graphene synthesis) shows to be largely the most impacting factor followed by the use-phase.

	Activated Carbon Supercapacitor 3 phases				rGO2C supercapacitor 3 phases				rGO2T supercapacitor 3 phases			
	Total	Production	Use Phase	EoL	**Total**	Production	Use Phase	EoL	**Total**	Production	Use Phase	EoL
Global Warming Potential [kg CO2-Equiv.]	2.16E-01	1.50E-01	8.76E-02	-2.15E-02	2.24E-01	2.70E-01	9.72E-02	-1.43E-01	2.21E-01	2.38E-01	9.72E-02	-1.14E-01
Ozone Depletion [kg CFC 11-Equiv.]	-1.57E-11	1.94E-10	6.43E-13	-2.10E-10	2.61E-10	1.87E-09	7.13E-13	-1.61E-09	2.61E-10	1.87E-09	7.13E-13	-1.61E-09
Human toxicity, cancer [CTUh]	7.72E-11	6.63E-11	3.17E-11	-2.08E-11	9.08E-11	2.68E-10	3.51E-11	-2.12E-10	9.01E-11	2.61E-10	3.51E-11	-2.06E-10
Human toxicity, non-canc. [CTUh]	1.06E-08	7.37E-09	5.25E-09	-2.06E-09	1.25E-08	3.01E-08	5.83E-09	-2.34E-08	1.26E-08	3.07E-08	5.83E-09	-2.40E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	7.08E-05	7.73E-05	2.00E-05	-2.64E-05	6.62E-05	9.24E-05	2.21E-05	-4.83E-05	6.65E-05	9.52E-05	2.21E-05	-5.08E-05
Ionising radiation, human health effect model, [kg U235 eq]	2.35E-01	2.06E-01	1.86E-03	2.72E-02	2.53E-01	2.51E-01	2.06E-03	-1.88E-04	2.53E-01	2.53E-01	2.06E-03	-1.60E-03
Photochemical ozone formation,[kg NMVOC]	3.52E-04	3.36E-04	7.86E-05	-6.26E-05	3.49E-04	5.39E-04	8.68E-05	-2.77E-04	3.48E-04	5.31E-04	8.68E-05	-2.70E-04
Acidification [Mole of H+ eq.]	8.47E-04	7.67E-04	2.13E-04	-1.32E-04	9.03E-04	1.54E-03	2.34E-04	-8.72E-04	9.08E-04	1.59E-03	2.34E-04	-9.17E-04
Terrestrial eutrophication, [Mole of N eq.]	1.54E-03	1.17E-03	5.86E-04	-2.15E-04	1.54E-03	1.75E-03	6.39E-04	-8.53E-04	1.52E-03	1.58E-03	6.39E-04	-6.94E-04
Freshwater eutrophication, [kg P eq]	2.28E-07	1.15E-07	1.17E-07	-4.44E-09	2.72E-07	6.81E-07	1.30E-07	-5.39E-07	2.57E-07	5.37E-07	1.30E-07	-4.10E-07
Ecotoxicity [CTUe]	1.63E-02	6.40E-03	1.12E-02	-1.33E-03	2.12E-02	5.33E-02	1.24E-02	-4.45E-02	2.09E-02	5.07E-02	1.24E-02	-4.22E-02
Resources depletion, water [kg]	1.96E-01	1.47E-01	6.50E-02	-1.56E-02	2.02E-01	2.22E-01	7.21E-02	-9.18E-02	2.00E-01	2.07E-01	7.21E-02	-7.83E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	5.15E-07	1.19E-06	2.91E-08	-7.02E-07	6.37E-07	5.13E-06	3.22E-08	-4.52E-06	7.01E-07	5.77E-06	3.22E-08	-5.10E-06

Table 5.8 – Summary and breakdown of the cradle to grave comparative LCA

When looking at the end-of-life, the impact of nitrogen is the third cause of concern only in the ionising radiation category. As the ionising radiation is generally driven by electricity production (mostly nuclear) it is legitimate to think that the main cause of impacts generation for the nitrogen is the electricity used to produce it. However there is no breakdown for its production process as data available in GaBi are commercially sensible.

For all other categories the impact of nitrogen is limited and sits generally between the fourth and the sixth impact, thus not penalising the recycling activity too much. Generally speaking, the fact that the recovered graphene is similar to the pristine one really boosts positively the environmental credits in all categories (except for the ionising radiation) as this recycled graphene displaces new graphene.

Something must be said about a strange value obtained for the ozone depletion impact category for the activated carbon supercapacitor rack. It presents a negative value, indicating that the recycling credits are bigger than the production burdens. This anomaly is linked to the waste incineration of plastics process used to model the rubber (supercapacitor seal) incineration. This process, according to GaBi 6 datasets, credits a large amount of ozone depleting emissions to the activated carbon supercapacitor.

The GaBi process of incineration of plastics, though, includes several types of plastics and not only rubber, but as the data set is aggregated there is no possibility to modify it. This leads to some imprecision in this impact category, but is not a big concern in the others as the impact of the rubber insulator and its recycling is fairly limited, moreover, it happens only in this impact category for the activated carbon supercapacitor as in the prototype there is no rubber.

The most important outcome of this analysis though is that, considering the whole life cycle, the graphene prototype could be already compared environmentally to an established technology like the activated carbon supercapacitors by simply minimising the heat losses and recycling it at the end of its life. This provided that the recycling process, when scaled up to industrial level, is able to recover high quality material that can displace new graphene production.

One additional comment can be done about the “AC Package” scenario presented in Chapter 4 (paragraph 4.1.5). The least impacting solution would be to include graphene electrodes in the commercial casing (that would reduce by around 50% in size). This solution would slightly decrease the production burden (Chapter 4 paragraph 4.2.4) and it would also decrease the use-phase halving it and making this scenario the least impacting. With reference to Figure 5.7, it would result in a total GWP of 0.181 CO_2eq divided into 0.25 CO_2eq for production, 0.05 CO_2eq for use-phase and -0.13 CO_2eq for recycling. However, experimental results on activated carbon showed a loss of about 60% specific capacitance when inside a commercial supercapacitor making these results unrealistic.

Results in Table 5.8 instead are based on real material performances and they are still very encouraging for this early-stage technology. However, these results do not include the heat losses from the pyrolysis process, thus the sensitivity analysis must be evaluated.

5.2.4 Sensitivity analysis

This section presents first the sensitivity analysis of the use-phase and end-of-life phase results. Two results are presented in each table, the variation of the single phase versus the parameter variation and what this variation means on the overall results presented in Table 5.8.

5.2.4.1 Use-phase sensitivity analysis

For the use-phase, the weight difference generated by a variation of specific capacitance is tested. The specific capacitance is varied to evaluate how material quality affects the results. The results are presented in Table 5.9 do not take into account the impact that a specific capacitance variation has on the other 2 phases.

As the weight is the only cause of use-phase environmental impacts, it is clear that a variation in weight of 43% will have a variation in the use-phase results of 43% showing a linear dependency. Nevertheless, it is interesting how the impact on the overall LCA is different depending on the impact category chosen. For example, a variation of 43% in weight causes a 16% variation in the GWP of the overall LCA results, but only a 2% in the case of resource depletion. This happens because the use-phase contributes very little in the resource depletion overall impact (dominated by the graphite use during graphene production and by the stainless steel case) and much more in the case of the global warming potential (more details in Appendix C paragraph C1).

Global Warming Potential [kg CO2-Equiv.]								
Impact reduction			**Sensitivity Variation**	**Sensitivity Results Use Phase**	**Sensitivity Variation**	**Impact increase**		
Overall LCA	**Final Value**	**%**				**%**	**Final Value**	**Overall LCA**
-16%	5.00E-02	-43%	-43%	AC Supercapacitor weight	0%	0%	8.76E-02	0%
-32%	2.53E-02	-74%	-74%	rGO2C supercapacitor weight	0%	0%	9.72E-02	0%
0%	9.72E-02	0%	0%	rGO2T supercapacitor weight	+46%	+46%	1.42E-01	20%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]								
-2%	1.66E-08	-43%	-43%	AC Supercapacitor weight	0%	0%	2.91E-08	0%
-4%	8.38E-09	-74%	-74%	rGO2C supercapacitor weight	0%	0%	3.22E-08	0%
0%	3.22E-08	0%	0%	rGO2T supercapacitor weight	+46%	+46%	4.71E-08	2%

Table 5.9 – Sensitivity results for the use-phase for GWP and resources depletion

The variation on the overall LCA, though, is just a theoretical exercise as a reduction in weight without a variation in the materials used for the production and consequent recycling or a reduction in their quantities is not possible. Therefore, this exercise must be considered a way to determine the implications on the LCA of a weight increase/reduction of a supercapacitor rack, assuming this variation in weight is totally disconnected from the material types or quantities.

5.2.4.2 End-of-life sensitivity analysis

Sensitivity analysis to the end-of-life is performed and the results for the GWP are shown in Table 5.10 (all categories in Appendix C paragraph C.2). They show what happens on the end-of-life phase and on the overall life cycle when size of the supercapacitors reduced according to the production sensitivity values. A negative percentage means a decrease in the environmental credits and therefore an increase in environmental impacts. Also in this case, a parameter variation is not perturbing the whole LCA but only the single phase.

	Global Warming Potential [kg CO2-Equiv.]									
	Impact reduction			Sensitivity Variation	Sensitivity Results End of Life*	Sensitivity Variation	Impact increase		
	Overall LCA	EoL	%				%	EoL	Overall LCA
AC	0%	-2.15E-02	0%	0%	Electricity	+8%	-0.4%	-2.14E-02	+0.04%
	+2%	-1.64E-02	-24%	-50%	Activated Carbon Recycling	0%	0%	-2.15E-02	0%
	-5%	-3.20E-02	49%	-50%	Nitrogen	0%	0%	-2.15E-02	0%
	+8%	-4.71E-03	-78%	-50%	Aluminium Recycling	0%	0%	-2.15E-02	0%
rGO2C	0%	-1.43E-01	0%	0%	Electricity	+6%	-0.01%	-1.43E-01	+0.01%
	+49%	-3.28E-02	-77%	-85%	Graphene Recycling	0%	0%	-1.43E-01	0%
	-9%	-1.62E-01	14%	-85%	Nitrogen	0%	0%	-1.43E-01	0%
	+11%	-1.18E-01	-17%	-85%	Stainless steel Recycling	0%	0%	-1.43E-01	0%
rGO2T	0%	-1.14E-01	0%	0%	Electricity	+6%	-0.02%	-1.14E-01	+0.01%
	0%	-1.14E-01	0%	0%	Graphene Recycling	+50%	44%	-1.64E-01	n/a
	0%	-1.14E-01	0%	0%	Nitrogen	+50%	-10%	-1.02E-01	+5%
	0%	-1.14E-01	0%	0%	Stainless steel Recycling	+50%	13%	-1.28E-01	n/a

Table 5.10 – Sensitivity results for End-of-life
(*negative percentages mean a reduction in the recycling credits thus an increased impact. The percaentage showed as Overall LCA is based on the overall value including the 3 pahses)

It is possible to notice how, for activated carbon, a reduction of 50% of the nitrogen used, would reduce the impact of the recycling process by almost 50%, while a reduction of 50% in the aluminium recycled would diminish by almost 80% the environmental credits and increases the overall life cycle impacts by 8%. It is possible also to notice how the heat losses have a very limited effect. The recycling of activated carbon does not affect the LCA significantly as a reduction of 50% in its recycling rate increases the overall impacts only by 2%.

In the case of the rGO2C the graphene recycling is the crucial activity that brings the largest environmental credit. A reduction of 85% of its recycling would bring a credit reduction of almost 80% and an increase of the overall impacts (Table 5.8) of almost 50%. On the contrary an increase of 50% of its recycling increases the benefit for the environment of 44%, but the benefit on the overall LCA cannot be calculated as it would mean to recycle more than it was produced[1].

The reduction of the nitrogen use and of the stainless steel recycling by 85% improves the end-of-life results by 14% and 17% respectively and the overall results by 9% and 11%. This is not a big share of the overall impacts, but is not negligible either especially if the graphene production will become more efficient. Should this happen, the recycling process would gain a smaller environmental credit since it would displace the production of a less impacting graphene. Hence, the share of nitrogen use and stainless steel recycling would increase.

Extending the analysis to all categories, the category in which the recycling has the highest share is the resource depletion (around 88% of the production plus use-phases for graphene and around 60% for activated carbon) because the recovery of material reduces the use of more material. In this case, the percentages related to the overall LCA values would show larger numbers (Appendix C paragraph C.2).

5.2.5 Alternative scenario

This scenario is generated combining all variations shown in the sensitivity analysis for both activated carbon and graphene technologies. Compared to the previous results this scenario shows the impact that a variation of specific capacitance has on the overall life cycle and not only on the single phase.

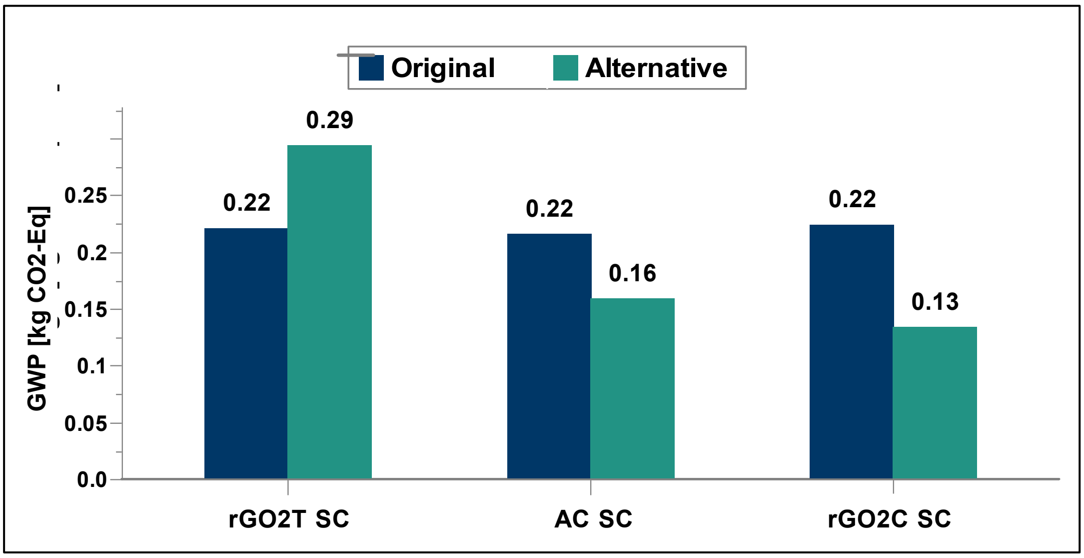

Figure 5.9 – Global warming potential: alternative scenario comparison. The graphene based supercapacitor becomes the least impacting technology reducing its GWP by 40% while the activated carbon solution improves it only by 25%. AC = activated carbon SC = supercapacitor

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[1] The variations are relative to the original results of the LCA. An increase of 50% in graphene recycling is not possible to test as the LCA result for GWP refers to a process in which the recovery rate is already set at 90%. It would mean to recycle more material than what was originally produced for a supercapacitor.

	ORIGINAL			ALTERNATIVE		
	AC	rGO2C	rGO2T	AC	rGO2C	rGO2T
Global Warming Potential [kg CO2-Equiv.]	0.216	0.224	0.221	0.159	0.134	0.294
Ozone Depletion [kg CFC 11-Equiv.]	-1.57E-11	2.61E-10	2.61E-10	-5.66E-11	1.08E-10	4.60E-10
Human toxicity, cancer [CTUh]	7.72E-11	9.08E-11	9.01E-11	5.81E-11	4.92E-11	1.31E-10
Human toxicity, non-canc. [CTUh]	1.06E-08	1.25E-08	1.26E-08	7.54E-09	6.18E-09	1.79E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	7.08E-05	6.62E-05	6.65E-05	5.38E-05	4.74E-05	8.83E-05
Ionising radiation, human health effect model, [kg U235 eq]	0.235	0.253	0.253	0.190	0.221	0.322
Photochemical ozone formation,[kg NMVOC]	3.52E-04	3.49E-04	3.48E-04	2.82E-04	2.50E-04	5.00E-04
Acidification [Mole of H+ eq.]	8.47E-04	9.03E-04	9.08E-04	6.54E-04	6.23E-04	1.23E-03
Terrestrial eutrophication, [Mole of N eq.]	1.54E-03	1.54E-03	1.52E-03	1.17E-03	9.46E-04	2.13E-03
Freshwater eutrophication, [kg P eq]	2.28E-07	2.72E-07	2.57E-07	1.68E-07	1.48E-07	4.49E-07
Ecotoxicity [CTUe]	1.63E-02	2.12E-02	2.09E-02	1.10E-02	8.13E-03	3.22E-02
Resources depletion, water [kg]	0.196	0.202	0.200	0.148	0.137	0.299
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	5.15E-07	6.37E-07	7.01E-07	4.21E-07	6.14E-07	2.62E-06

Table 5.11 – Alternative scenario comparison all categories. In the alternative scenario the rGO2C becomes the least impacting device in 10 impact categories (green)

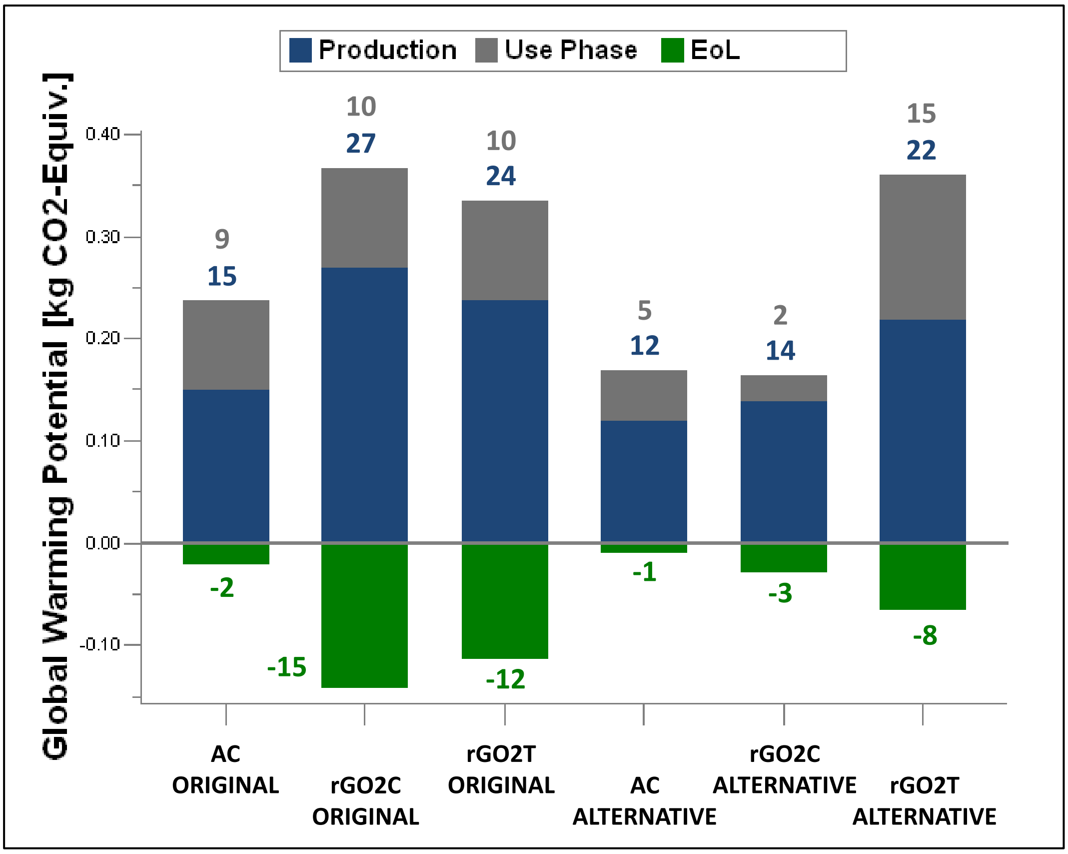

Figure 5.10 – Break down of the two scenarios into Production, Use-phase and End-of-life. The sum of values returns the values in Figure 5.9.
(AC = Activated Carbon)

The results for the global warming potential category are shown in Figure 5.9. They favour the graphene technology that offers a larger margin for specific capacitance improvement. This means that when the graphene production would synthesise high quality material, it would be feasible to create a less impacting device (rGO2C based) than today's commercial activated carbon supercapacitors. Less impacting than the technologically advanced supercapacitors too (using activated carbon that reaches its theoretical limit of specific capacitance).

All categories are presented in Table 5.11 (breakdown of the three phases for the alternative scenario in Appendix C paragraph C.3). In the alternative scenario, the rGO2C based supercapacitor becomes the least impacting in 10 out of 13 impact categories proving that a reduced material input combined with a reduced weight will benefit this technology more than it would be possible for the activated carbon solution also when considering the smaller environmental credits coming from a reduced quantity of recyclable material.

The fact that the graphene technology impacts less than the activated carbon is made possible by the recycling activity that allows the material recovered to displace a more energy intensive production process. This is clear from Figure 5.10 where the breakdown of the impacts for both scenarios is shown divided into production, use-phase and recycling. From this picture it is possible to say that the main contributor is always the production phase in both scenarios (consistently more than 50% for the activated carbon and more than 80% for graphene when considering all impact categories. Appendix C paragraph C.3). For the rGO2T, the production and recycling phases reduce their contribution due to a reduction in the acid usage (and neutralisation), but the use-phases increases as the weight of the supercapacitor increases (lower specific capacitance, bigger electrodes).

Improvements in the production process of graphene are needed to allow the graphene supercapacitors to be least impacting than the activated carbon ones without considering both recycling processes. Though, it is possible to speculate that the graphene synthesis process is still under development and thus it is possible that, when optimised as much as the activated carbon production, it could become the best environmental choice between the two materials.

For the time being, the use-phase is important for the graphene solution as it allows it to become less impacting over time. To quantify this importance it is possible to calculate a breakeven point beyond which the graphene device becomes less impacting than the activated carbon based one. Figure 5.11 shows the global warming potential variation over the lifetime of a vehicle when recycling is not considered. It is possible to deduct that in the alternative scenario the activated carbon supercapacitor (less impacting production at 0 Km) becomes more impacting after 120,000 Km. This is because the increased specific capacitance of graphene allows for a smaller and lighter supercapacitor that generates a lower impact per kilometre driven. When adding the recycling (Figure 5.12), the scenario changes completely. Considering only production and recycling (km 0) activated carbon is the best technology but only for 600 km.

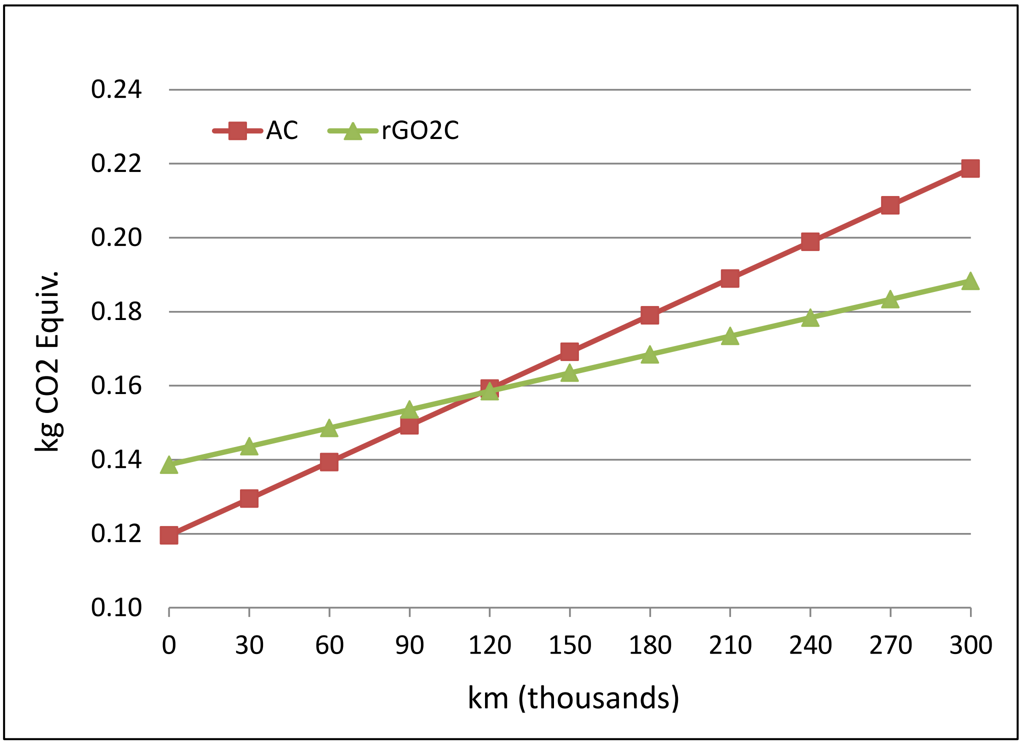

Figure 5.11 – Global Warming Potential over a lifetime of a vehicle: Production and use-phase. The lighter supercapacitor (rGO2C) becomes less impacting over 116,000 km driven

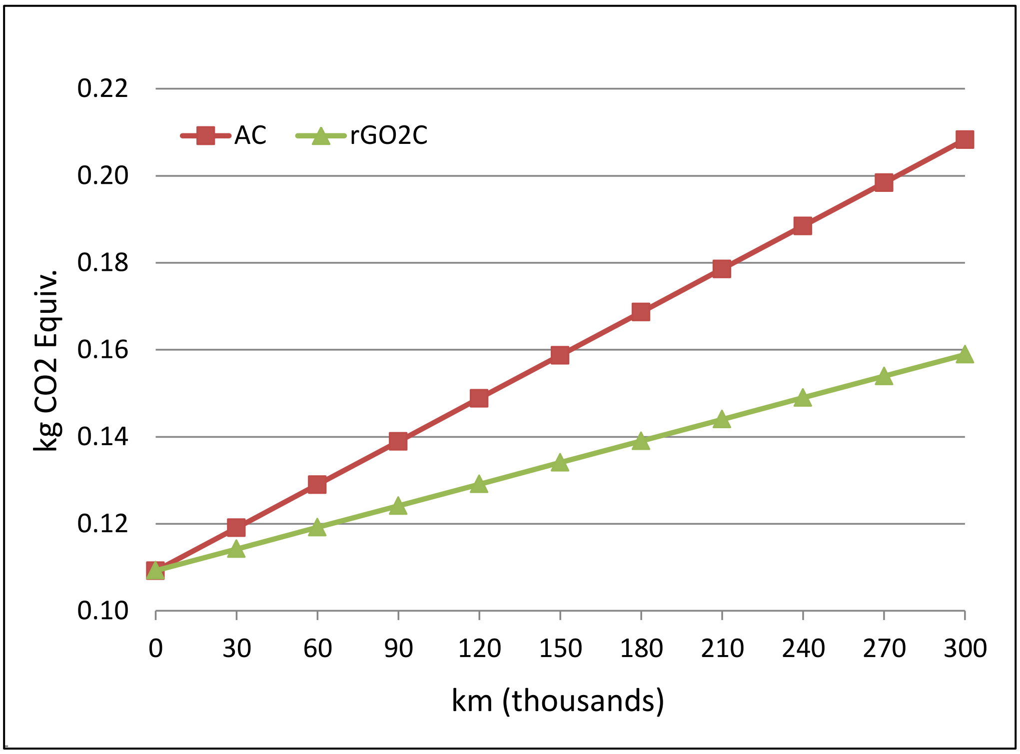

Figure 5.12 – Global Warming Potential over a lifetime of a vehicle: 3 phases (cradle to grave). When including recycling, the graphene technology is the least impacting after 571 km.

	BREAKEVEN POINTS IN Km	
	W/O Recycling	W Recycling
Global Warming Potential [kg CO2-Equiv.]	115,927	571
Ozone Depletion [kg CFC 11-Equiv.]	Never	Never
Human toxicity, cancer [CTUh]	550,191	Always
Human toxicity, non-canc. [CTUh]	401,338	13,172
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	Always	Always
Ionising radiation, human health effect model, [kg U235 eq]	Never	Never
Photochemical ozone formation,[kg NMVOC]	135,359	Always
Acidification [Mole of H+ eq.]	374,523	72,963
Terrestrial eutrophication, [Mole of N eq.]	31,306	Always
Freshwater eutrophication, [kg P eq]	474,752	58,180
Ecotoxicity [CTUe]	393,785	12,279
Resources depletion, water [kg]	180,904	59,279
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	Never	Never

Table 5.12 – Summary of breakeven points for all categories

Table 5.12 shows, for all impact categories, after how many kilometres the rGO2C based prototype becomes less impacting than the activated carbon based device. In some cases it will never happen (i.e.: above one million kilometres as no car would be driven for such long distance), while in some others is likely to happen. It is important to remember, though, that FIAT sets the theoretical maximum lifetime for a petrol vehicle at 150,000 km and 300,000 km for a diesel engine and that Table 5.12 is based on the consumption of a petrol engine (1.4 L or less).

Nevertheless, it is an interesting overview and indication of how impacts change over a vehicle lifetime and shows that, for this application, it is possible to accept an increase in environmental impacts during the production phase, in favour of their decrease during the use-phase. When doing this type of reasoning, though, it is important to evaluate after how many kilometres the higher production impacts will be absorbed by a less impacting use-phase.

5.3 Normalisation and Weighting

When results are normalised, it is possible to better understand which categories suffer the most from the production and use of the supercapacitors. Table 5.13 shows the results presented in Table 5.11 normalised using to the latest values released by the European Commission during the first half of the year 2015. The values mean that the higher the number is, the larger is the share of the impact in relation to the European impact (per person per year).

The normalised values show how the ionising radiation is the most problematic part of the production of these supercapacitors followed by the global warming potential. The following four are non-carcinogenic human toxicity, acidification, particulate matter and photochemical ozone formation. They ranked in different order in different scenarios, but they are always present in the top 6 list.

On the normalised values the weighting sets are applied to rank the impact categories in order of importance. In this case three sets are applied: the first set is obtained averaging the values presented in a document connected to the Joint Research Centre (JRC) of the EU Commission [7] (results are shown in Table 5.14), the second set is the one proposed by Thinkstep[2] (formerly PE international – results in Table 5.15). The third set, instead, it is created merging standard weighting sets (TRACI 2.1 and ReCiPe – Results in Table 5.16).

	ORIGINAL			ALTERNATIVE		
	AC	**rGO2C**	**rGO2T**	**AC**	**rGO2C**	**rGO2T**
Global Warming Potential	2.34E-05	2.43E-05	2.40E-05	1.72E-05	1.45E-05	3.19E-05
Ozone Depletion	-7.29E-10	1.21E-08	1.21E-08	-2.62E-09	4.98E-09	2.13E-08
Human toxicity, cancer	2.09E-06	2.46E-06	2.44E-06	1.58E-06	1.33E-06	3.54E-06
Human toxicity, non-canc.	1.98E-05	2.35E-05	2.36E-05	1.41E-05	1.16E-05	3.35E-05
Particulate matter/Respiratory inorganics	1.86E-05	1.74E-05	1.74E-05	1.42E-05	1.25E-05	2.31E-05
Ionising radiation, human health effect model	2.08E-04	2.24E-04	2.24E-04	1.68E-04	1.95E-04	2.85E-04
Photochemical ozone formation	1.11E-05	1.10E-05	1.10E-05	8.89E-06	7.90E-06	1.58E-05
Acidification	1.79E-05	1.91E-05	1.92E-05	1.38E-05	1.32E-05	2.60E-05
Terrestrial eutrophication	8.75E-06	8.75E-06	8.65E-06	6.62E-06	5.38E-06	1.21E-05
Freshwater eutrophication	1.54E-07	1.84E-07	1.74E-07	1.14E-07	1.00E-07	3.03E-07
Ecotoxicity	1.86E-06	2.42E-06	2.39E-06	1.26E-06	9.30E-07	3.68E-06
Resources depletion, water	2.41E-06	2.48E-06	2.46E-06	1.82E-06	1.69E-06	3.67E-06
Resource Depletion, fossil and mineral	5.13E-06	6.28E-06	6.92E-06	4.20E-06	6.07E-06	2.59E-05

Table 5.13 – Normalised values: scenario comparison, all categories.
Values are normalised vs the total EU impact per person per year.
Colours vary per column from the largest share (red) to the smalles (green)

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[2] Thinkstep is a multinational consultancy firm for corporate sustainability; it is the owner and developer of the GaBi software and LCA dataset and database provider.

	ORIGINAL			ALTERNATIVE		
	AC	**rGO2C**	**rGO2T**	**AC**	**rGO2C**	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	5.46E-04	5.67E-04	5.59E-04	4.02E-04	3.39E-04	7.43E-04
Ozone Depletion [kg CFC 11-Equiv.]	-2.67E-09	4.43E-08	4.44E-08	-9.61E-09	1.83E-08	7.81E-08
Human toxicity, cancer [CTUh]	1.40E-05	1.64E-05	1.63E-05	1.05E-05	8.88E-06	2.36E-05
Human toxicity, non-canc. [CTUh]	7.92E-05	9.39E-05	9.43E-05	5.66E-05	4.64E-05	1.34E-04
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.24E-04	1.16E-04	1.16E-04	9.44E-05	8.32E-05	1.54E-04
Ionising radiation, human health effect model, [kg U235	7.64E-04	8.22E-04	8.22E-04	6.17E-04	7.16E-04	1.05E-03
Photochemical ozone formation,[kg NMVOC]	5.93E-05	5.86E-05	5.85E-05	4.74E-05	4.21E-05	8.41E-05
Acidification [Mole of H+ eq.]	7.76E-05	8.28E-05	8.32E-05	5.99E-05	5.71E-05	1.13E-04
Terrestrial eutrophication, [Mole of N eq.]	6.13E-05	6.13E-05	6.06E-05	4.64E-05	3.76E-05	8.47E-05
Freshwater eutrophication, [kg P eq]	1.08E-06	1.28E-06	1.22E-06	7.97E-07	7.01E-07	2.12E-06
Ecotoxicity [CTUe]	2.05E-05	2.67E-05	2.63E-05	1.39E-05	1.02E-05	4.05E-05
Resources depletion, water [kg]	1.20E-05	1.24E-05	1.23E-05	9.12E-06	8.43E-06	1.84E-05
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	3.59E-05	4.39E-05	4.84E-05	2.94E-05	4.25E-05	1.81E-04

Table 5.14 – Weighted values: JRC weighting set applied, all categories

	ORIGINAL			ALTERNATIVE		
	AC	**rGO2C**	**rGO2T**	**AC**	**rGO2C**	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	2.06E-04	2.14E-04	2.11E-04	1.51E-04	1.28E-04	2.80E-04
Ozone Depletion [kg CFC 11-Equiv.]	-7.29E-10	1.21E-08	1.21E-08	-2.62E-09	4.98E-09	2.13E-08
Human toxicity, cancer [CTUh]	1.36E-05	1.60E-05	1.59E-05	1.02E-05	8.66E-06	2.30E-05
Human toxicity, non-canc. [CTUh]	1.29E-04	1.53E-04	1.53E-04	9.19E-05	7.54E-05	2.18E-04
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.21E-04	1.13E-04	1.13E-04	9.21E-05	8.11E-05	1.50E-04
Ionising radiation, human health effect model, [kg U235	1.08E-03	1.17E-03	1.17E-03	8.74E-04	1.02E-03	1.48E-03
Photochemical ozone formation,[kg NMVOC]	7.12E-05	7.04E-05	7.02E-05	5.69E-05	5.06E-05	1.01E-04
Acidification [Mole of H+ eq.]	1.02E-04	1.09E-04	1.09E-04	7.88E-05	7.51E-05	1.48E-04
Terrestrial eutrophication, [Mole of N eq.]	5.69E-05	5.69E-05	5.62E-05	4.30E-05	3.49E-05	7.87E-05
Freshwater eutrophication, [kg P eq]	1.00E-06	1.19E-06	1.13E-06	7.40E-07	6.51E-07	1.97E-06
Ecotoxicity [CTUe]	1.15E-05	1.50E-05	1.48E-05	7.82E-06	5.76E-06	2.28E-05
Resources depletion, water [kg]	2.41E-06	2.48E-06	2.46E-06	1.82E-06	1.69E-06	3.67E-06
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	2.93E-05	3.58E-05	3.94E-05	2.40E-05	3.46E-05	1.48E-04

Table 5.15 – Weighted values: Thinkstep weighting set applied, all categories

	ORIGINAL			ALTERNATIVE		
	AC	**rGO2C**	**rGO2T**	**AC**	**rGO2C**	**rGO2T**
Global Warming Potential [kg CO2-Equiv.]	2.18E-04	2.26E-04	2.23E-04	1.60E-04	1.35E-04	2.96E-04
Ozone Depletion [kg CFC 11-Equiv.]	-4.52E-09	7.49E-08	7.50E-08	-1.62E-08	3.09E-08	1.32E-07
Human toxicity, cancer [CTUh]	1.49E-05	1.75E-05	1.73E-05	1.12E-05	9.46E-06	2.52E-05
Human toxicity, non-canc. [CTUh]	1.41E-04	1.67E-04	1.67E-04	1.00E-04	8.24E-05	2.38E-04
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.23E-04	1.15E-04	1.15E-04	9.35E-05	8.23E-05	1.53E-04
Ionising radiation, human health effect model, [kg U235 eq]	1.08E-03	1.17E-03	1.17E-03	8.74E-04	1.02E-03	1.48E-03
Photochemical ozone formation,[kg NMVOC]	7.12E-05	7.04E-05	7.02E-05	5.69E-05	5.06E-05	1.01E-04
Acidification [Mole of H+ eq.]	1.09E-04	1.16E-04	1.17E-04	8.44E-05	8.03E-05	1.59E-04
Terrestrial eutrophication, [Mole of N eq.]	5.78E-05	5.78E-05	5.71E-05	4.37E-05	3.55E-05	7.99E-05
Freshwater eutrophication, [kg P eq]	1.00E-06	1.19E-06	1.13E-06	7.40E-07	6.51E-07	1.97E-06
Ecotoxicity [CTUe]	1.27E-05	1.65E-05	1.63E-05	8.58E-06	6.32E-06	2.51E-05
Resources depletion, water [kg]	2.41E-06	2.48E-06	2.46E-06	1.82E-06	1.69E-06	3.67E-06
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	3.59E-05	4.39E-05	4.84E-05	2.94E-05	4.25E-05	1.81E-04

Table 5.16 – Weighted values: newly developed weighting set applied, all categories

After applying three different weighting sets, it is possible to notice that the ranking of the impact categories is almost identical for all three sets of results. Thus, it can be said that for the three devices analysed the ionising radiation (mostly driven by nuclear electricity generation) is the main source of concerns. This is true provided the normalisation factors will remain the same in the future. Also aluminium and graphite contribute to this category, likely due to the electricity consumption during their production. However, is not possible to give a definite answer due to data aggregation in the LCA datasets.

The second most problematic category is the global warming potential and also in this case the problems are mostly linked to the electricity and the graphene production (graphite and electricity). Third is the particulate matter for the first weighting set, acidification for the second and human toxicity for the third (each set gives a different importance to these categories.

Summarising, for the three sets, the top five categories are: ionising radiation, global warming potential, particulate matter, human toxicity (non-carcinogenic) and acidification, this last three have a different order of importance in the three sets. The sixth position also differs depending on the weighting set among resource depletion, photochemical ozone formation or terrestrial eutrophication.

Figure 5.13 represents the sum of the results for the alternative scenario using the Thinkstep weighting. It was chosen because believed to be more reliable as it involved more than 500 experts for its creation. The chart shows how, when summing all weighted impact categories of the alternate scenario, the activated carbon supercapacitor rack results in being the best option overall. This is due to the very large contribution of the ionising radiation (more than 60%) to the overall results. Excluding this impact category will make the graphene supercapacitor rack the technology with the lowest environmental impact (11% less).

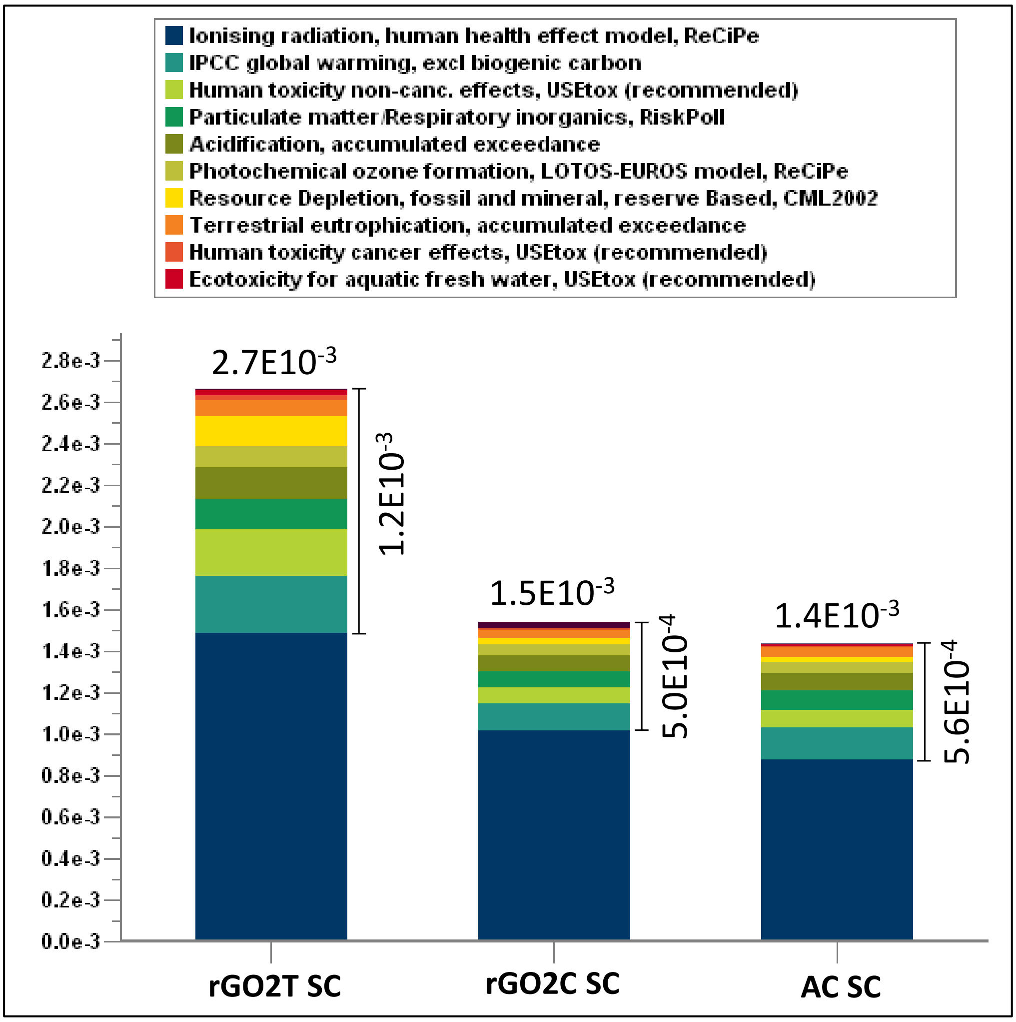


Figure 5.13 – Aggregated results with the Thinkstep weighting set applied: alternative scenario

On this topic, it is important to highlight that the ionising radiation normalisation value given by the JRC (EU centre of reference for LCA and developer of the ILCD methodology) is fostering some debates on whether it is a reliable value or not as it returns a very large normalised impact [10]. The given normalisation factor (per person per year) seems to be too low and therefore generate this enormous difference between this category and all the others. It is evident from Figure 5.13 how the ionising radiation outweighs all other categories combined. This is also proven by the fact that even if using the German mix that has less nuclear power and has a larger share of renewables (36% less ionising radiation per MJ produced than the EU27 mix), the ionising radiation still contributes for more than 50% of the impacts (50% for AC and 57% rGO2C).

According to the presented results, it is likely that a shift from stainless steel to aluminium for the prototype case would increase the ionising radiation value of more than 20% and therefore the gap with the activated carbon based device (Table 4.22 of Chapter 4). This analysis overturns the conclusions deducted from Table 4.22 that showed more categories benefitting from the shift between stainless steel and aluminium. However, it is clear now that those categories have a minor weight if compared to the ionising radiation.

Before concluding this chapter, it is worth stressing again the fact that all those values applied for the normalisation and weighting are still under development and subject to changes together with the impact categories characterisation methods recommended by the JRC in the ILCD handbook that are always under continuous refinement and improvement.

5.4 Conclusions

This chapter has proven how the use-phase and end-of-life phase give an important contribution to the impacts generated by both supercapacitors. The results of the cradle-to-gate LCA showed that, even at this early stage of technological development, it is possible to say that the two technologies are comparable, even though the graphene supercapacitor impacts the environment slightly more than the activated carbon one (from an almost equal value in terrestrial eutrophication to 23% less in ecotoxicity and 4% in GWP).

Recycling contributes to this as it allows the recovery of high purity graphene that showed the same properties as pristine graphene if used as polymer reinforcement. The sensitivity analysis showed how the graphene recovery, besides graphene production, is the parameter that, if varied, gives the largest variation in the results, proving how crucial is this activity in the abatement of the environmental impacts of the graphene technology. In fact, when the recycling is taken into account the activated carbon technology still has the lowest environmental impact but the impact values of the two technologies can be considered very similar.

The use-phase is also important as for the selected application the weight of the components determines the fuel consumption of the vehicle. Thus the lighter component is advantaged by a less impacting use-phase. It impacts, in case of the activated carbon supercapacitor, up to 64% in the case of ecotoxicity, 37% for the global warming potential down to the 1% of the ionising radiation (driven mostly by electricity usage). In the case of the graphene based device, though, its impact is almost similar in absolute values, but is smaller in percentage due to a larger share of impacts due to the production phase. As a general statement it is possible to say that when the graphene technology improves to the point of allowing the production of devices lighter than the activated carbon based (in this case 2.3 g), a more impacting production phase can be accepted if its impacts would be offset by the use-phase during the lifetime of the vehicle.

When the alternative scenario is applied (specific capacitances reaching their maximum theoretical value) it is possible to estimate that the least impacting technology would be the graphene based one in 10 out of 13 impact categories by percentages ranging from 7% in the water depletion to almost 20% in human toxicity and terrestrial eutrophication. It shows also a 16% advantage over the activated carbon device in the global warming category. Moreover, even if the theoretical numbers would not be reached, the graphene technology offers more room for improvement. This is because while the activated carbon production is based on an efficient state of the art production process, the simulated graphene production is based on the laboratory process that could be made more efficient in the future and therefore reduce its environmental impacts even further.

Normalisation and weighting are applied to appreciate the relevance of the impacts in relation to average European impacts per person per year (and per impact category). When summing together all weighted impact categories, the activated carbon based supercapacitor rack overturns the results by being 5% less impacting than the competing technology. The graphene based supercapacitor suffers from a larger contribution of the ionising radiation (14% more) that pushes the results in favour of activated carbon. However, this impact category alone covers more than 60% of the total aggregated impacts for both technologies (61% for AC and 67% forrGO2C) and if this impact category is removed, the sum of all remaining impacts is in favour of the graphene supercapacitor (11% lower impact). It must be said that the normalisation values are still under development and they cannot be considered official or very reliable yet.

Concerning this cradle-to-grave LCA it is possible to conclude that the production of graphene remains the most critical phase for the graphene supercapacitor. It showed how important is to minimise the heat losses as much as possible and to reduce the quantity of graphene needed to reach the necessary capacitance (85% quantity reduction would make the graphene supercapacitor the favourable choice). This would consequentially reduce the quantity of material used for the whole package reducing the capacitor weight and therefore both production and use-phase impacts. It is also crucial that the recycling process, when performed at commercial-scale, could still recover very high quality material (similar to pristine) in order to displace new graphene production and gain environmental credits.

5.5 References

1. Veca, A., *Personal communication*, 2013: CRT (Centro Ricerche FIAT).
2. Hankin, S. and S. Billet, *Electrograph final report (EU project FP7)*, 2014.
3. Jiang, G. and S.J. Pickering, *Recycling supercapacitors based on shredding and mild thermal treatment.* Waste Management, 2015.
4. Jiang, G., *Personal communication*, 2014: University of Nottingham.
5. Simon, C.M. and W. Kaminsky, *Chemical recycling of polytetrafluoroethylene by pyrolysis.* Polymer Degradation and Stability, 1998. **62**(1): p. 1-7.
6. *Product Environmental Footprint Pilot Guidance - Guidance for the implementation of the EU Product Environmental Footprint (PEF) during the Environmental Footprint (EF) pilot phase. EU Commission.* 2015 [cited 2015 03]; Available from: http://ec.europa.eu/environment/eussd/smgp/pdf/Guidance_products.pdf.
7. Huppes, G., et al., *Weighting environmental effects: Analytic survey with operational evaluation methods and a meta-method.* The International Journal of Life Cycle Assessment, 2012. **17**(7): p. 876-891.
8. ScrapSales. *Find the Best Scrap Metal Prices in the UK*. 2016 [cited 2016 03]; Available from: http://www.scrapsales.co.uk/.
9. Weinstein, L. and R. Dash, *Supercapacitor carbons.* Materials Today, 2013. **16**(10): p. 356-357.
10. Thinkstep, *PEF test kit 4.0 Webminar*, 2014.

CHAPTER 6: Conclusions

This chapter summarises the results of the LCA study and provides the general conclusions for the main parts of the LCA: graphene comparison, supercapacitor production comparison including scale up of graphene production and supercapacitor cradle to grave life cycle including use phase and recycling.

It also highlights the original contribution of this study to the research on life cycle assessment of graphene and provides some suggestions about future studies that would help reducing the environmental impacts of graphene while it is still in its infancy and would help filling data gaps for studies on life cycle assessment of graphene.

6.1 Conclusions

The graphene production analysis showed how the processes to make the rGO2x type of graphene are the least impacting in all impact categories analysed if compared – per unit of mass produced – to electrochemical exfoliation and to chemical vapour deposition. Moreover, the chemical routes offer the highest specific capacitance (20 F/g) that is one of the most important properties for supercapacitor application. It also showed that the main contributor to the environmental impacts is the electricity consumption.

The graphene materials with lowest impacts and highest specific capacitance were used as electrode for supercapacitors and the prototypes manufactured were compared to the state of the art commercial supercapacitors produced by Maxwell Technologies Inc. Before comparing the devices, though, it was necessary to scale up the laboratory graphene production to a commercial-scale industrial process in order to compare it to Maxwell production of activated carbon, the material currently used in the electrodes of commercial supercapacitors.

The results of the cradle-to-gate LCA, from raw material extraction to supercapacitor assembly, showed that activated carbon technology is currently the least impacting and therefore the best solution in terms of environmental impacts for all impact categories. This is not only true when considering the current status of graphene research but also in a possible alternative scenario where both graphene and activated carbon specific capacitance is increased to their maximum upper limit. In this case, however, the impacts generated by graphene prototype become comparable to the ones generated by the activated carbon supercapacitor and slightly better in the case of particulate matter.

This is an encouraging result in the light of the fact that the alternative scenario did not consider any efficiency improvement in the graphene production process that remains the one performed in the laboratory. However, it also clearly showed that improving only the specific capacitance of the graphene would not be enough to make this technology the least impacting and that the production process must be made more efficient.

When considering a cradle-to-gate approach, therefore including the use phase and recycling phase, this analysis showed that currently the two technologies generate very similar environmental impacts while in the alternative scenario the graphene technology proved to be the least impacting solution in almost all impact categories, demonstrating the good potential of the technology.

Considering the LCA from raw material extraction to the recycling of the devices, it is possible to appreciate the important contribution of the recycling and use phase. Especially the recycling activity is fundamental for the graphene technology to become the least impacting solution in most of the impact categories. This is possible because the material recovered proved to be of a very high quality when used as polymer reinforcement, hence it can displace the production of pristine material generating environmental credits.

Graphene production still remains the process with the largest environmental impact confirming it to be the most problematic area of the whole life cycle and where development is mostly needed to reduce environmental burdens. Production was found to be responsible for at least 50% of the impacts for the activated carbon device and generally more than 80% for the graphene supercapacitor production when considering all impact categories. If the recycling was excluded, the activated carbon technology would still be the least impacting solution in the original scenario while in the alternative one the two technologies would show similar results.

The use phase plays also an important role for the selected application (powering a car door mirror). Transporting the additional supercapacitor rack increases the fuel consumption since more weight must be carried and even little additional weight can make a difference over a lifetime of 150,000 km.

The activated carbon supercapacitor is lighter making the impacts of its use phase smaller compared to the graphene prototype. However, in the alternative scenario the graphene technology could become lighter and this would mean that, over the life cycle, the activated carbon supercapacitor would be slightly less impacting during production, but the more a car is driven, the more the graphene solution becomes a better choice for reducing the environmental burdens. It was calculated that after roughly 120,000 km the graphene based device would impact less than its competitor in all impact categories, excluding the ozone depletion, the ionising radiation and the resource depletion (mineral and fossil).

When results for the alternative scenario are normalised according to the latest values issued by the European Commission, weighted according to Thinkstep waiting set for ranking them in order of importance, ionising radiation is by far the most troublesome impact category. Its impact is larger than all other impact categories combined (roughly 60% of the total). Since this impact is mostly generated by nuclear electricity production, these normalisation and weighting factors favour the activated carbon supercapacitor that needs less electricity during its lifecycle. However, if the ionising radiation category is taken out of the picture, the graphene technology becomes the best solution for limiting the environmental impacts (11% less than the activated carbon supercapacitor). Though, the normalisation values and weighting sets used are provisional as they are still under development thus very up to date but not entirely reliable yet.

As general conclusion it is possible to say that today the graphene technology could compete with the activated carbon only if heat losses during production and recycling are minimised and if recycling is performed to recover high quality graphene to use as polymer reinforcement. In this study it was shown that graphene technology will become better than activated carbon from an environmental perspective when its production is optimised and its specific capacitance is increased. Graphene is also likely to be the material with the largest room for improvement since it is just at an early stage of development and limited research has been done to develop and optimise commercial production. For these reasons, graphene can be looked at as a promising and valuable alternative to activated carbon for supercapacitors to be developed in the years to come.

6.2 Original contribution

This research has followed the examples of other studies for process modelling and scale up to commercial-scale industrial processes. Uncertainties are assessed via sensitivity analysis and scenario modelling. However, it is the first study applying this theory to the graphene synthesis. Moreover, the production phase and the recycling activity are scaled up by designing potential industrial processes using a process simulation tool.

The most important contribution though is to offer a complete life cycle assessment of graphene including: a comparative study of production methods on the basis of the quantity produced, a comparative study of graphene applied to supercapacitors and a case study in which the supercapacitors are used to power a car door mirror in order to offer a cradle-to-grave comparative life cycle assessment of a graphene based product.

Considering the analysis of the production methods, the approach used was very helpful in comparing the different processes on the base of a common quantity of material produced. What is important is that this study contributes in closing some gaps in data availability for graphene synthesis. Compared to the only other study found on the subject, this offers an analysis based on data measured directly in laboratories rather than data from literature and it shows an analysis of several impact categories and not limited only to four.

This is one of the few studies that incorporates a function in the life cycle assessment and therefore does not judge the production methods purely on the quantity of material produced, but also quality. This analysis is important as a comparison made purely on quantity produced penalises those processes that might need more resources, but produce a high quality material of which less quantity might be required to perform the same function. This thesis not only provides some new data in relation to graphene use for supercapacitors, but also provides the information on the environmental burdens of these two technologies for an extensive list of impact categories.

Moreover, this is also one of the few studies in which a graphene based device is included in a case study in order to present a full life cycle of graphene with a cradle-to-grave approach. A whole life cycle analysis is performed and also a ranking of environmental impacts via normalisation and weighting is presented and this level of detail was not found in any other study in literature.

Summarising, this is the first study on graphene that offers a whole cradle-to-grave life cycle assessment on graphene and supercapacitors, it offers an extensive list of impact categories weighted for importance and offers a set of valuable data to cover some gaps of data availability for the graphene synthesis process. It is also the first study of graphene that offers an analysis on possible commercial-scale graphene production and recycling processes.

6.3 Future work

From this study, it is clear that graphene synthesis should be improved in order to increase the efficiency of the processes and reduce waste. To do so, more studies are needed to understand the reactions mechanism. This would be of help in estimating the optimum quantities of materials and energy inputs needed to maximise the output (also in terms of quality) and in understanding wastes and emissions composition and quantity. This additional information would also be important to improve the quality and precision of the LCA presented.

For electrochemical exfoliation, larger batches should be tested in order to understand what impact the size has on the production rate and efficiency. Studies should be carried on the electrode size and disposition in order to optimise the electrolytic cell. Research is needed also to investigate the cell performance when electrodes are reused or used continuously (with an increased number of cracks) in order to evaluate how this impacts the graphene quality and process efficiency. Research should also find a way to recycle substance or reuse them. For example, in the case of the electrochemical exfoliation, oxygen and hydrogen are by-products that could be used to produce electricity in a fuel cell to reduce the energy consumption of graphene production.

It would be also very important to understand what would happen if the material produced with the electrochemical exfoliation is reduced to remove oxygen groups as the material produced with this process is a mix of oxidised graphite and oxidised graphene. A reduction might increase its low specific capacitance and may enhance this process making it more attractive for supercapacitors.

For the chemical reactions the most important improvement is to reduce the energy consumption, and related environmental impacts, by simply minimising the heat required during production by minimising the heat losses. Further impact reductions might also be achieved by recycling/reusing the chemicals, optimising their quantities and shortening reaction time (reduced energy consumption) without compromising the material quality.

Tests should also be performed on the supercapacitor performance while using different electrolytes. During this study only acetonitrile was considered but it was never investigated if its coupling with graphene is the optimal solution. It is possible that a different electrolyte would enhance the performance of the supercapacitor and this could affect the LCA.

Some more tests should be performed on the rGO2T material in order to measure how it performs in a supercapacitor configuration. It was thought to be as good as the rGO2C material, but as it showed a flat surface it is also possible that its performance are not as good as those of the rGO2C as it offers a low surface area per unit volume and thus be not good for storing electrical charge. This flat surface was speculated to be due to the drying process that produced a very thin foil of material. In fact, the wet graphite oxide was dried in a furnace inside a flat container. Tests should be performed in order to understand what would happen if the wet material would be dried in a rotary drum or a stirred reactor. This might result in a dry material presenting randomly oriented nanoplatelets and therefore increasing its specific capacitance.

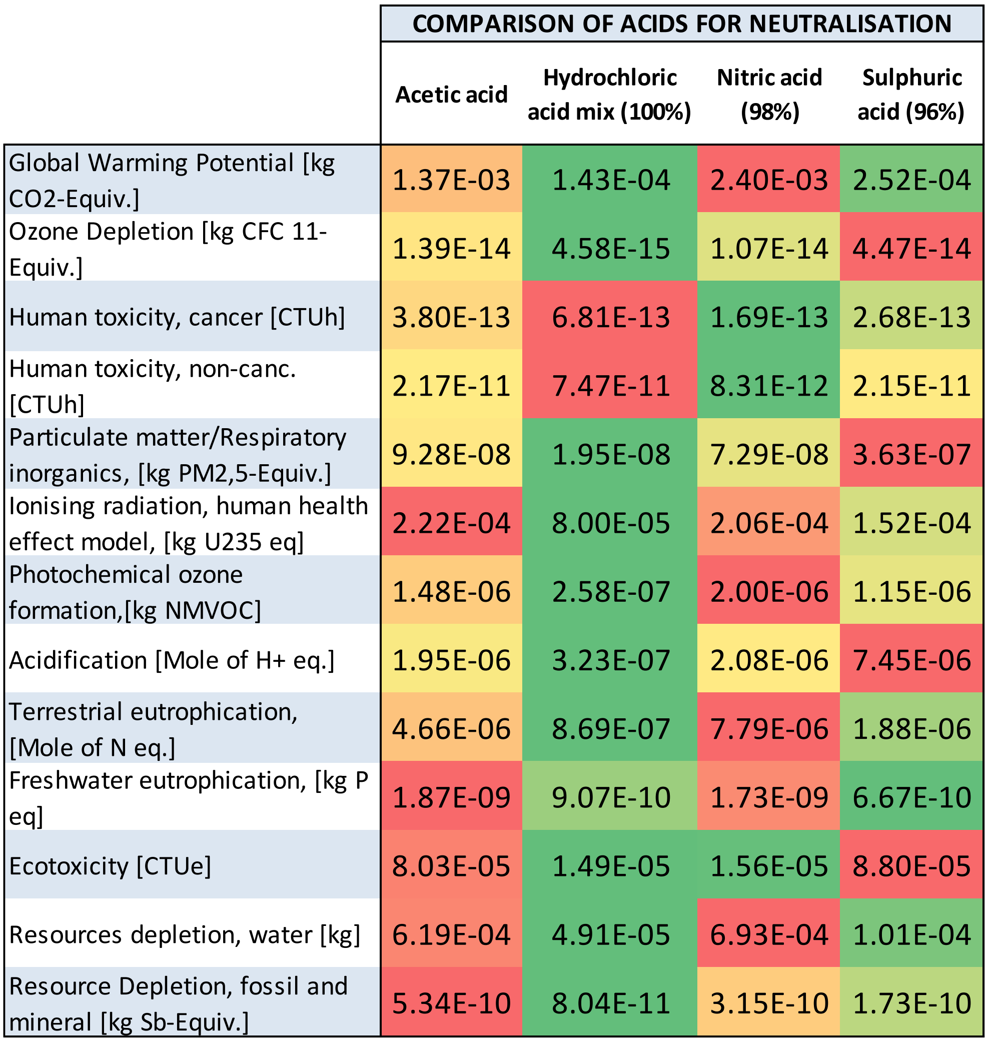
For the end of life phase, some more tests should be carried for evaluating the possibility of reducing the quantity of nitrogen used. Nitrogen is the largest contributor to the environmental impacts of the recycling phase but most likely it is used in excess. Hence, if reduced, the environmental credits generated by the recycling activity could be further increased. Besides, further work should be carried on further optimising the recycling process making it less energy intensive.

Finally, a crucial area of research is linked with the toxicology of the exposure to nanoparticles for both environment and human beings. In fact, one limitation of this LCA, but also of most (if not all) LCA studies on nanomaterials is the lack of knowledge on the possible impacts connected with nanoscale materials since nano particles might show altered properties if compared to their macro counterparts.

APPENDIX A – Graphene synthesis

A.1 Electrolyte neutralisation

Table A.1 presents the results for the acids necessary to neutralise the electrolyte for the electrochemical exfoliation. If compared to the overall results presented in Chapter 3 Table 3.2 it is possible to see how these impact values are few orders of magnitude smaller than the overall values, showing a minor contribution of the neutralisation process.



	COMPARISON OF ACIDS FOR NEUTRALISATION			
	Acetic acid	**Hydrochloric acid mix (100%)**	**Nitric acid (98%)**	**Sulphuric acid (96%)**
Global Warming Potential [kg CO2-Equiv.]	1.37E-03	1.43E-04	2.40E-03	2.52E-04
Ozone Depletion [kg CFC 11-Equiv.]	1.39E-14	4.58E-15	1.07E-14	4.47E-14
Human toxicity, cancer [CTUh]	3.80E-13	6.81E-13	1.69E-13	2.68E-13
Human toxicity, non-canc. [CTUh]	2.17E-11	7.47E-11	8.31E-12	2.15E-11
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	9.28E-08	1.95E-08	7.29E-08	3.63E-07
Ionising radiation, human health effect model, [kg U235 eq]	2.22E-04	8.00E-05	2.06E-04	1.52E-04
Photochemical ozone formation,[kg NMVOC]	1.48E-06	2.58E-07	2.00E-06	1.15E-06
Acidification [Mole of H+ eq.]	1.95E-06	3.23E-07	2.08E-06	7.45E-06
Terrestrial eutrophication, [Mole of N eq.]	4.66E-06	8.69E-07	7.79E-06	1.88E-06
Freshwater eutrophication, [kg P eq]	1.87E-09	9.07E-10	1.73E-09	6.67E-10
Ecotoxicity [CTUe]	8.03E-05	1.49E-05	1.56E-05	8.80E-05
Resources depletion, water [kg]	6.19E-04	4.91E-05	6.93E-04	1.01E-04
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	5.34E-10	8.04E-11	3.15E-10	1.73E-10

Table A.1 – Acids comparison for neutralisation of KOH or NaOH solutions

A.2 Acid neutralisation for the chemical oxidation of graphite

Table A.2 presents the results of the environmental impact of 4 bases (sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate (or washing soda Na_2CO_3) and (or slaked lime $Ca(OH)_2$) that can be used to neutralise the totality of sulphuric acid used to oxidise the graphite during the first step of the chemical (and thermal) route for graphene production. The values presented are those needed to neutralise the sulphuric acid in the case of the GO2 material. What is important to notice is that the calcium hydroxide is always the least impacting solution except for the two human toxicity categories. For this reason the calcium hydroxide was selected as neutralising agent for the chemical oxidation of graphite.

	COMPARISON OF BASES FOR NEUTRALISATION			
	Calcium hydroxide (Ca(OH)2; slaked lime)	**Potassium hydroxide (KOH)**	**Sodium hydroxide (NaOH caustic soda)**	**Soda (Na2CO3)**
Global Warming Potential [kg CO2-Equiv.]	2.04E-02	4.53E-02	3.00E-02	4.63E-02
Ozone Depletion [kg CFC 11-Equiv.]	3.03E-14	1.70E-11	1.98E-12	1.44E-12
Human toxicity, cancer [CTUh]	1.35E-11	1.69E-11	1.51E-11	8.55E-12
Human toxicity, non-canc. [CTUh]	1.66E-09	2.25E-09	1.81E-09	1.41E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	8.24E-07	1.41E-05	5.36E-06	2.21E-05
Ionising radiation, human health effect model, [kg U235 eq]	5.40E-04	4.01E-02	3.63E-02	6.95E-03
Photochemical ozone formation,[kg NMVOC]	7.16E-06	9.04E-05	6.19E-05	1.67E-04
Acidification [Mole of H+ eq.]	8.49E-06	1.11E-04	8.22E-05	3.55E-04
Terrestrial eutrophication, [Mole of N eq.]	2.93E-05	3.69E-04	2.63E-04	1.24E-03
Freshwater eutrophication, [kg P eq]	2.01E-09	9.74E-08	9.91E-08	6.61E-08
Ecotoxicity [CTUe]	2.10E-04	1.34E-03	1.30E-03	1.41E-03
Resources depletion, water [kg]	1.79E-03	2.56E-02	2.22E-02	2.73E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	2.11E-09	4.23E-06	2.21E-08	2.06E-08

Table A.2 – Bases comparison for neutralisation of H_2SO_4 solution

A.3 Reduction of graphene oxide all categories

The results presented in Table A.3 show in detail all categories for the reduction processes (chemical and thermal) only, without including the prior oxidation of graphite. It is the expansion of Figure 3.13 and Figure 3.15 of Chapter 3 and shows the results for the reductions in the base and in the optimised lab scenarios. It is important to notice the consistency in all categories as referred in Chapter 3.

	REDUCED MATERIALS BASE SCENARIO	
	Chemical rGOxC	Thermal rGOxT
Global Warming Potential [kg CO2-Equiv.]	0.25	0.73
Ozone Depletion [kg CFC 11-Equiv.]	1.5E-10	5.3E-10
Human toxicity, cancer [CTUh]	7.7E-11	2.0E-10
Human toxicity, non-canc. [CTUh]	8.6E-09	2.7E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	7.5E-05	2.6E-04
Ionising radiation, human health effect model, [kg U235 eq]	0.5	1.8
Photochemical ozone formation,[kg NMVOC]	4.7E-04	1.5E-03
Acidification [Mole of H+ eq.]	1.1E-03	3.8E-03
Terrestrial eutrophication, [Mole of N eq.]	1.6E-03	5.1E-03
Freshwater eutrophication, [kg P eq]	2.9E-07	4.8E-07
Ecotoxicity [CTUe]	9.8E-03	2.3E-02
Resources depletion, water [kg]	0.26	0.79
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	1.2E-07	3.6E-07
	IMPROVED LAB SCENARIO	
Global Warming Potential [kg CO2-Equiv.]	0.10	0.04
Ozone Depletion [kg CFC 11-Equiv.]	3.7E-11	2.7E-11
Human toxicity, cancer [CTUh]	3.6E-11	1.1E-11
Human toxicity, non-canc. [CTUh]	3.1E-09	1.5E-09
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	2.3E-05	1.3E-05
Ionising radiation, human health effect model, [kg U235 eq]	0.14	0.10
Photochemical ozone formation,[kg NMVOC]	1.7E-04	8.8E-05
Acidification [Mole of H+ eq.]	3.6E-04	2.0E-04
Terrestrial eutrophication, [Mole of N eq.]	5.9E-04	2.8E-04
Freshwater eutrophication, [kg P eq]	2.0E-07	3.0E-08
Ecotoxicity [CTUe]	5.2E-03	1.3E-03
Resources depletion, water [kg]	0.10	0.04
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	4.5E-08	2.1E-08

Table A.3 – Reduction processes: scenario comparison, all categories. This table only includes the reduction process and does not include the oxidation step.

A.4 Breakdown for rGO2C and rGO2T

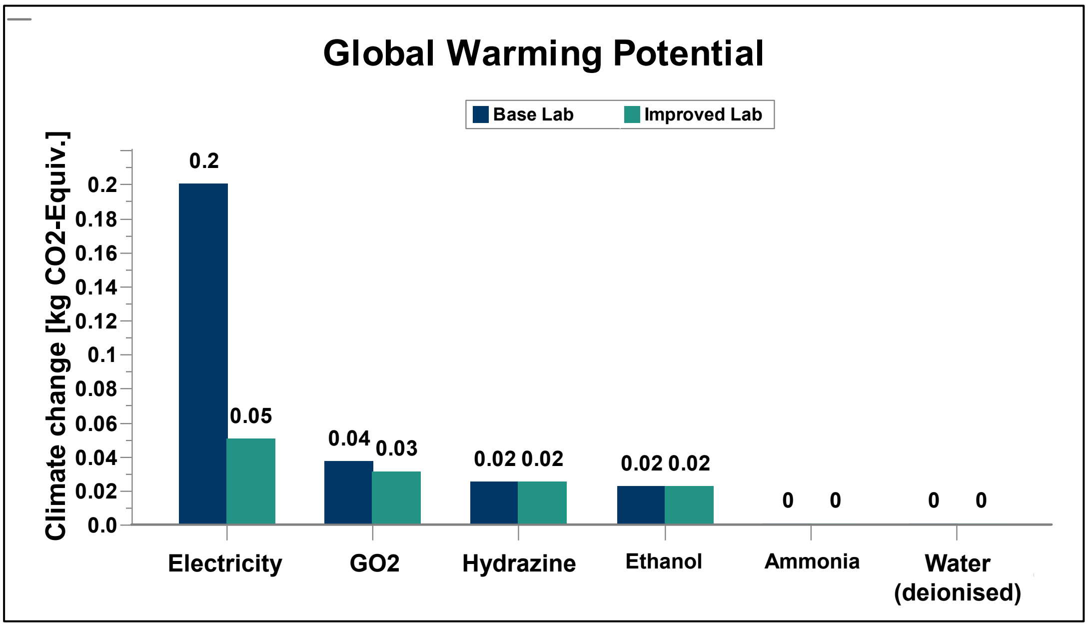


Figure A.1 – Global warming potential: scenario comparison, rGO2T breakdown

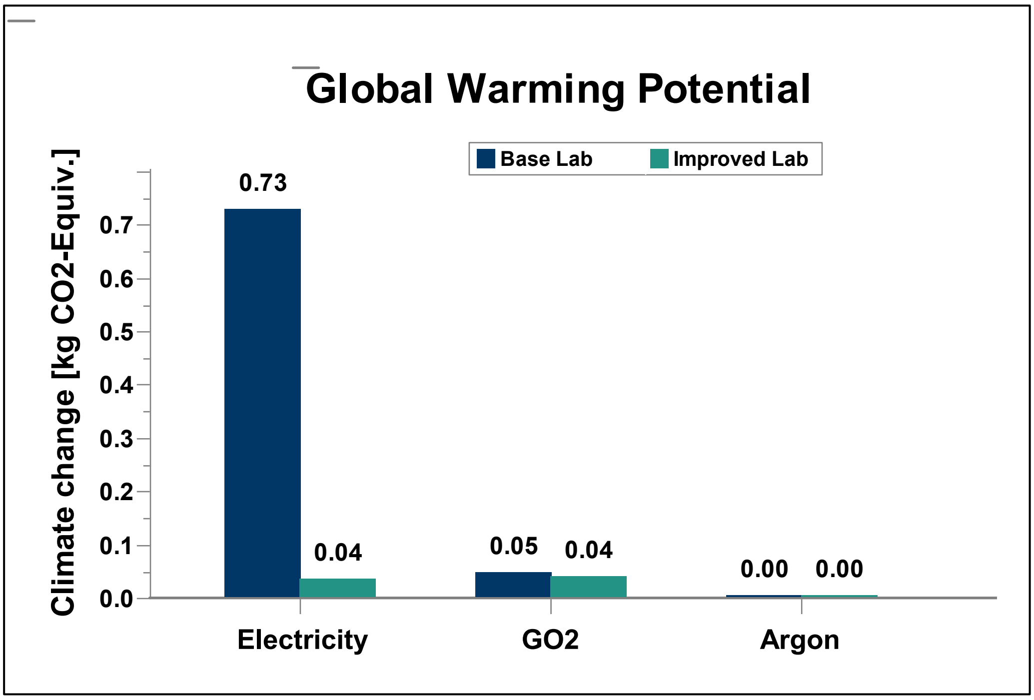


Figure A.2 – Global warming potential: scenario comparison, rGO2T breakdown

A.5 Normalisation and weighting

To further analyse the results presented in Chapter 3 paragraph 3.5 it is possible to normalise them according to the latest European guidelines. Normalisation it is normally couple with weighting, that it is normally applied to impact categories in order to set priorities. For more detail on the normalisation and weighting techniques please refer to Chapter 5 paragraph 5.1.5. Weightings are generally decided by policy makers and institutional bodies.

Normalising the results according to the ILCD test factors, shows that the contribution of these processes to the overall EU27 pollution per person is quite minimal. However, this normalisation is not really significant when the processes analysed are related to one gram of graphene production. The values become more interesting when the processes are scaled up to commercial production. Nonetheless, even if these numbers are not important in absolute terms, they are crucial to decide which categories are more impacted by the graphene production.

	COMPARISON NORMALISED VALUES				
	CH3OONa 15V	**KOH 15V**	**NaOH 7V - Used**	**rGO2H**	**rGO2T**
Global Warming Potential	4.75E-05	3.67E-05	5.35E-05	1.43E-05	9.07E-06
Ozone Depletion	1.34E-08	1.04E-08	1.54E-08	2.13E-09	1.77E-09
Human toxicity, cancer	3.28E-06	2.60E-06	3.86E-06	1.68E-06	1.25E-06
Human toxicity, non-canc.	2.97E-05	2.31E-05	3.38E-05	1.04E-05	8.91E-06
Particulate matter/Respiratory inorganics	2.90E-05	2.17E-05	3.23E-05	8.47E-06	7.75E-06
Ionising radiation, human health effect model	8.42E-04	6.49E-04	9.68E-04	1.47E-04	1.18E-04
Photochemical ozone formation	2.63E-05	1.99E-05	2.93E-05	7.96E-06	6.15E-06
Acidification	4.48E-05	3.35E-05	5.03E-05	1.52E-05	1.43E-05
Terrestrial eutrophication	1.77E-05	1.29E-05	1.90E-05	4.63E-06	3.22E-06
Freshwater eutrophication	2.65E-07	2.22E-07	3.33E-07	2.02E-07	1.11E-07
Ecotoxicity	1.51E-06	1.18E-06	1.74E-06	1.08E-06	7.89E-07
Resources depletion, water	6.29E-06	5.00E-06	7.35E-06	1.77E-06	1.27E-06
Resource Depletion, fossil and mineral	5.99E-05	6.82E-05	7.44E-05	1.53E-05	2.00E-05

Table A.4 – Graphene production, best case scenario normalised values

Table A.4 shows how the impact categories relevancy remains consistent for all synthesis processes and sets the ionising radiation as main contributor to the overall EU27 values. The other relevant categories are, in no particular order: acidification, resource depletion, global warming potential, human toxicity (non-carcinogenic) and particulate matter. In Figure A.3 it is possible to see the relative importance for all impact categories analysed and how they are dominated by the ionising radiation while the second concern is the resource depletion followed by the global warming potential and acidification.

Besides the resource depletion that is linked to graphite use, all other impact categories are mostly linked with energy consumption, nuclear and fossil fuel burning. In some cases, like acidification and toxicity, there is a contribution from the acids used.

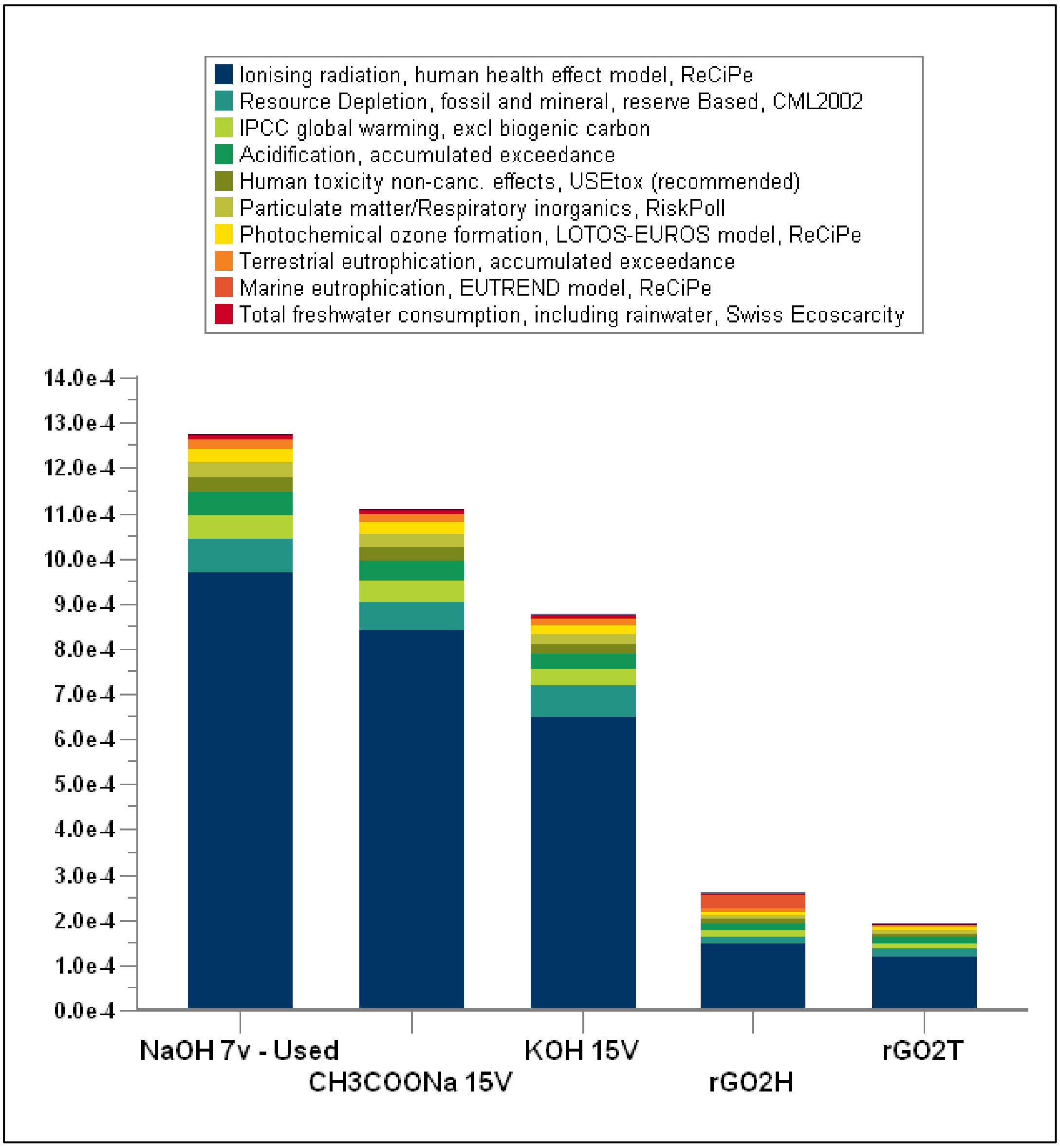


Figure A.3 – Graphene production, normalised impact relevance

When weighting is applied, the results remain consistent with the normalised results. This is because for the EU standard, for the moment, the weighting is politically set to 1 for all categories, while pilot projects are running to determine some more realistic values.

	COMPARISON WEIGHTED VALUES				
	CH3OONa 15V	KOH 15V	NaOH 7V - Used	rGO2H	rGO2T
Global Warming Potential [kg CO2-Equiv.]	4.18E-04	3.23E-04	4.70E-04	1.26E-04	7.99E-05
Ozone Depletion [kg CFC 11-Equiv.]	7.22E-08	5.60E-08	8.31E-08	1.15E-08	9.54E-09
Human toxicity, cancer [CTUh]	2.14E-05	1.69E-05	2.51E-05	1.09E-05	8.13E-06
Human toxicity, non-canc. [CTUh]	1.93E-04	1.50E-04	2.20E-04	6.77E-05	5.79E-05
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	1.88E-04	1.41E-04	2.10E-04	5.51E-05	5.03E-05
Ionising radiation, human health effect model, [kg U235 eq]	4.38E-03	3.38E-03	5.03E-03	7.65E-04	6.12E-04
Photochemical ozone formation,[kg NMVOC]	1.68E-04	1.27E-04	1.88E-04	5.09E-05	3.94E-05
Acidification [Mole of H+ eq.]	2.56E-04	1.91E-04	2.87E-04	8.65E-05	8.16E-05
Terrestrial eutrophication, [Mole of N eq.]	1.15E-04	8.40E-05	1.23E-04	3.01E-05	2.09E-05
Freshwater eutrophication, [kg P eq]	1.72E-06	1.45E-06	2.16E-06	1.31E-06	7.24E-07
Ecotoxicity [CTUe]	9.38E-06	7.30E-06	1.08E-05	6.69E-06	4.89E-06
Resources depletion, water [kg]	6.29E-06	5.00E-06	7.35E-06	1.77E-06	1.27E-06
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	3.41E-04	3.89E-04	4.24E-04	8.71E-05	1.14E-04

Table A.5 – Graphene production, best case scenario weighted values

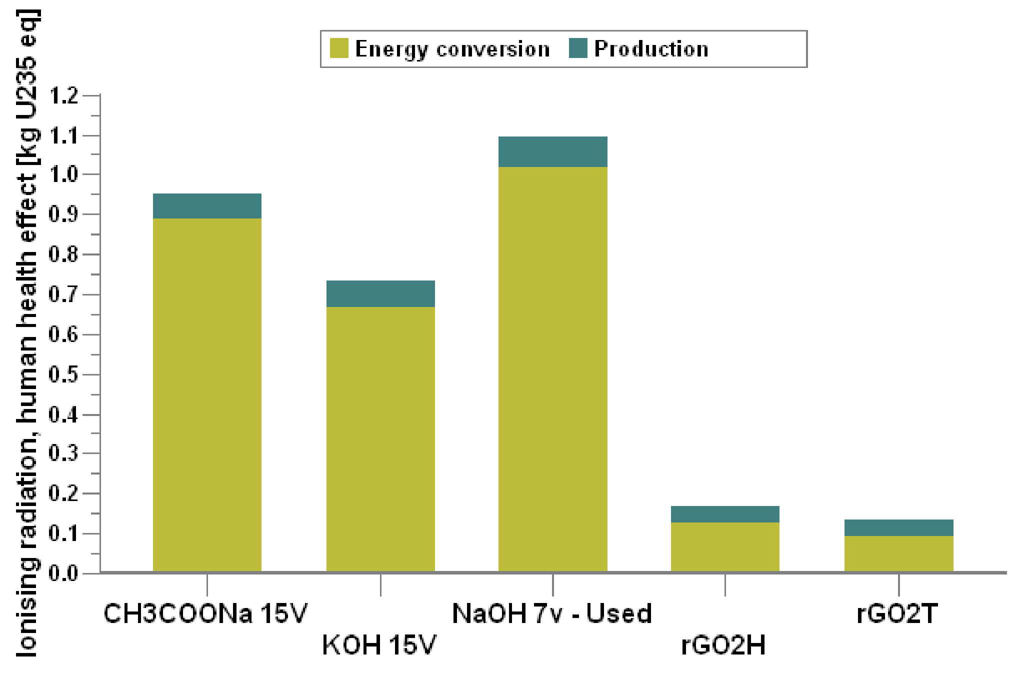


Figure A.4 – Graphene production. Ionising radiation: electricity contribution Vs material used

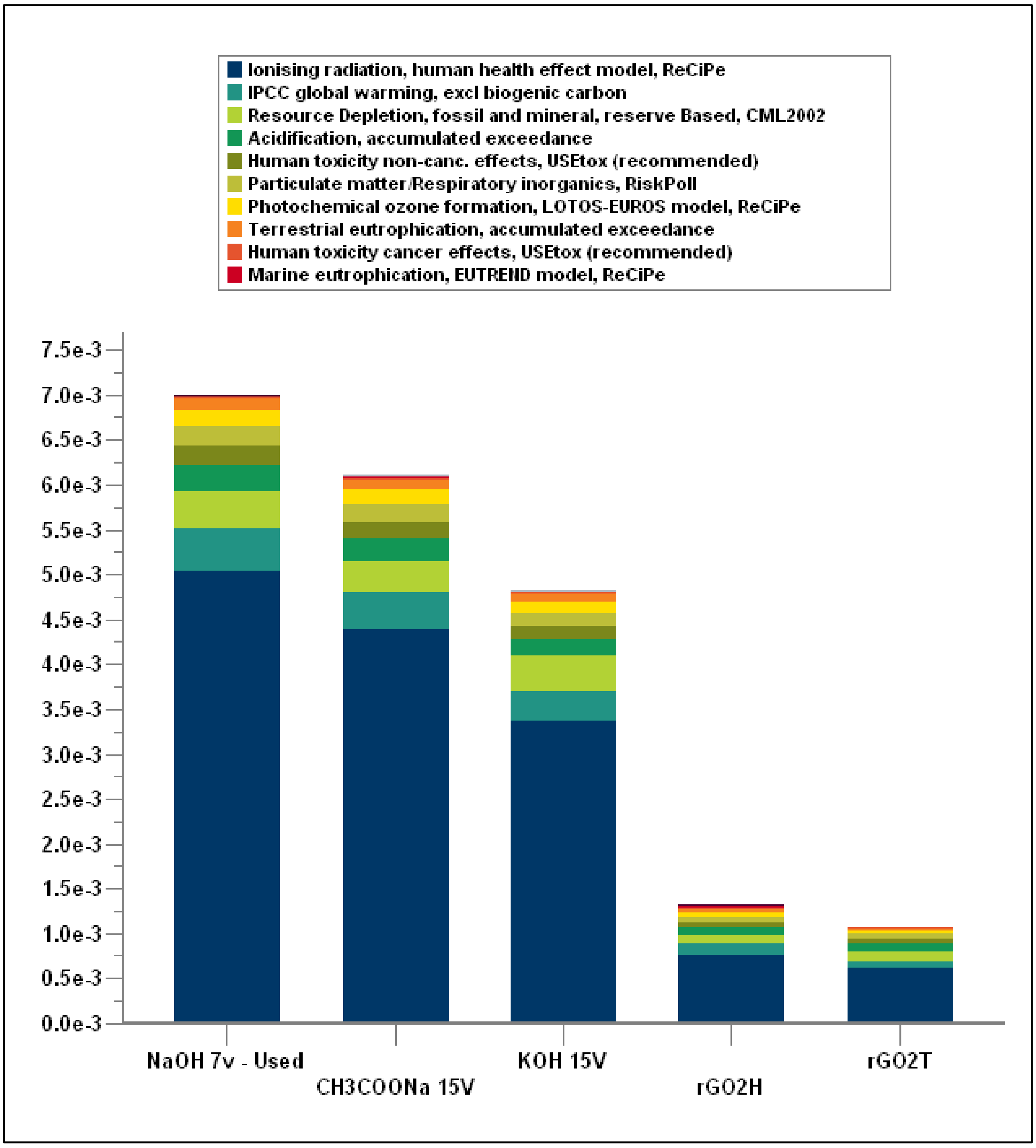


Figure A.5 – Graphene production, weighted impact relevance

When applying the Thinkstep suggested weighting set the table is not changing in the substance as the top 5 impact categories remain the ionising radiation, the global warming potential, the resource depletion, the acidification and the non-carcinogenic human toxicity as it is possible to see from Table A.5.

Also in this case the ranking of the impact is better displayed in Figure A.5 but in this case the resource depletion is not the second most important category but is the global warming potential while the acidification and non-carcinogenic human toxicity remain the fourth and fifth.

Some questions remain on the ionising radiation relevance as it results as the most important impact category. This is quite strange as this impact is mostly caused by the electricity production (Figure A.4). Since the ionising radiations emitted during power generation it is only linked with nuclear power, this normalisation factor implies that in the current European energy mix is impacting the environment mostly because of a high release of radioactive material more than for particulate matter, for example.

It must be said, though, that both the official normalisation and the weighting values are still under development and therefore will most likely change in the near future.

APPENDIX B – Production of supercapacitors

B.1 Possible scaled up graphene production

This section is just to exemplify how the graphene production processes can be optimised to match Maxwell Technologies annual production of activated carbon (around 3 ton/year). The examples are not based on any financial analysis to support this possible configuration.

B.1.1 Chemical oxidation and chemical reduction route

To obtain a production of 3 tonnes per year, it is enough to process 2 kg of graphene per batch when operating with 6 reduction vessels in parallel for 250 days a year. As the reduction procedure is the longest one, in this way it is possible to constantly run reductions while the oxidation vessel maintains some idle time.

Another way of achieving the same numbers is by having a unique but bigger reduction vessel and having several oxidations running in parallel while the reduction runs, but this solution is less flexible when there is a need to have a mix production. However, it can be more cost efficient and needs less maintenance. It all depends on the needs of the plant.

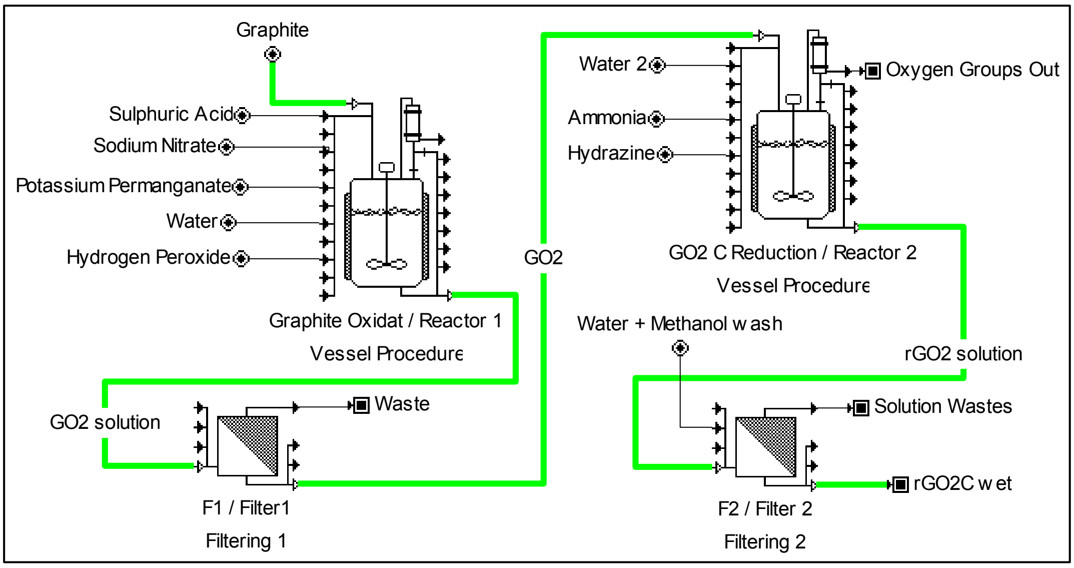


Figure B.1 – Process simulation: rGO2C production

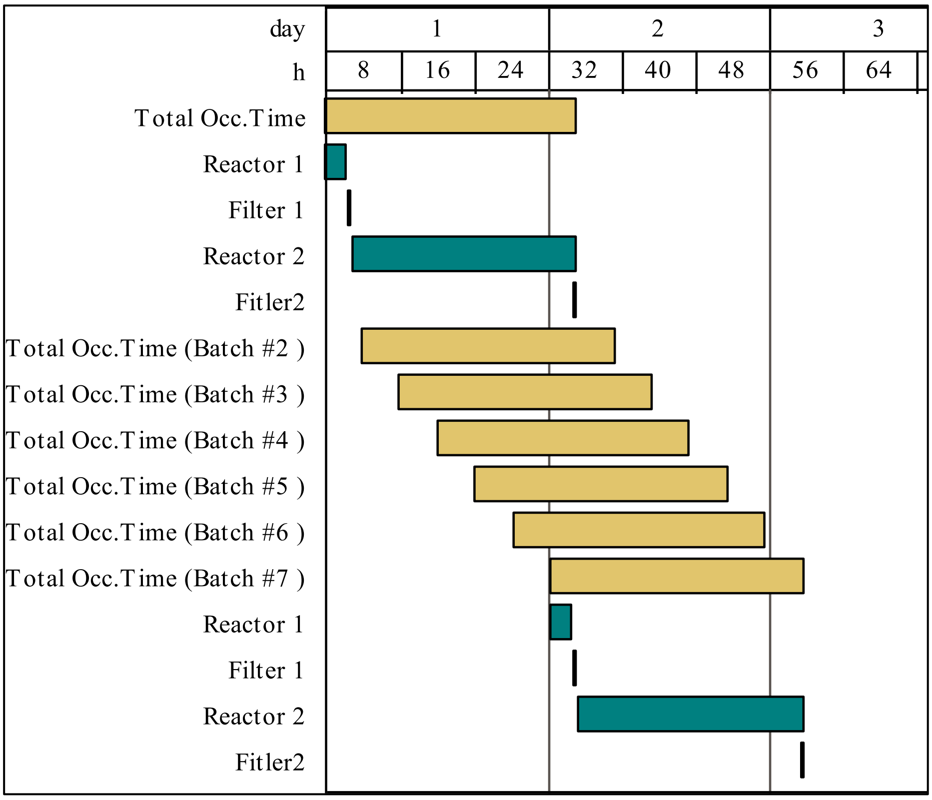


Figure B.2 – rGO2C production scheduling of multiple batches (Gantt chart)

OVERALL PROCESS DATA	
Annual Throughput	3,037.94kg/yr
Batch Throughput	2.06 kg
Reactor 1	61.07% capacity
Reactor 2	100% capacity
Limiting Equipment	Reactor 2

Table B.1 – rGO2C production process data

As it is possible to see from Figure B.2 the two reduction processes (two long green lines) perfectly match after 6 batches assuring a continuous batch process when needed.

While Table B.1 shows a summary of the overall process data with the throughput showing 3 tonnes of graphene produced per year and 100% utilisation for the second reactor used for the reduction of GO2.

B.1.2 Chemical oxidation and thermal reduction

This process consists of an oxidation and a thermal reduction. The process is sized to run batches of 2 kg in order to produce 3 tonnes of graphene per year. In the diagram in Figure B.3 the thermal reduction is divided into three different furnaces (here shown as rectors for matching the Gantt chart in Figure B.4) in order to have a more flexible process. Three furnaces for three heating stages (25°C - 140°C, 140°C - 350°C, 350°C - 700°C) allow to run several batches at a time.

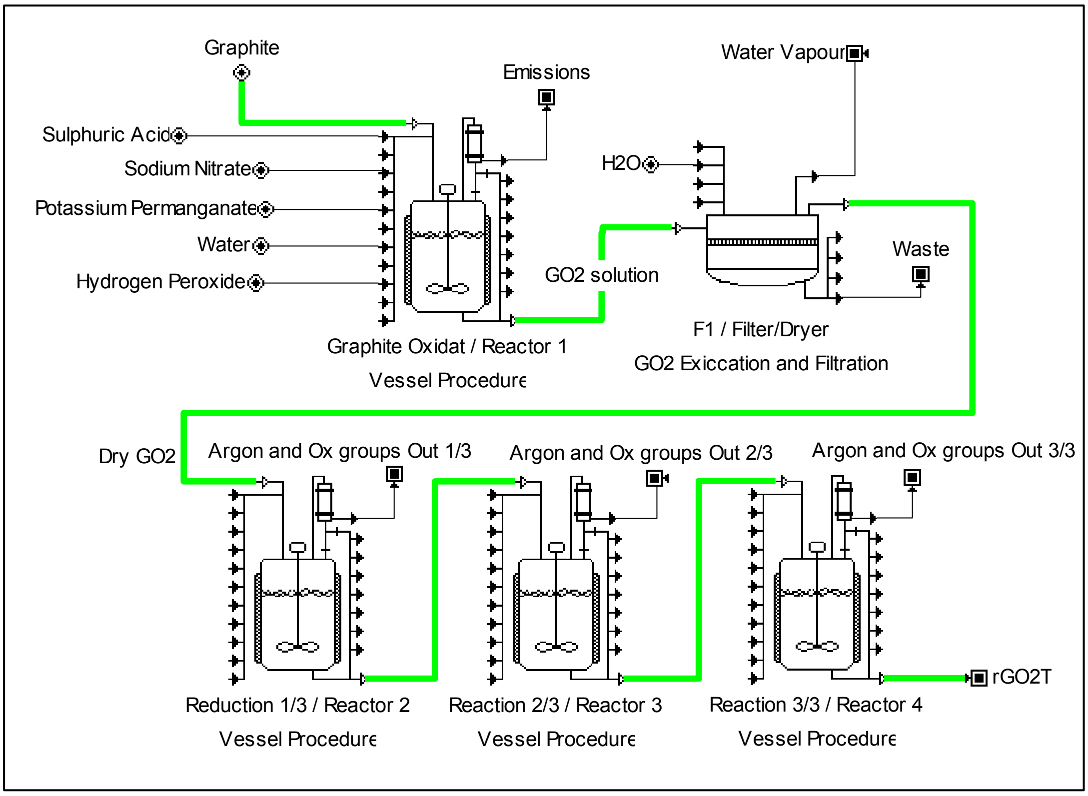


Figure B.3 – Process simulation: rGO2T production

To perform the whole process with the chosen layout, there is a need of 1 furnace for the first step, 4 furnaces for the second step - the longest - and 2 furnaces for the last step. There is also the need for 3 drying filters as they also require long time to dry the graphite oxide.

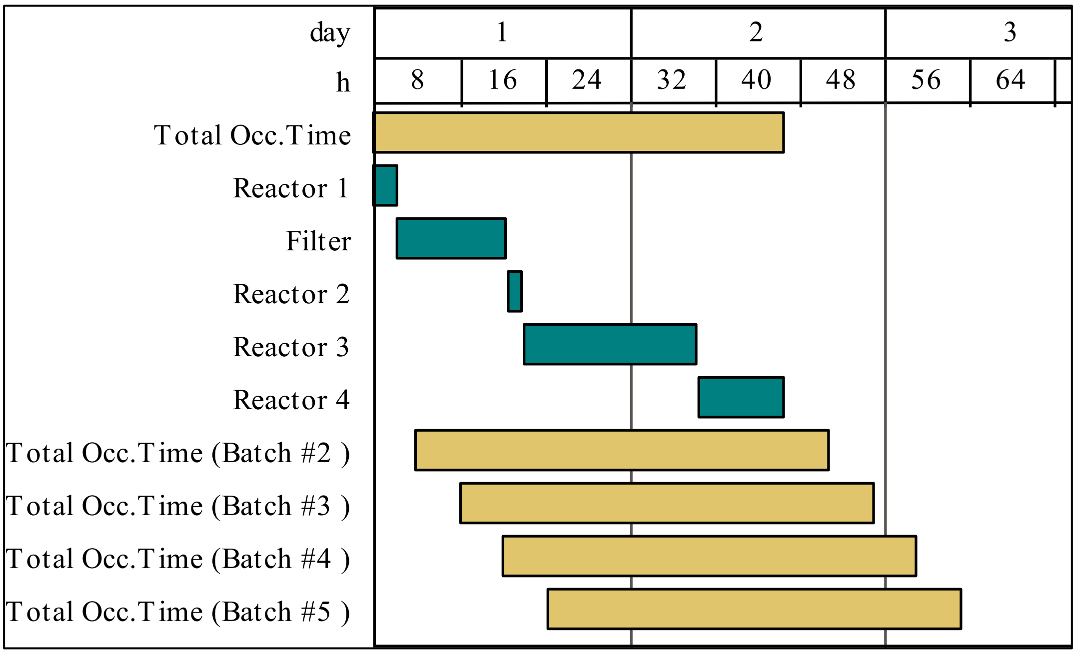


Figure B.4 – rGO2T production scheduling of multiple batches (Gantt chart)

Also in this case, everything could be done in a single furnace and one single big furnace might also be less expensive to operate (e.g.: less heat losses overall), but once again it all depends on the plant needs of cost Vs throughput. The Gantt chart in Figure B.4 shows that the downtime between each batch is very limited using this configuration. Also in this case the process is considered to be running for 250 days in a year, excluding weekends and possible closures.

OVERALL PROCESS DATA	
Annual Throughput	2,994.60kg/yr
Batch Throughput	2.06 kg
Reactor 1	60.32% capacity
Filter	84.18% capacity
Reactor 2	40.65% capacity
Reactor 3	98.93% capacity
Reactor 4	100.00% capacity
Limiting Equipment	Reactor 4

Table B.2 – rGO2T production process data

Table B.2 shows the overall data for the process simulated. As requested, the yearly throughput is three tonnes per year with a batch throughput of 2kg and this guarantees that the equipment does not need big equipment. The important thing, though, is to notice how the process runs almost always above 50% of its capacity showing a well optimised process.

B.2 Example of measurements performed on electrochemically exfoliated graphene

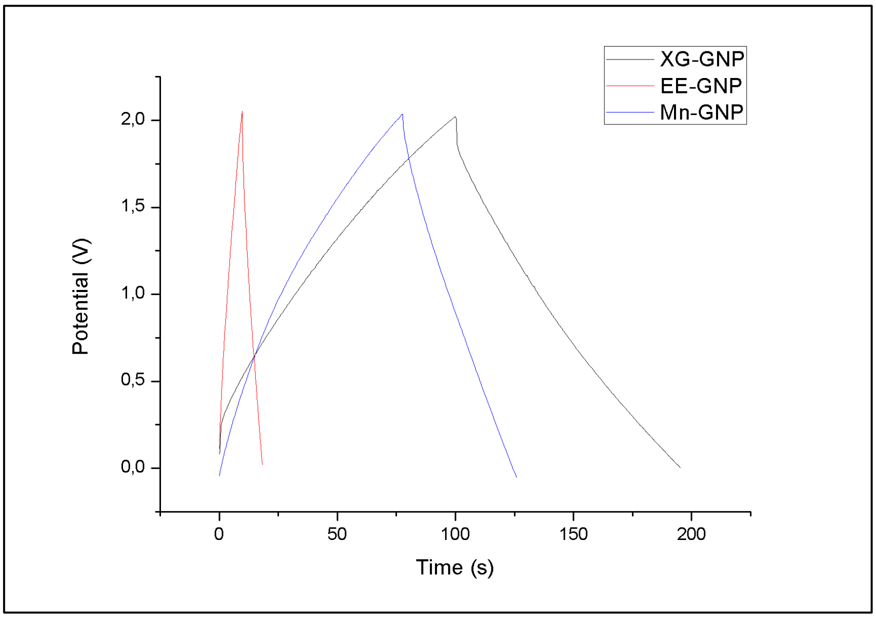


Figure B.5 – Constant current charge and discharge time

In Figure B.5 is possible to see the plot of a constant current charge and discharge for three different types of graphene:

- XG = commercial
- EE = electrochemically exfoliated material
- Mn = commercial functionalised with MnO

As the capacitance is given by the formula C = I/(dV/dt), it is possible to understand that if the variation of the voltage in time is large (i.e. steeper slope), the capacitance is low.

B.3 Examples of measurements performed at INCAR for specific capacitance

The measurements are based con cyclic voltammetry (Figure B.6) and charge-discharge cycles (Figure B.7)

For Figure B.6 the formula applied is:

$$C_{condenser}(Fg^{-1}) = \frac{(q_a + |q_c|)}{m_c \Delta V}$$

where q_a and q_c are the quantity of charge at the anode and the cathode, m_c is the mass of the material and ΔV is the potential difference during the cycling.

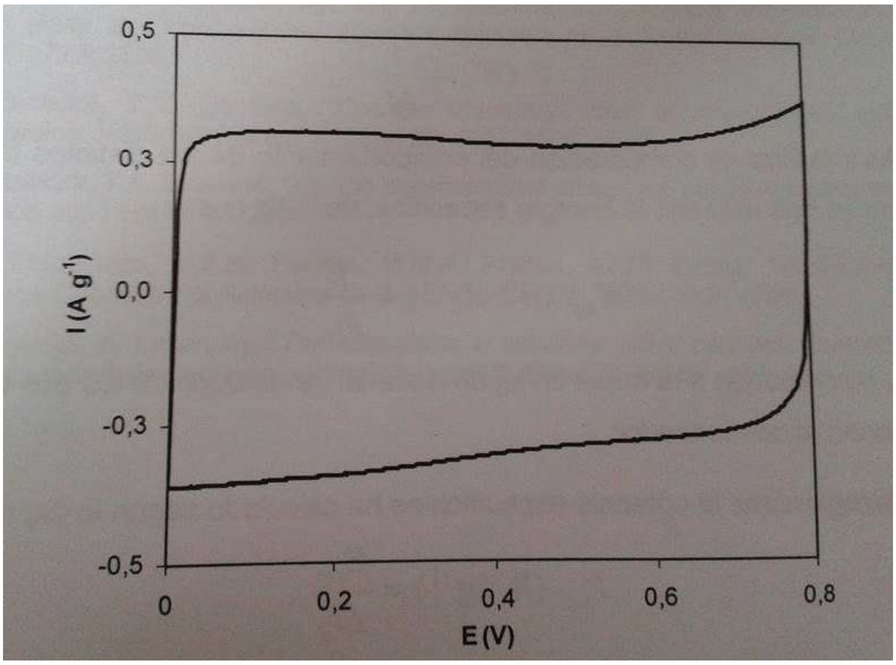


Figure B.6 – Example of cyclic voltammetry from CSIC

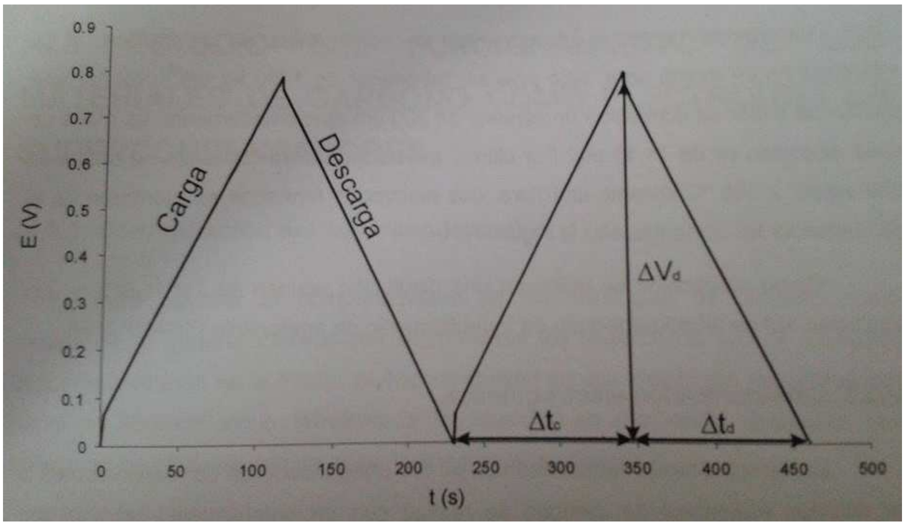


Figure B.7 – Example of charge-discharge cycles from CSIC

For Figure B.7 instead the formula used is:

$$C_{condenser}(Fg^{-1}) = \frac{(2\, i\, \Delta t_d)}{m_c \Delta V_d}$$

where Δt_d is the time needed to discharge the device and ΔV_d is the potential difference during the charge discharge cycle.

B.4 From material specific capacitance to supercapacitor specific capacitance

Because of the double layer forming at each electrode, the capacitance of a supercapacitor behaves as two capacitors in series:

$$\frac{1}{C_{Capacitor}} = \frac{1}{C_{Electrode}} + \frac{1}{C_{Electrode}}$$

Assuming both electrodes provide the same capacitance:

$$\frac{1}{C_{Capacitor}} = \frac{2}{C_{Electrode}}$$

or

$$C_{Capacitor} = \frac{C_{Electrode}}{2}$$

Dividing by the total mass of carbon in the capacitor:

$$\frac{2C_{Capacitor}}{m_{sc}} = \frac{C_{Electrode}}{m_{sc}}$$

but the total mass of carbon in the capacitor equals twice the mass of carbon at each electrode ($2m_e$):

$$\frac{2C_{Capacitor}}{m_{sc}} = \frac{C_{Electrode}}{2m_e}$$

or

$$\frac{4C_{Capacitor}}{m_{sc}} = \frac{C_{Electrode}}{m_e}$$

that shows how the specific capacitance of the electrode material is four times the specific capacitance of the supercapacitor.

B.5 Sensitivity analysis additional tables

	Ozone Depletion [kg CFC11-Equiv.]						
	Impact reduction		**Sensitivity Variation**	**Sensitivity Results Production**	**Sensitivity Variation**	**Impact increase**	
	Final Value	**%**				**%**	**Final Value**
AC	2.45E-11	-36.7%	-50%	Quantity of Activated Carbon	0%	0.0%	3.87E-11
	3.77E-11	-2.5%	-50%	Case Size	0%	0.0%	3.87E-11
rGO2C	3.70E-10	-0.9%	-85%	Quantity of Graphene	0%	0.0%	3.73E-10
	8.55E-11	-77.1%	-85%	Case Size	0%	0.0%	3.73E-10
	3.73E-10	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	3.73E-10
	3.73E-10	0.0%	0%	Electricity - Chemical Reduction	+240%	0.5%	3.75E-10
	3.73E-10	0.0%	-90%	Acid Use and Neutralisation	0%	0.0%	3.73E-10
rGO2T	3.74E-10	0.0%	0%	Quantity of Graphene	+50%	0.6%	3.76E-10
	3.74E-10	0.0%	0%	Case Size	+ 50%	48.2%	5.54E-10
	3.74E-10	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	3.74E-10
	3.74E-10	0.0%	0%	Electricity - Thermal Reduction	+110%	0.1%	3.74E-10
	3.74E-10	0.0%	-90%	Acid Use and Neutralisation	0%	0.0%	3.74E-10

Table B.3 – Sensitivity analysis results for ozone depletion

	Human toxicity, cancer [CTUh]						
	Impact reduction		**Sensitivity Variation**	**Sensitivity Results Production**	**Sensitivity Variation**	**Impact increase**	
	Final Value	**%**				**%**	**Final Value**
AC	1.24E-11	-6.7%	-50%	Quantity of Activated Carbon	0%	0.0%	1.33E-11
	1.10E-11	-16.9%	-50%	Case Size	0%	0.0%	1.33E-11
rGO2C	3.74E-11	-30.2%	-85%	Quantity of Graphene	0%	0.0%	5.36E-11
	2.90E-11	-45.8%	-85%	Case Size	0%	0.0%	5.36E-11
	5.36E-11	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	5.36E-11
	5.36E-11	0.0%	0%	Electricity - Chemical Reduction	+240%	1.2%	5.42E-11
	4.79E-11	-10.5%	-90%	Acid Use and Neutralisation	0%	0.0%	5.36E-11
rGO2T	5.22E-11	0.0%	0%	Quantity of Graphene	+50%	16.9%	6.10E-11
	5.22E-11	0.0%	0%	Case Size	+ 50%	29.4%	6.75E-11
	5.22E-11	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	5.22E-11
	5.22E-11	0.0%	0%	Electricity - Thermal Reduction	+110%	0.2%	5.23E-11
	4.47E-11	-14.4%	-90%	Acid Use and Neutralisation	0%	0.0%	5.22E-11
	1.02E-06		-0.1%	Acid Use (for rGO2C)		0.0%	1.03E-06
	1.15E-06		-0.1%	Acid use (for rGO2T)		0.0%	1.15E-06

Table B.4 – Sensitivity analysis results for human toxicity (cancer)

	Human toxicity, non-canc. [CTUh]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	1.37E-09	-6.9%	-50%	Quantity of Activated Carbon	0%	0.0%	1.47E-09
	1.22E-09	-16.9%	-50%	Case Size	0%	0.0%	1.47E-09
rGO2C	4.52E-09	-24.9%	-85%	Quantity of Graphene	0%	0.0%	6.02E-09
	3.04E-09	-49.5%	-85%	Case Size	0%	0.0%	6.02E-09
	6.02E-09	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	6.02E-09
	6.02E-09	0.0%	0%	Electricity - Chemical Reduction	+240%	1.4%	6.10E-09
	5.39E-09	-10.5%	-90%	Acid Use and Neutralisation	0%	0.0%	6.02E-09
rGO2T	6.14E-09	0.0%	0%	Quantity of Graphene	+50%	15.3%	7.09E-09
	6.14E-09	0.0%	0%	Case Size	+ 50%	30.3%	8.01E-09
	6.14E-09	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	6.14E-09
	6.14E-09	0.0%	0%	Electricity - Thermal Reduction	+110%	0.2%	6.16E-09
	5.30E-09	-13.7%	-90%	Acid Use and Neutralisation	0%	0.0%	6.14E-09

Table B.5 – Sensitivity analysis results for human toxicity (non-cancer)

	Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	1.38E-05	-10.9%	-50%	Quantity of Activated Carbon	0%	0.0%	1.55E-05
	1.29E-05	-16.7%	-50%	Case Size	0%	0.0%	1.55E-05
rGO2C	1.13E-05	-39.0%	-85%	Quantity of Graphene	0%	0.0%	1.85E-05
	1.45E-05	-21.7%	-85%	Case Size	0%	0.0%	1.85E-05
	1.85E-05	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.85E-05
	1.85E-05	0.0%	0%	Electricity - Chemical Reduction	+240%	4.4%	1.93E-05
	1.63E-05	-11.6%	-90%	Acid Use and Neutralisation	0%	0.0%	1.85E-05
rGO2T	1.90E-05	0.0%	0%	Quantity of Graphene	+50%	23.8%	2.36E-05
	1.90E-05	0.0%	0%	Case Size	+ 50%	13.1%	2.15E-05
	1.90E-05	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	1.91E-05
	1.90E-05	0.0%	0%	Electricity - Thermal Reduction	+110%	0.7%	1.92E-05
	1.62E-05	-15.0%	-90%	Acid Use and Neutralisation	0%	0.0%	1.90E-05

Table B.6 – Sensitivity analysis results for particulate matter

	Ionising radiation, human health effect model, [kg U235 eq]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	3.85E-02	-6.7%	-50%	Quantity of Activated Carbon	0%	0.0%	4.12E-02
	3.78E-02	-8.3%	-50%	Case Size	0%	0.0%	4.12E-02
rGO2C	3.56E-02	-29.1%	-85%	Quantity of Graphene	0%	0.0%	5.03E-02
	4.95E-02	-1.5%	-85%	Case Size	0%	0.0%	5.03E-02
	1.85E-05	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	5.03E-02
	5.03E-02	0.0%	0%	Electricity - Chemical Reduction	+240%	11.3%	5.59E-02
	4.93E-02	-1.9%	-90%	Acid Use and Neutralisation	0%	0.0%	5.03E-02
rGO2T	5.06E-02	0.0%	0%	Quantity of Graphene	+50%	17.3%	5.93E-02
	5.06E-02	0.0%	0%	Case Size	+ 50%	0.9%	5.10E-02
	5.06E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	5.06E-02
	5.06E-02	0.0%	0%	Electricity - Thermal Reduction	+110%	1.9%	5.15E-02
	1.62E-05	-15.0%	-90%	Acid Use and Neutralisation	0%	0.0%	5.06E-02

Table B.7 – Sensitivity analysis results for Ionising radiation

	Photochemical ozone formation,[kg NMVOC]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	6.15E-05	-8.6%	-50%	Quantity of Activated Carbon	0%	0.0%	6.73E-05
	5.98E-05	-11.1%	-50%	Case Size	0%	0.0%	6.73E-05
rGO2C	6.45E-05	-40.2%	-85%	Quantity of Graphene	0%	0.0%	1.08E-04
	8.42E-05	-21.8%	-85%	Case Size	0%	0.0%	1.08E-04
	1.08E-04	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.08E-04
	1.08E-04	0.0%	0%	Electricity - Chemical Reduction	+240%	4.3%	1.12E-04
	9.95E-05	-7.6%	-90%	Acid Use and Neutralisation	0%	0.0%	1.08E-04
rGO2T	1.06E-04	0.0%	0%	Quantity of Graphene	+50%	23.3%	1.31E-04
	1.06E-04	0.0%	0%	Case Size	+ 50%	13.8%	1.21E-04
	1.06E-04	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	1.06E-04
	1.06E-04	0.0%	0%	Electricity - Thermal Reduction	+110%	0.7%	1.07E-04
	9.53E-05	-10.3%	-90%	Acid Use and Neutralisation	0%	0.0%	1.06E-04

Table B.8 – Sensitivity analysis results for photochemical ozone formation

	Acidification [Mole of H+ eq.]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	1.41E-04	-8.0%	-50%	Quantity of Activated Carbon	0%	0.0%	1.53E-04
	1.33E-04	-13.2%	-50%	Case Size	0%	0.0%	1.53E-04
rGO2C	1.87E-04	-39.5%	-85%	Quantity of Graphene	0%	0.0%	3.08E-04
	2.34E-04	-24.1%	-85%	Case Size	0%	0.0%	3.08E-04
	3.08E-04	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	3.08E-04
	3.08E-04	0.0%	0%	Electricity - Chemical Reduction	+240%	4.0%	3.21E-04
	2.67E-04	-13.4%	-90%	Acid Use and Neutralisation	0%	0.0%	3.08E-04
rGO2T	3.18E-04	0.0%	0%	Quantity of Graphene	+50%	24.1%	3.95E-04
	3.18E-04	0.0%	0%	Case Size	+ 50%	14.6%	3.65E-04
	3.18E-04	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	3.18E-04
	3.18E-04	0.0%	0%	Electricity - Thermal Reduction	+110%	0.6%	3.20E-04
	2.63E-04	-17.3%	-90%	Acid Use and Neutralisation	0%	0.0%	3.18E-04

Table B.9 – Sensitivity analysis results for acidification

	Terrestrial eutrophication, [Mole of N eq.]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	2.15E-04	-8.2%	-50%	Quantity of Activated Carbon	0%	0.0%	2.34E-04
	2.08E-04	-10.9%	-50%	Case Size	0%	0.0%	2.34E-04
rGO2C	2.19E-04	-37.7%	-85%	Quantity of Graphene	0%	0.0%	3.51E-04
	2.71E-04	-22.6%	-85%	Case Size	0%	0.0%	3.51E-04
	3.51E-04	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	3.51E-04
	3.51E-04	0.0%	0%	Electricity - Chemical Reduction	+240%	4.7%	3.67E-04
	3.32E-04	-5.4%	-90%	Acid Use and Neutralisation	0%	0.0%	3.51E-04
rGO2T	3.16E-04	0.0%	0%	Quantity of Graphene	+ 50%	19.1%	3.76E-04
	3.16E-04	0.0%	0%	Case Size	+ 50%	15.7%	3.65E-04
	3.16E-04	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	3.16E-04
	3.16E-04	0.0%	0%	Electricity - Thermal Reduction	+110%	0.9%	3.18E-04
	2.90E-04	-8.0%	-90%	Acid Use and Neutralisation	0%	0.0%	3.16E-04

Table B.10 – Sensitivity analysis results for terrestrial eutrophication

Freshwater eutrophication, [kg P eq]

	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	2.18E-08	-5.5%	-50%	Quantity of Activated Carbon	0%	0.0%	2.31E-08
	2.23E-08	-3.4%	-50%	Case Size	0%	0.0%	2.31E-08
rGO2C	7.75E-08	-43.1%	-85%	Quantity of Graphene	0%	0.0%	1.36E-07
	8.98E-08	-34.1%	-85%	Case Size	0%	0.0%	1.36E-07
	1.36E-07	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.36E-07
	1.36E-07	0.0%	0%	Electricity - Chemical Reduction	+240%	1.1%	1.38E-07
	1.32E-07	-3.0%	-90%	Acid Use and Neutralisation	0%	0.0%	1.36E-07
rGO2T	1.07E-07	0.0%	0%	Quantity of Graphene	+ 50%	18.8%	1.28E-07
	1.07E-07	0.0%	0%	Case Size	+ 50%	27.1%	1.37E-07
	1.07E-07	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.07E-07
	1.07E-07	0.0%	0%	Electricity - Thermal Reduction	+110%	0.2%	1.08E-07
	1.02E-07	-5.1%	-90%	Acid Use and Neutralisation	0%	0.0%	1.07E-07

Table B.11 – Sensitivity analysis results for freshwater eutrophication

Ecotoxicity [CTUe]

	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	1.21E-03	-5.3%	-50%	Quantity of Activated Carbon	0%	0.0%	1.28E-03
	1.14E-03	-10.9%	-50%	Case Size	0%	0.0%	1.28E-03
rGO2C	8.71E-03	-18.3%	-85%	Quantity of Graphene	0%	0.0%	1.07E-02
	4.30E-03	-59.7%	-85%	Case Size	0%	0.0%	1.07E-02
	1.07E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.07E-02
	1.07E-02	0.0%	0%	Electricity - Chemical Reduction	+240%	0.7%	1.07E-02
	1.01E-02	-4.9%	-90%	Acid Use and Neutralisation	0%	0.0%	1.07E-02
rGO2T	1.01E-02	0.0%	0%	Quantity of Graphene	+ 50%	8.8%	1.10E-02
	1.01E-02	0.0%	0%	Case Size	+ 50%	39.2%	1.41E-02
	1.01E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.01E-02
	1.01E-02	0.0%	0%	Electricity - Thermal Reduction	+110%	0.1%	1.01E-02
	9.44E-03	-6.9%	-90%	Acid Use and Neutralisation	0%	0.0%	1.01E-02

Table B.12 – Sensitivity analysis results for ecotoxicity

Resources depletion, water [kg]

	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	2.60E-02	-11.5%	-50%	Quantity of Activated Carbon	0%	0.0%	2.93E-02
	1.99E-02	-32.3%	-50%	Case Size	0%	0.0%	2.93E-02
rGO2C	3.27E-02	-26.2%	-85%	Quantity of Graphene	0%	0.0%	4.43E-02
	4.41E-02	-0.6%	-85%	Case Size	0%	0.0%	4.43E-02
	4.43E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	4.44E-02
	4.43E-02	0.0%	0%	Electricity - Chemical Reduction	+240%	6.9%	4.74E-02
	4.38E-02	-1.2%	-90%	Acid Use and Neutralisation	0%	0.0%	4.43E-02
rGO2T	4.13E-02	0.0%	0%	Quantity of Graphene	+ 50%	16.7%	4.82E-02
	4.13E-02	0.0%	0%	Case Size	+ 50%	0.4%	4.15E-02
	4.13E-02	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.1%	4.14E-02
	4.13E-02	0.0%	0%	Electricity - Thermal Reduction	+110%	1.2%	4.18E-02
	4.06E-02	-1.7%	-90%	Acid Use and Neutralisation	0%	0.0%	4.13E-02

Table B.13 – Sensitivity analysis results for resources depletion (water)

	Resource Depletion, fossil and mineral [kg Sb-Equiv.]						
	Impact reduction		Sensitivity Variation	Sensitivity Results Production	Sensitivity Variation	Impact increase	
	Final Value	%				%	Final Value
AC	1.97E-07	-17.0%	-50%	Quantity of Activated Carbon	0%	0.0%	2.38E-07
	1.92E-07	-19.2%	-50%	Case Size	0%	0.0%	2.38E-07
rGO2C	6.58E-07	-35.9%	-85%	Quantity of Graphene	0%	0.0%	1.03E-06
	5.61E-07	-45.3%	-85%	Case Size	0%	0.0%	1.03E-06
	1.03E-06	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.03E-06
	1.03E-06	0.0%	0%	Electricity - Chemical Reduction	+240%	0.1%	1.03E-06
	1.02E-06	-0.2%	-90%	Acid Use and Neutralisation	0%	0.0%	1.03E-06
rGO2T	1.15E-06	0.0%	0%	Quantity of Graphene	+ 50%	24.3%	1.44E-06
	1.15E-06	0.0%	0%	Case Size	+ 50%	25.2%	1.45E-06
	1.15E-06	0.0%	0%	Electricity - Graphite Oxidation (GO2)	+8%	0.0%	1.15E-06
	1.15E-06	0.0%	0%	Electricity - Thermal Reduction	+110%	0.0%	1.15E-06
	1.15E-06	-0.2%	-90%	Acid Use and Neutralisation	0%	0.0%	1.15E-06

Table B.14 – Sensitivity analysis results for resources depletion (fossil and mineral)

APPENDIX C – Use phase and end of life of supercapacitors

C.1 Values for sensitivity analysis of use phase

This table completes the results for the sensitivity analysis of the use phase.

Impact reduction			Sensitivity Variation	Sensitivity Results Use Phase	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
Ozone Depletion [kg CFC 11-Equiv.]								
0%	3.66E-13	-43%	-43%	AC Supercapacitor weight	0%	0%	6.43E-13	0%
0%	1.85E-13	-74%	-74%	rGO2C supercapacitor weight	0%	0%	7.13E-13	0%
0%	7.13E-13	0%	0%	rGO2T supercapacitor weight	46%	+46%	1.04E-12	0%
Human toxicity, cancer [CTUh]								
-14%	1.81E-11	-43%	-43%	AC Supercapacitor weight	0%	0%	3.17E-11	0%
-9%	9.14E-12	-74%	-74%	rGO2C supercapacitor weight	0%	0%	3.51E-11	0%
0%	3.51E-11	0%	0%	rGO2T supercapacitor weight	46%	+46%	5.13E-11	+5%
Human toxicity, non-canc. [CTUh]								
-18%	3.00E-09	-43%	-43%	AC Supercapacitor weight	0%	0%	5.25E-09	0%
-12%	1.51E-09	-74%	-74%	rGO2C supercapacitor weight	0%	0%	5.83E-09	0%
0%	5.83E-09	0%	0%	rGO2T supercapacitor weight	46%	+46%	8.51E-09	+7%
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]								
-9%	1.14E-05	-43%	-43%	AC Supercapacitor weight	0%	0%	2.00E-05	0%
-14%	5.75E-06	-74%	-74%	rGO2C supercapacitor weight	0%	0%	2.21E-05	0%
0%	2.21E-05	0%	0%	rGO2T supercapacitor weight	46%	+46%	3.23E-05	+9%
Ionising radiation, human health effect model, [kg U235 eq]								
0%	1.06E-03	-43%	-43%	AC Supercapacitor weight	0%	0%	1.86E-03	0%
-1%	5.36E-04	-74%	-74%	rGO2C supercapacitor weight	0%	0%	2.06E-03	0%
0%	2.06E-03	0%	0%	rGO2T supercapacitor weight	46%	+46%	3.01E-03	0%
Photochemical ozone formation,[kg NMVOC]								
-8%	4.48E-05	-43%	-43%	AC Supercapacitor weight	0%	0%	7.86E-05	0%
-10%	2.26E-05	-74%	-74%	rGO2C supercapacitor weight	0%	0%	8.68E-05	0%
0%	8.68E-05	0%	0%	rGO2T supercapacitor weight	46%	+46%	1.27E-04	+6%
Acidification [Mole of H+ eq.]								
-9%	1.22E-04	-43%	-43%	AC Supercapacitor weight	0%	0%	2.13E-04	0%
-10%	6.08E-05	-74%	-74%	rGO2C supercapacitor weight	0%	0%	2.34E-04	0%
0%	2.34E-04	0%	0%	rGO2T supercapacitor weight	46%	+46%	3.41E-04	+6%
Terrestrial eutrophication, [Mole of N eq.]								
-14%	3.34E-04	-43%	-43%	AC Supercapacitor weight	0%	0%	5.86E-04	0%
-20%	1.66E-04	-74%	-74%	rGO2C supercapacitor weight	0%	0%	6.39E-04	0%
0%	6.39E-04	0%	0%	rGO2T supercapacitor weight	46%	+46%	9.33E-04	+13%
Freshwater eutrophication, [kg P eq]								
-22%	6.67E-08	-43%	-43%	AC Supercapacitor weight	0%	0%	1.17E-07	0%
-12%	3.37E-08	-74%	-74%	rGO2C supercapacitor weight	0%	0%	1.30E-07	0%
0%	1.30E-07	0%	0%	rGO2T supercapacitor weight	46%	+46%	1.89E-07	+9%
Ecotoxicity [CTUe]								
-27%	6.39E-03	-43%	-43%	AC Supercapacitor weight	0%	0%	1.12E-02	0%
-14%	3.23E-03	-74%	-74%	rGO2C supercapacitor weight	0%	0%	1.24E-02	0%
0%	1.24E-02	0%	0%	rGO2T supercapacitor weight	46%	+46%	1.81E-02	+9%
Resources depletion, water [kg]								
-14%	3.71E-02	-43%	-43%	AC Supercapacitor weight	0%	0%	6.50E-02	0%
-26%	1.87E-02	-74%	-74%	rGO2C supercapacitor weight	0%	0%	7.21E-02	0%
0%	7.21E-02	0%	0%	rGO2T supercapacitor weight	46%	+46%	1.05E-01	+17%
Resource Depletion, fossil and mineral [kg Sb-Equiv.]								
-2%	1.66E-08	-43%	-43%	AC Supercapacitor weight	0%	0%	2.91E-08	0%
-4%	8.38E-09	-74%	-74%	rGO2C supercapacitor weight	0%	0%	3.22E-08	0%
0%	3.22E-08	0%	0%	rGO2T supercapacitor weight	+46%	+46%	4.71E-08	2%

Table C.1 – Sensitivity analysis results for the use phase

C.2 Values for sensitivity analysis of EoL phase

These tables complete the results presented for the sensitivity analysis of the use phase. Negative percentages mean a reduction in the recycling credits thus an increased impact. The percaentage showed as Overall LCA is based on the overall value including the 3 pahses

Ozone Depletion [kg CFC 11-Equiv.]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-2.10E-10	0%	0%	Electricity (AC)	+8%	-0.03%	-2.10E-10	0.03%
28%	-1.56E-10	-26%	-50%	Activated Carbon Recycling	0%	0%	-2.10E-10	0%
-5%	-2.20E-10	5%	-50%	Nitrogen (AC)	0%	0%	-2.10E-10	0%
-5%	-2.19E-10	4%	-50%	Aluminium Recycling (AC)	0%	0%	-2.10E-10	0%
0%	-1.61E-09	0%	0%	Electricity (rGO2C)	+6%	0.00%	-1.61E-09	0.00%
1%	-1.60E-09	-1%	-85%	Graphene Recycling (rGO2C)	0%	0%	-1.61E-09	0%
-1%	-1.62E-09	1%	-85%	Nitrogen (rGO2C)	0%	0%	-1.61E-09	0%
74%	-2.31E-10	-86%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-1.61E-09	0%
0%	-1.61E-09	0%	0%	Electricity (rGO2T)	+6%	0.00%	-1.61E-09	0.00%
0%	-1.14E-01	0%	0%	Graphene Recycling (rGO2T)	+50%	2%	-1.61E-09	n/a
0%	-1.14E-01	0%	0%	Nitrogen (rGO2T)	+50%	-1%	-1.61E-09	0.5%
0%	-1.14E-01	0%	0%	Stainless steel Recycling (rGO2T)	+50%	1%	-1.61E-09	n/a

Table C.2 – Sensitivity analysis results for ozone depletion

Human toxicity, cancer [CTUh]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-2.08E-11	0%	0%	Electricity (AC)	+8%	-0.4%	-2.07E-11	0.04%
1%	-2.01E-11	-3%	-50%	Activated Carbon Recycling	0%	0%	-2.08E-11	0%
-3%	-2.33E-11	12%	-50%	Nitrogen (AC)	0%	0%	-2.08E-11	0%
13%	-8.52E-12	-59%	-50%	Aluminium Recycling (AC)	0%	0%	-2.08E-11	0%
0%	-2.12E-10	0%	0%	Electricity (rGO2C)	+6%	-0.01%	-2.12E-10	0.01%
22%	-1.46E-10	-31%	-85%	Graphene Recycling (rGO2C)	0%	0%	-2.12E-10	0%
-2%	-2.17E-10	2%	-85%	Nitrogen (rGO2C)	0%	0%	-2.12E-10	0%
38%	-9.81E-11	-54%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-2.12E-10	0%
0%	-2.06E-10	0%	0%	Electricity (rGO2T)	+6%	0.00%	-2.06E-10	0.00%
0%	-2.06E-10	0%	0%	Graphene Recycling (rGO2T)	+50%	18%	-2.42E-10	n/a
0%	-2.06E-10	0%	0%	Nitrogen (rGO2T)	+50%	-1%	-2.03E-10	1%
0%	-2.06E-10	0%	0%	Stainless steel Recycling (rGO2T)	+50%	28%	-2.64E-10	n/a

Table C.3 – Sensitivity analysis results for human toxicity (cancer)

Human toxicity, non-canc. [CTUh]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-2.06E-09	0%	0%	Electricity (AC)	+8%	-0.1%	-2.06E-09	0.04%
1%	-1.99E-09	-4%	-50%	Activated Carbon Recycling	0%	0%	-2.06E-09	0%
-3%	-2.47E-09	20%	-50%	Nitrogen (AC)	0%	0%	-2.06E-09	0%
11%	-6.91E-10	-66%	-50%	Aluminium Recycling (AC)	0%	0%	-2.06E-09	0%
0%	-2.34E-08	0%	0%	Electricity (rGO2C)	+6%	0.00%	-2.34E-08	0.00%
17%	-1.74E-08	-26%	-85%	Graphene Recycling (rGO2C)	0%	0%	-2.34E-08	0%
-2%	-2.42E-08	3%	-85%	Nitrogen (rGO2C)	0%	0%	-2.34E-08	0%
39%	-9.35E-09	-60%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-2.34E-08	0%
0%	-2.40E-08	0%	0%	Electricity (rGO2T)	+6%	0.00%	-2.40E-08	0.00%
0%	-2.40E-08	0%	0%	Graphene Recycling (rGO2T)	+50%	16%	-2.78E-08	n/a
0%	-2.40E-08	0%	0%	Nitrogen (rGO2T)	+50%	-2%	-2.35E-08	5%
0%	-2.40E-08	0%	0%	Stainless steel Recycling (rGO2T)	+50%	25%	-3.01E-08	n/a

Table C.4 – Sensitivity analysis results for human toxicity (non-cancer)

Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-2.64E-05	0%	0%	Electricity (AC)	+8%	-0.1%	-2.64E-05	0.03%
3%	-2.32E-05	-12%	-50%	Activated Carbon Recycling	0%	0%	-2.64E-05	0%
-4%	-3.08E-05	17%	-50%	Nitrogen (AC)	0%	0%	-2.64E-05	0%
15%	-1.22E-05	-54%	-50%	Aluminium Recycling (AC)	0%	0%	-2.64E-05	0%
0%	-4.83E-05	0%	0%	Electricity (rGO2C)	+6%	-0.01%	-4.83E-05	0.01%
22%	-2.32E-05	-52%	-85%	Graphene Recycling (rGO2C)	0%	0%	-4.83E-05	0%
-7%	-5.60E-05	16%	-85%	Nitrogen (rGO2C)	0%	0%	-4.83E-05	0%
16%	-3.00E-05	-38%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-4.83E-05	0%
0%	-5.08E-05	0%	0%	Electricity (rGO2T)	+6%	-0.01%	-5.08E-05	0.01%
0%	-5.08E-05	0%	0%	Graphene Recycling (rGO2T)	+50%	32%	-6.69E-05	n/a
0%	-5.08E-05	0%	0%	Nitrogen (rGO2T)	+50%	-9%	-4.64E-05	4%
0%	-5.08E-05	0%	0%	Stainless steel Recycling (rGO2T)	+50%	20%	-6.10E-05	n/a

Table C.5 – Sensitivity analysis results for particulate matter

Ionising radiation, human health effect model, [kg U235 eq]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	2.72E-02	0%	0%	Electricity (AC)	+8%	0.7%	2.74E-02	0.09%
1%	2.95E-02	8%	-50%	Activated Carbon Recycling	0%	0%	2.72E-02	0%
-5%	-4.52E-03	-117%	-50%	Nitrogen (AC)	0%	0%	2.72E-02	0%
8%	4.39E-02	61%	-50%	Aluminium Recycling (AC)	0%	0%	2.72E-02	0%
0%	-1.88E-04	0%	0%	Electricity (rGO2C)	+6%	-0.01%	-1.88E-04	0.01%
49%	4.77E-02	-25473%	-85%	Graphene Recycling (rGO2C)	0%	-26%	-1.88E-04	0%
-21%	-5.47E-02	28943%	-85%	Nitrogen (rGO2C)	0%	0%	-1.88E-04	0%
1%	1.33E-03	-808%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-1.88E-04	0%
0%	-1.60E-03	0%	0%	Electricity (rGO2T)	+6%	-3.01%	-1.55E-03	0.02%
0%	-1.60E-03	0%	0%	Graphene Recycling (rGO2T)	+50%	1807%	-3.05E-02	n/a
0%	-1.60E-03	0%	0%	Nitrogen (rGO2T)	+50%	-2007%	3.05E-02	13%
0%	-1.60E-03	0%	0%	Stainless steel Recycling (rGO2T)	+50%	56%	-2.50E-03	n/a

Table C.6 – Sensitivity analysis results for Ionising radiation

The ionising radiation is a special case, where the nitrogen use generates a larger burden than all the credits generated by all recycling activities. This EoL phase is not adding any credit but it is a burden, but its contribution is almost zero and that's why to the large percentages shown for the EoL phase correspond small percentages for the overall LCA value.

Photochemical ozone formation,[kg NMVOC]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-6.26E-05	0%	0%	Electricity (AC)	+8%	-0.3%	-6.24E-05	0.04%
2%	-5.23E-05	-16%	-50%	Activated Carbon Recycling	0%	0%	-6.26E-05	0%
-4%	-8.04E-05	29%	-50%	Nitrogen (AC)	0%	0%	-6.26E-05	0%
9%	-2.42E-05	-61%	-50%	Aluminium Recycling (AC)	0%	0%	-6.26E-05	0%
0%	-2.77E-04	0%	0%	Electricity (rGO2C)	+6%	-0.01%	-2.77E-04	0.01%
27%	-1.09E-04	-61%	-85%	Graphene Recycling (rGO2C)	0%	0%	-2.77E-04	0%
-6%	-3.13E-04	13%	-85%	Nitrogen (rGO2C)	0%	0%	-2.77E-04	0%
14%	-1.88E-04	-32%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-2.77E-04	0%
0%	-2.70E-04	0%	0%	Electricity (rGO2T)	+6%	-0.01%	-2.70E-04	0.01%
0%	-2.70E-04	0%	0%	Graphene Recycling (rGO2T)	+50%	35%	-3.66E-04	n/a
0%	-2.70E-04	0%	0%	Nitrogen (rGO2T)	+50%	-8%	-2.50E-04	3%
0%	-2.70E-04	0%	0%	Stainless steel Recycling (rGO2T)	+50%	19%	-3.23E-04	n/a

Table C.7 – Sensitivity analysis results for photochemical ozone formation

Acidification [Mole of H+ eq.]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-1.32E-04	0%	0%	Electricity (AC)	+8%	-0.3%	-1.32E-04	0.04%
2%	-1.16E-04	-12%	-50%	Activated Carbon Recycling	0%	0%	-1.32E-04	0%
-6%	-1.94E-04	46%	-50%	Nitrogen (AC)	0%	0%	-1.32E-04	0%
11%	-2.39E-05	-82%	-50%	Aluminium Recycling (AC)	0%	0%	-1.32E-04	0%
0%	-8.72E-04	0%	0%	Electricity (rGO2C)	+6%	-0.01%	-8.72E-04	0.01%
27%	-3.90E-04	-55%	-85%	Graphene Recycling (rGO2C)	0%	0%	-8.72E-04	0%
-6%	-9.82E-04	13%	-85%	Nitrogen (rGO2C)	0%	0%	-8.72E-04	0%
19%	-5.42E-04	-38%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-8.72E-04	0%
0%	-9.17E-04	0%	0%	Electricity (rGO2T)	+6%	-0.01%	-9.17E-04	0.01%
0%	-9.17E-04	0%	0%	Graphene Recycling (rGO2T)	+50%	33%	-1.22E-03	n/a
0%	-9.17E-04	0%	0%	Nitrogen (rGO2T)	+50%	-7%	-8.53E-04	4%
0%	-9.17E-04	0%	0%	Stainless steel Recycling (rGO2T)	+50%	21%	-1.11E-03	n/a

Table C.8 – Sensitivity analysis results for acidification

Terrestrial eutrophication, [Mole of N eq.]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-2.15E-02	0%	0%	Electricity (AC)	+8%	-0.3%	-2.14E-02	0.03%
2%	-1.81E-02	-16%	-50%	Activated Carbon Recycling	0%	0%	-2.15E-02	0%
-3%	-2.76E-02	28%	-50%	Nitrogen (AC)	0%	0%	-2.15E-02	0%
8%	-8.21E-03	-62%	-50%	Aluminium Recycling (AC)	0%	0%	-2.15E-02	0%
0%	-1.43E-01	0%	0%	Electricity (rGO2C)	+6%	-0.02%	-1.43E-01	0.01%
21%	-5.80E-02	-59%	-85%	Graphene Recycling (rGO2C)	0%	0%	-1.43E-01	0%
-5%	-1.63E-01	14%	-85%	Nitrogen (rGO2C)	0%	0%	-1.43E-01	0%
12%	-9.35E-02	-34%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-1.43E-01	0%
0%	-1.14E-01	0%	0%	Electricity (rGO2T)	+6%	-0.02%	-1.14E-01	0.01%
0%	-1.14E-01	0%	0%	Graphene Recycling (rGO2T)	+50%	31%	-1.50E-01	n/a
0%	-1.14E-01	0%	0%	Nitrogen (rGO2T)	+50%	-10%	-1.02E-01	3%
0%	-1.14E-01	0%	0%	Stainless steel Recycling (rGO2T)	+50%	25%	-1.42E-01	n/a

Table C.9 – Sensitivity analysis results for terrestrial eutrophication

Freshwater eutrophication, [kg P eq]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-4.44E-09	0%	0%	Electricity (AC)	+8%	-1.2%	-4.39E-09	0.02%
1%	-1.62E-09	-63%	-50%	Activated Carbon Recycling	0%	0%	-4.44E-09	0%
-2%	-8.90E-09	100%	-50%	Nitrogen (AC)	0%	0%	-4.44E-09	0%
2%	-9.34E-10	-79%	-50%	Aluminium Recycling (AC)	0%	0%	-4.44E-09	0%
0%	-5.39E-07	0%	0%	Electricity (rGO2C)	+6%	0.00%	-5.39E-07	0.00%
32%	-2.79E-07	-48%	-85%	Graphene Recycling (rGO2C)	0%	0%	-5.39E-07	0%
-1%	-5.50E-07	2%	-85%	Nitrogen (rGO2C)	0%	0%	-5.39E-07	0%
26%	-3.31E-07	-39%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-5.39E-07	0%
0%	-4.10E-07	0%	0%	Electricity (rGO2T)	+6%	0.00%	-4.10E-07	0.00%
0%	-4.10E-07	0%	0%	Graphene Recycling (rGO2T)	+50%	22%	-4.98E-07	n/a
0%	-4.10E-07	0%	0%	Nitrogen (rGO2T)	+50%	-2%	-4.04E-07	1%
0%	-4.10E-07	0%	0%	Stainless steel Recycling (rGO2T)	+50%	29%	-5.29E-07	n/a

Table C.10 – Sensitivity analysis results for freshwater eutrophication

In the freshwater eutrophication the value for the EoL phase is negative and it is therefore a credit, however it is very proximate to zero and therefore, a 50% reduction in the use of nitrogen increases the credits by 100% (it doubles then) but it reduces the overall impacts only by 2%

Ecotoxicity [CTUe]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-1.33E-03	0%	0%	Electricity (AC)	+8%	-0.2%	-1.33E-03	0.01%
0%	-1.27E-03	-4%	-50%	Activated Carbon Recycling	0%	0%	-1.33E-03	0%
-1%	-1.47E-03	10%	-50%	Nitrogen (AC)	0%	0%	-1.33E-03	0%
4%	-5.83E-04	-56%	-50%	Aluminium Recycling (AC)	0%	0%	-1.33E-03	0%
0%	-4.45E-02	0%	0%	Electricity (rGO2C)	+6%	0.00%	-4.45E-02	0.00%
13%	-3.62E-02	-19%	-85%	Graphene Recycling (rGO2C)	0%	0%	-4.45E-02	0%
-1%	-4.49E-02	1%	-85%	Nitrogen (rGO2C)	0%	0%	-4.45E-02	0%
45%	-1.49E-02	-67%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-4.45E-02	0%
0%	-4.22E-02	0%	0%	Electricity (rGO2T)	+6%	0.00%	-4.22E-02	0.00%
0%	-4.22E-02	0%	0%	Graphene Recycling (rGO2T)	+50%	9%	-4.59E-02	n/a
0%	-4.22E-02	0%	0%	Nitrogen (rGO2T)	+50%	-1%	-4.20E-02	0%
0%	-4.22E-02	0%	0%	Stainless steel Recycling (rGO2T)	+50%	26%	-5.32E-02	n/a

Table C.11 – Sensitivity analysis results for ecotoxicity

Resources depletion, water [kg]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-1.56E-02	0%	0%	Electricity (AC)	+8%	-0.8%	-1.55E-02	0.06%
1%	-1.41E-02	-10%	-50%	Activated Carbon Recycling	0%	0%	-1.56E-02	0%
-10%	-3.73E-02	139%	-50%	Nitrogen (AC)	0%	0%	-1.56E-02	0%
31%	5.02E-02	-422%	-50%	Aluminium Recycling (AC)	0%	0%	-1.56E-02	0%
0%	-9.18E-02	0%	0%	Electricity (rGO2C)	+6%	-0.04%	-9.18E-02	0.01%
11%	-5.86E-02	-36%	-85%	Graphene Recycling (rGO2C)	0%	0%	-9.18E-02	0%
-13%	-1.29E-01	40%	-85%	Nitrogen (rGO2C)	0%	0%	-9.18E-02	0%
0%	-9.17E-02	0%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-9.18E-02	0%
0%	-7.83E-02	0%	0%	Electricity (rGO2T)	+6%	-0.04%	-7.83E-02	0.01%
0%	-7.83E-02	0%	0%	Graphene Recycling (rGO2T)	+50%	25%	-9.81E-02	n/a
0%	-7.83E-02	0%	0%	Nitrogen (rGO2T)	+50%	-28%	-5.64E-02	8%
0%	-7.83E-02	0%	0%	Stainless steel Recycling (rGO2T)	+50%	0%	-7.83E-02	n/a

Table C.12 – Sensitivity analysis results for resources depletion (water)

Resource Depletion, fossil and mineral [kg Sb-Equiv.]								
Impact reduction			Sensitivity Variation	Sensitivity Results End of Life	Sensitivity Variation	Impact increase		
Overall LCA	EoL	%				%	EoL	Overall LCA
0%	-7.02E-07	0%	0%	Electricity (AC)	+8%	0.0%	-7.02E-07	0.00%
9%	-5.88E-07	-16%	-50%	Activated Carbon Recycling	0%	0%	-7.02E-07	0%
-0.4%	-7.07E-07	1%	-50%	Nitrogen (AC)	0%	0%	-7.02E-07	0%
20%	-4.63E-07	-34%	-50%	Aluminium Recycling (AC)	0%	0%	-7.02E-07	0%
0%	-4.52E-06	0%	0%	Electricity (rGO2C)	+6%	0.00%	-4.52E-06	0.00%
30%	-2.97E-06	-34%	-85%	Graphene Recycling (rGO2C)	0%	0%	-4.52E-06	0%
0%	-4.53E-06	0%	-85%	Nitrogen (rGO2C)	0%	0%	-4.52E-06	0%
43%	-2.32E-06	-49%	-85%	Stainless steel Recycling (rGO2C)	0%	0%	-4.52E-06	0%
0%	-5.10E-06	0%	0%	Electricity (rGO2T)	+6%	0.00%	-5.10E-06	0.00%
0%	-5.10E-06	0%	0%	Graphene Recycling (rGO2T)	+50%	14%	-5.82E-06	n/a
0%	-5.10E-06	0%	0%	Nitrogen (rGO2T)	+50%	0%	-5.10E-06	0%
0%	-5.10E-06	0%	0%	Stainless steel Recycling (rGO2T)	+50%	14%	-5.81E-06	n/a

Table C.13 – Sensitivity analysis results for resources depletion (fossil and mineral)

C.3 Breakdown of the three phases for the alternative scenario

	ALTERNATIVE SCENARIO											
	Activated Carbon Supercapacitor 3 phases				rGO2C supercapacitor 3 phases				rGO2T supercapacitor 3 phases			
	Total	Production	Use Phase	EoL	**Total**	Production	Use Phase	EoL	**Total**	Production	Use Phase	EoL
Global Warming Potential [kg CO2-Equiv.]	1.59E-01	1.20E-01	4.96E-02	-1.04E-02	1.34E-01	1.39E-01	2.48E-02	-2.94E-02	2.94E-01	2.18E-01	1.42E-01	-6.64E-02
Ozone Depletion [kg CFC 11-Equiv.]	-5.66E-11	1.18E-10	3.63E-13	-1.75E-10	1.08E-10	4.25E-10	1.82E-13	-3.18E-10	4.60E-10	2.86E-09	1.04E-12	-2.40E-09
Human toxicity, cancer [CTUh]	5.81E-11	5.07E-11	1.79E-11	-1.05E-11	4.92E-11	8.35E-11	8.98E-12	-4.33E-11	1.31E-10	3.13E-10	5.13E-11	-2.34E-10
Human toxicity, non-canc. [CTUh]	7.54E-09	5.61E-09	2.97E-09	-1.04E-09	6.18E-09	9.57E-09	1.49E-09	-4.88E-09	1.79E-08	3.74E-08	8.50E-09	-2.80E-08
Particulate matter/Respiratory inorganics, [kg PM2,5-Equiv.]	5.38E-05	5.60E-05	1.13E-05	-1.35E-05	4.74E-05	5.57E-05	5.64E-06	-1.39E-05	8.83E-05	9.70E-05	3.22E-05	-4.09E-05
Ionising radiation, human health effect model, [kg U235 eq]	1.90E-01	1.75E-01	1.05E-03	1.36E-02	2.21E-01	2.27E-01	5.27E-04	-6.65E-03	3.22E-01	2.60E-01	3.01E-03	5.93E-02
Photochemical ozone formation,[kg NMVOC]	2.82E-04	2.70E-04	4.44E-05	-3.25E-05	2.50E-04	2.90E-04	2.22E-05	-6.18E-05	5.00E-04	5.79E-04	1.27E-04	-2.06E-04
Acidification [Mole of H+ eq.]	6.54E-04	6.04E-04	1.21E-04	-7.05E-05	6.23E-04	7.56E-04	5.97E-05	-1.93E-04	1.23E-03	1.63E-03	3.41E-04	-7.41E-04
Terrestrial eutrophication, [Mole of N eq.]	1.17E-03	9.45E-04	3.31E-04	-1.11E-04	9.46E-04	9.80E-04	1.63E-04	-1.97E-04	2.13E-03	1.77E-03	9.32E-04	-5.73E-04
Freshwater eutrophication, [kg P eq]	1.68E-07	1.05E-07	6.62E-08	-2.79E-09	1.48E-07	2.10E-07	3.31E-08	-9.45E-08	4.49E-07	6.97E-07	1.89E-07	-4.38E-07
Ecotoxicity [CTUe]	1.10E-02	5.37E-03	6.34E-03	-6.75E-04	8.13E-03	1.37E-02	3.17E-03	-8.72E-03	3.22E-02	6.97E-02	1.81E-02	-5.57E-02
Resources depletion, water [kg]	1.48E-01	1.19E-01	3.67E-02	-7.43E-03	1.37E-01	1.41E-01	1.84E-02	-2.23E-02	2.99E-01	2.27E-01	1.05E-01	-3.37E-02
Resource Depletion, fossil and mineral [kg Sb-Equiv.]	4.21E-07	7.58E-07	1.64E-08	-3.54E-07	6.14E-07	1.51E-06	8.23E-09	-9.02E-07	2.62E-06	7.76E-06	4.70E-08	-5.19E-06

Table c.14 – Alternative scenario 3 phases breakdown of results