Review of environmental life cycle assessment studies of graphene production

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Abstract

Environmentally benign production processes are required in order to ensure a sustainable graphene supply. Life cycle assessment (LCA) is an established method for assessing life cycle environmental impacts of products and production processes. In this paper, life cycle impacts of five production processes for graphene are reviewed: Chemical reduction of graphite oxide, ultrasonication exfoliation, thermal exfoliation, chemical vapour deposition, and epitaxial growth. The reduction step, including the production of the reduction agent hydrazine, was the main contributor for most impacts in the chemical reduction of graphite oxide. Production of the solvent diethyl ether was the step that contributed the most for ultrasonication exfoliation, so solvent recovery is advised. For thermal exfoliation, microwave heating was the step that contributed the most to environmental impacts of graphene nanoplatelets. For chemical vapour deposition, the methane feedstock production step contributed the most, but methane recovery could reduce the energy use considerably. The environmental impacts of epitaxial graphene were dominated by electricity use for production of the silicon wafer substrate, which means that a 'greener' electricity mix can reduce impacts considerably. Overall, it is shown that graphene need not be an energy-intensive material compared to conventional materials used in society today. Copyright © 2017 VBRI Press.

Keywords: Graphene, LCA, environmental impacts, resource use, energy use.

Introduction

Graphene is a recently discovered carbon-based nanomaterial, which brings promises of many useful applications **[1-4]**. The maybe most promising long-term application is in electronics, where graphene has been suggested as a new semiconductor material that may replace silicon in the future **[5, 6]**. A more near-term applications is the use of graphene in composite materials to enhance their strength and electric properties **[7-11]**. Another near-term application is the replacement of indium tin oxide (ITO) in liquid crystal displays with graphene **[12, 13]**. Additional potential applications include corrosion protection **[14, 15]**, flame retardants **[16]**, fuel cells **[17]**, capacitors **[18]**, and biosensors in health care diagnostics **[19]**. In parallel with the development of such promising applications, environmental and resource impacts related to nanomaterials in general **[20-22]** and graphene in particular **[23-25]** have been investigated. In general, many nanomaterials have been shown to have notable environmental impacts during their production, for example high energy use **[26]**. Considering the potentially high cumulative need for graphene in these applications in the future, it is important to investigate environmental impacts of graphene and its production in order to guide towards feasible and environmentally benign production processes.

Life cycle assessment (LCA) is an established environmental assessment method that can be used to calculate the environmental and resource impacts of products **[27, 28]**. This method can be used to assess impacts occurring throughout a product's life cycle, from raw material extraction, over production and use, to its end of life. The importance of evaluating nanotechnology using LCA has been highlighted in an early report about environmental impacts of nanotechnology by the United Kingdom's Royal Society, where they state **[21]** "We recommend that a series of life cycle assessments be undertaken for the applications and product groups arising from existing and expected developments in nanotechnologies, to ensure that savings in resource consumption during the use of the product are not offset by increased consumption during manufacture and disposal."

The potential use of LCA in the context of nanotechnology has been further discussed in a report by Curran et al. **[29]**, where they confirmed the applicability and relevance of LCA for assessing environmental impacts of nanomaterials. They also state that there are two interesting types of LCA studies of nanomaterials that can be conducted. The first is a so-called cradle-to-grave study, where the whole life cycle of a product containing nanomaterials is considered (including raw material extraction, production, use, and end of life). The second is a so - called cradle – to - gate study, where only the production system of the nanomaterial is considered (including raw material extraction and production). The later type of studies can be used to compare different production routes, and results can be used as part of future cradle-to-grave studies of nanomaterial-containing products. A number of LCA studies of nanomaterials have already been conducted, as is evident from the review studies by Gavankar *et al.* **[30]**, Miseljic and Olsen **[31]**, Hischier and Walser **[32]**, Theis **[33]** and Arvidsson **[34]**. Nanomaterials included in these studies are, for example, carbon nanotubes, fullerenes, nanoclay, quantum dots, silver nanoparticles and titanium dioxide nanoparticles, but not graphene.

Considering that many potential applications and high production rates of graphene are expected in the future, this nanomaterial is particularly relevant to investigate using LCA. The aim of this study is to review the limited number of LCA studies of graphene production (i.e. cradle-to-gate studies) that have been conducted to date. The focus of the review is on how the LCA studies were conducted and which the main results were, including which step in the production system that contributed the most to environmental and resource impacts. First, however, a brief description of the most patented graphene production processes is provided. Then, the LCA method is briefly described. This is followed by a detailed review and comparison of LCA studies of graphene production. Suggestions for future research are finally provided.

Graphene production processes

A patent analysis by Sivudu and Mahajan **[35]** revealed which three groups of graphene production processes are the most patented: Exfoliation (39%), chemical vapour deposition (38%), and epitaxial growth (7%). These three types of processes are also often mentioned in reviews of graphene production in scientific papers **[4, 36, 37]**. A brief description of these processes is provided below. They are also illustrated schematically in **Fig. 1**.

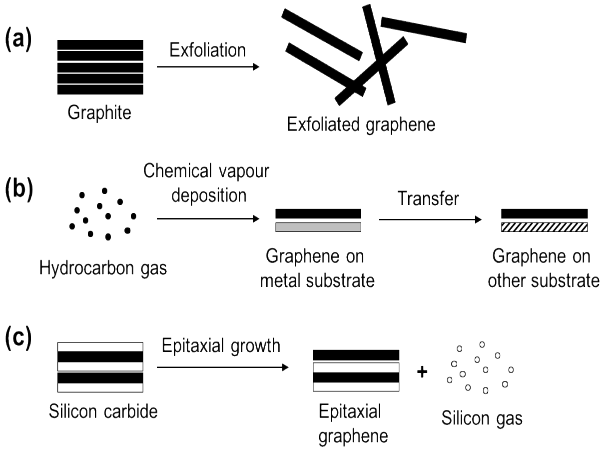

Fig. 1. Schematic illustration of the three most patented types of graphene production processes: Exfoliation (a), chemical vapour deposition (b), and epitaxial growth (c).

Exfoliation processes

Exfoliation processes produce graphene from graphite, and the produced graphene has a potential application in composite materials **[38]**. Graphite consists of many graphene sheets stuck together **[39]**. Exfoliation processes are all about separating (i.e. exfoliating) individual graphene sheets from graphite by braking the van der Waal bonds that hold the graphene layers together. This can be done in several ways, of which most suggested occur in liquid phase.

One often-mentioned way is through reduction of graphite oxide **[38, 40]**. Graphite is then first oxidized into graphite oxide. This is done by the so-called Hummers' process and similar processes, and these typically require inputs of a strong acid as solvent, potassium permanganate as oxidizing agent, and hydrogen peroxide in order to reduce excess permanganate **[41]**. The increased electrostatic repulsion between the oxygen atoms then causes the oxidized graphene sheets to begin to exfoliate. When exposed to a chemical reduction agent, such as hydrazine, the graphite oxide sheets are reduced and fully separated into graphene sheets or stacks of graphene sheets **[42]**. Other substances can also be used as reducing agents (e.g. sodium acetate trihydrate **[43]** and rose water **[44]**), and reduction of the graphite oxide can also be conducted by applying heat **[45]**. The synthesis procedure and degree of oxidation in the graphite oxide have a strong influence on the resulting graphene properties **[46]**.

Another way to exfoliate graphene sheets from graphite in liquid is by ultrasonication **[47, 48]**. The energy in the ultrasound is used to overcome the van der Waals forces that hold the graphene layers in graphite together, causing the graphene sheets to become exfoliated **[49]**. In order to stabilise the exfoliated graphene sheets and prevent reaggregation, different substances can be added, which can be categorized into solvents **[50-52]** and surfactants **[51, 53, 54]**. The quality of graphene produced by ultrasonication facilitated by solvents can be further improved by addition of inorganic salts **[55]**. Ultrasound exfoliation can induce oxidation and defect onto the graphene **[56]**.

Thermal exfoliation by applying high temperatures or microwaves to graphite in liquid solution has also been conducted **[57]**. Such heating may result in nanometre-sized stacks of graphene sheets, also called graphite nanoplatelets (GnP) **[8]**, rather than single-layered graphene.

Additional ways of liquid exfoliation exist, such as applying mechanical shear forces and exfoliating by supercritical carbon dioxide **[40, 48, 57]**. Note that these processes are not always mutually exclusive, but can sometimes be used together or in sequence. For example, ultrasonication can be used to improve the exfoliation of reduced graphite oxide **[42, 58, 59]**. There are also exfoliation processes that do are not conducted in liquid, such as micromechanical cleavage, where graphene sheets are peeled of a graphite crystal by adhesive tape **[3]**.

Chemical vapour deposition

Rather than exfoliating graphene sheets from graphite, the CVD process creates graphene sheets from gaseous carbon sources, and the graphene formed is suitable for use in electronics in general and liquid crystal displays in particular **[12, 60]**. The carbon-containing gas can be methane, ethane, or similar, and is deposited onto a metal substrate under low pressure **[61]**. Even fatty acids from waste chicken fat have been shown to function as feedstock in CVD of graphene **[62]**. The substrate can be made from metals such as copper (also in liquid form **[63]**), nickel, iridium, and ruthenium **[64]**. When exposed to high temperatures (~1000°C), the gas deposits onto the metal substrate and forms a graphene layer. The reaction is self-saturating, and an excess amount of gaseous carbon is required. Hydrogen gas is also added to maintain a reducing reaction environment and thereby avoiding oxidation, which could otherwise damage the graphene structure. Once formed, the graphene sheet will often need to be transferred from the metal substrate in order to be used in different applications. This can be done by etching away the metal **[64]** or by more gentle separations, such as hydrogen bubbling **[65]**, which enables reuse of the metal. The material poly(methyl methacrylate) (PMMA) is often used as supporting material during transfer to a new substrate **[66]**. If the graphene layer is to be used in a transparent electrode in liquid crystal display applications, which is a main envisioned application of CVD-made graphene, the graphene layer will need to be transferred to a transparent quartz layer specifically **[64]**.

Epitaxial growth

Graphene produced on silicon carbide via epitaxial growth is suitable for use as a semiconductor in electronic circuitry **[67]**. Epitaxial growth is similar to CVD in the sense that it gives graphene as a thin surface layer, and this reaction is also self-limiting. However, rather than using a gaseous carbon feedstock, epitaxial growth departs from solid silicon carbide, which is a material consisting of one-atom thick alternating layers of silicon and carbon **[68]**. When exposed to high temperatures (>1000°C), the top silicon layers sublimate, and the then-exposed top carbon layers form a graphene sheet on top of the remaining silicon carbide wafer **[69-71]**. To ensure a high quality of the graphene layer, it is important to limit the sublimation rate of silicon. This can be done in several ways, such as by confining the reaction so that the sublimated silicon gases provide a counter pressure, or providing a counter pressure by adding argon gas **[69]**.

Fundamentals of life cycle assessment

Some fundamentals of LCA are described here, and shown graphically in **Fig. 2**. LCA is a systematic method for assessing environmental and resource impacts of products, services and processes. It follows a defined structure containing four steps **[28, 72]**. The first step is the goal and scope formulation, where the reason for conducting the study and the expected audience are stated. These aspects influence methodological choices throughout the LCA study **[73]**. Which processes that are included in the studied product system are also clarified by setting up a so-called system boundary that delimits the studied product system (**Fig. 2**). As described earlier, cradle-to-grave and cradle-to-gate are two common system boundaries. The functional unit is defined, which is the unit to which all environmental and resource impacts are related. A functional unit could be 1 computer in an LCA study of a computer, and 1 kg of steel in an LCA study of steel production.

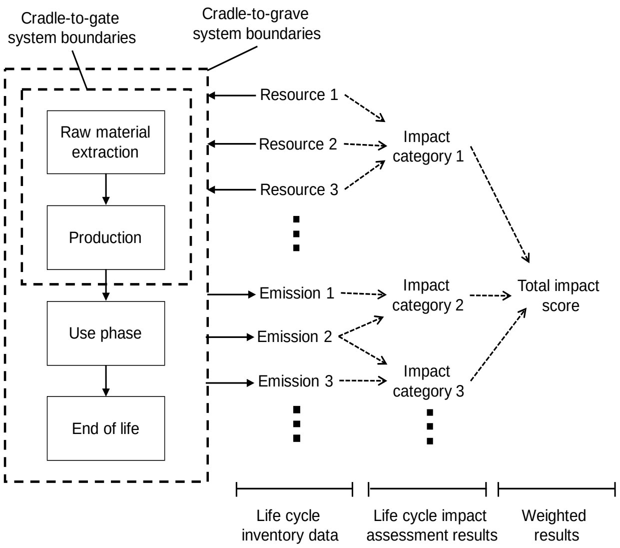

Fig. 2. Graphical representation of some key concepts in life cycle assessment. Ordinary arrows show material and energy flows, and dashed arrows show the impact assessment procedure in life cycle assessment.

The second step is called inventory analysis, where data on inputs and outputs for the now-defined system is acquired and related to the functional unit of the study **[74]**. This is the most time-consuming step in an LCA study, and the result is typically a long list of input materials (such as electricity, heat, and raw materials), emissions (such as carbon dioxide, nitrogen oxides and hazardous chemicals), by-products, and waste. The third step is the impact assessment. Here, the inventory data is translated into impact categories using the following equation **[75]**:

$$I = \sum_{i,j} m_{i,j} \times CF_i \qquad \text{(Eq. 1)}$$

where, I is the impact, m is a quantity of emissions or resources, CF is a so-called characterization factor relating the quantity to an impact category, i is a specific substance emitted or resource used, and j is a certain phase in the product's life cycle (e.g. raw material extraction or end of life). Some commonly included environmental impact categories are climate change from emissions of greenhouse gases, acidification from emissions of acidic substances, eutrophication from emissions of nutrients, ground-level ozone formation from hydrocarbon emissions, depletion of the ozone layer due to emissions of ozone-disrupting chemicals, as well as human toxicity and ecotoxicity from emissions that are toxic to humans and organisms in the environment, respectively **[72, 76, 77]**. Some commonly included resource impact categories are energy use, land use, water use, and use of abiotic resources such as metals and cement **[72, 76, 77]**.

How much a quantity contributes to an impact category – for example, how much a greenhouse gas contributes to climate change – is determined by the CF in Eq. 1. One emission or resource can contribute to several impact categories (**Fig. 2**). For example, emissions of nitrogen oxides contribute to both acidification and eutrophication **[76]**. For many emission-based impact categories, impacts are related to an equivalent amount of a certain emission contributing to the impact, such as CO_2 for climate change and SO_2 for acidification. The units of the impact categories can thus be kg CO_2 equivalents and kg SO_2 equivalents for climate change and acidification, respectively. The unit of a CF for climate change is thus kg CO_2 equivalents per kg emitted greenhouse gas. For resource use-related impact categories, the unit is often a quantity of the resource, such as MJ for energy use and m^2 for land use.

Although not always used, the different impact categories assessed in the impact assessment step can be weighted together into one single unit of environmental and resource impact **[78]**. Such weighting must be based on some sort of values. One variant is to relate the impact categories to policy goal, another is to base it on the economic value that is destroyed by the environmental deterioration and resource use **[79]**.

The fourth step in an LCA study is the interpretation, where impact assessment results are put into context, a sensitivity analysis is conducted (e.g. according to **[80]**), and conclusions are drawn from the study **[72]**.

In addition to environmental and resource impacts, there is ongoing work in the LCA community to extend LCA to enable the assessment of social and economic impacts as well **[81, 82]**. These variants of LCA are called social LCA and life cycle costing (LCC), respectively. When LCA, social LCA, and LCC are used together, this can be referred to as life cycle sustainability assessment (LCSA) **[83]**. However, these approaches are only in an early stage of development and have not been applied to nanomaterials yet. They will therefore not be discussed further in this paper.

Life cycle assessment studies of graphene production

To date, there exist four published LCA studies of five different types of graphene production: Chemical reduction of graphite oxide, ultrasonication exfoliation, thermal exfoliation, CVD, and epitaxial growth. These five processes cover the most patented types of production processes – liquid exfoliation, CVD, and epitaxial growth – although there exist other specific variants of these as well. The four studies are described in detail below, and a summary of the five studied production processes is presented in **Table. 1**. All studies are recent, with the oldest being published in 2014. Only results for the impact category energy use exist for all five production processes studied, so only life cycle energy use results are shown in **Table. 1**.

Life cycle assessment of chemical reduction of graphite oxide and ultrasonication exfoliation

Arvidsson et al. **[84]** compared life cycle impacts of two liquid exfoliation processes for graphene production. One was chemical reduction of graphite oxide by hydrazine as described in a patent **[85]**, and the other was ultrasonication of graphite as described in another patent **[52]**. Different variants of the Hummers' process were considered for production of graphite oxide from graphite **[41]**, and both synthetic and natural graphite were considered as raw materials. For the ultrasonication process, diethyl ether was assumed to be used as solvent, since it is a common industry chemical and one of the solvents with most advantageous surface properties for facilitating exfoliation **[52]**. The functional unit of the study was 1 kg of graphene in solution (water for the reduction of graphite oxide process and diethyl ether for the ultrasonication process). Four impact categories were considered: Energy use, water use, human toxicity and ecotoxicity. The results of the study showed that for the baseline cases studied, it was difficult to rank the two processes with regard to environmental performance. The ultrasonication required approximately half as much the energy and water as the chemical reduction of graphite oxide, but caused approximately twice as high human toxicity impacts. Ecotoxicity impacts were similar for the two processes. For chemical reduction of graphite oxide, the chemical reduction reaction contributed the most to energy use (about 80%), human toxicity (almost 100%), and ecotoxicity (almost 100%), while Hummers' process contributed the most to water use (about 80%). For ultrasonication, the diethyl ether solvent production was the largest contributor to all impact categories (almost 100%). In a sensitivity analysis, a number of parameters were varied, including transport distances, electricity mixes, and solvent recovery. This analysis made it clear which one of the two production processes that could be environmentally preferable. Assuming a 90% solvent recovery of the diethyl ether solvent used in the ultrasonication made this process superior for all four

Table 1. Summary of existing life cycle assessment studies of five graphene production processes.

Study characteristics	Chemical reduction of graphite oxide [84]	Ultrasonication exfoliation [84]	Thermal exfoliation [86]	Chemical vapour deposition [88]	Epitaxial growth [91]
Graphene produced	Reduced graphene sheets in water	Graphene sheets in diethyl ether	Pulverized graphite nanoplatelets	Graphene on a quartz substrate	Graphene on a silicon carbide wafer
Carbon feedstock	Graphite	Graphite	Graphite	Methane	Silicon carbide
Functional unit	1 kg	1 kg	1 kg	1 cm^2	1 cm^2
Number of impact categories considered	4: Energy use, water use, human toxicity and ecotoxicity	4: Energy use, water use, human toxicity and ecotoxicity	12, including: Energy use, climate change, acidification, human toxicity and ecotoxicity	2: Energy use and metal use	4: Energy use, climate change, acidification and ecotoxicity
Step with largest contribution to impacts	Reduction step (Hummers' process for water use)	Diethyl ether solvent production	Microwave heating	Methane production	Silicon carbide wafer production
Energy use results	900-1000 MJ/kg	70-500 MJ/kg	2000 MJ/kg	0.007-0.2 MJ/cm^2	2-80 MJ/cm^2

impact categories. The main recommendation of the study was thus for industry and research to focus development efforts on ultrasonication with high solvent recovery in order to limit impacts from liquid exfoliation of graphene.

Life cycle assessment of thermal exfoliation

Pizza *et al.* **[86]** conducted a cradle-to-grave assessment of an epoxy-based nanocomposite material containing GnP to improve thermal conductivity. The functional unit of the study was 1 kg of nanocomposite. As part of that study, a cradle-to-gate assessment of GnP production was conducted and results were also shown for 1 kg of GnP. In fact, the production of GnP turned out to be a major contribution to the overall impacts of the nanocomposite. The GnP production process studied was thermal exfoliation with sulphate intercalation **[87]**. The graphite feedstock was first exposed to sulfuric and nitric acid, thereby forming a sulphate-graphite intercalated compound of partly separated stacks of graphene. This is done in order to facilitate the exfoliation. After furnace heating, carbon dioxide and water gases are formed, which expand and separate the GnP. Further heating by microwaves are then conducted to stabilize the exfoliated graphene. The produced GnP are then pulverized. A large number of impact categories were considered: Metal depletion, fossil depletion, energy use, water depletion, climate change, ozone depletion, human toxicity, ecotoxicity, photochemical oxidant formation, acidification, freshwater eutrophication, marine eutrophication and hazardous waste. The results for the thermal exfoliation clearly shows that the electricity for microwave heating accounts for the largest share of the energy use of the GnP production (>90%). The authors state that this step and the duration of the heating is necessary in order to achieve sufficient exfoliation. The second largest contribution to energy use is pulverization, accounting for 3% of the energy use. Contribution from production of graphite, sulphuric acid, nitric acid and transport were minor. Considering that the heat was produced with electricity, the authors state that the electricity mix is of crucial importance.

Life cycle assessments of chemical vapour deposition

In an assessment of CVD-made graphene, Arvidsson *et al.* **[88]** considered methane as carbon feedstock and copper as metal substrate, with input of hydrogen gas to ensure a reducing environment. The study was based on experimental work by a group at the University of Texas at Austin **[61, 64, 89]**. The functional unit was 1 cm^2 of graphene on a quartz substrate. Consequently, the transfer of the graphene sheet from the copper onto quartz was included. This transfer was modelled as a sequence containing the application of PMMA, etching away copper by iron nitrate, transfer onto quartz and then washing away PMMA with acetone. Two impact categories deemed to be of particular relevance were included: Energy use and the use of scarce metals. These two resource impacts of CVD-made graphene were compared to those of a currently used material in transparent electrodes: Indium tin oxide (ITO). In a previous study, the life cycle energy use of ITO had been calculated to be 18-68 kJ/cm^2 **[90]**. The baseline result for CVD-made graphene was 22 kJ/cm^2, which is thus at the lower end of the energy use range of ITO. A sensitivity analysis revealed that given recovery of excess methane feedstock and low residence time in the reactor, the energy use of CVD-made graphene could become as low as 6.6 kJ/cm^2. In addition, CVD-made graphene was found to be beneficial compared to ITO from a scarce metal use point of view. Although copper was required in order to produce graphene, the much scarcer material indium is required to produce ITO. CVD-made graphene thus seems to be a beneficial alternative to ITO both regarding energy use and use of scarce metals.

Life cycle assessment of epitaxial growth

Arvidsson and Molander **[91]** conducted an assessment of epitaxial growth with a functional unit of 1 cm^2. Three different production scenarios were investigated: Lab-scale, pilot-scale, and industrial scale. The lab-scale scenario was based on an experimental setting **[69]**, and the pilot-scale scenario was based on a small production facility in Sweden. The industrial scale was modelled based on assumptions about future improvements. The raw material for this process is a high-grade silicon carbide wafer, which consists of alternate layers of carbon and silicon. The silicon carbide wafer can in turn be produced via two different production processes **[68]**. The one currently most used in industry is called physical vapour transfer, where coke and crude silicon carbide made from silica sand are vaporised and deposited onto a high-grade silicon carbide crystal, thereby expanding the crystal with similarly high-grade silicon carbide. The other process is called high temperature vapour deposition, in which methane and silane gases are deposited on a high-grade silicon carbide crystal at high temperatures. In the epitaxial growth process, argon distilled from air can be applied to prevent too rapid silicon sublimation. The four impact categories energy use, climate change, acidification and ecotoxicity were investigated. The results vary notable between the best and worst cases. It was shown that electricity use during the production of the silicon carbide wafer was the largest contributor to all impacts (>70%). Reducing the amount of silicon carbide wafer could reduce impacts by one order of magnitude at most. Using a less impacting (‘greener’) electricity mix during silicon carbide wafer production could further reduce all impacts by up to several orders of magnitude, especially for climate change, acidification, and ecotoxicity, which all depend heavily on choice of electricity mix.

Comparisons and future work

Here, results from the five studied production processes are compared and recommendations for future work are provided. The energy use results in **Table 1** can be compared to existing ‘bulk’ materials. For example, aluminium requires approximately 200 MJ/kg **[26]**, and is a relatively energy-intensive metal to produce. Notably, most of the energy use results in **Table 1** are higher than this. Only graphene produced from ultrasonication, given solvent recovery, has a lower energy use than that.

However, **Table 1** consequently also shows that graphene does not need to be more energy-intensive than existing materials. This goes not only for the graphene produced by ultrasonication with solvent recovery, but also for the CVD-made graphene that was shown to require less energy than the currently used ITO, especially given efficient use of the methane feedstock. Comparing the two surface-based production processed CVD and epitaxial growth to each other, it is clear that the epitaxial growth has impacts that are orders of magnitude higher per cm^2.

It is important to note that the types of graphene produced are not completely identical. For example, the thermal exfoliation produces 1 kg of GnP powder, while the ultrasonication exfoliation and chemical reduction of graphite oxide produce 1 kg of graphene in diethyl ether and water, respectively. The graphene produced by reducing graphite oxide may also have residual oxygen bound to it, which graphene produced by ultrasonication should not have to the same extent **[84]**. There may also be quality differences between CVD-made and epitaxial graphene **[92]**. Direct comparisons between the results of the reviewed studies are therefore difficult, since differences in properties between the graphene produced by different processes may affect the technical performance of subsequent products in which the graphene is used. Still, it gives a rough indication about which of the production processes have high impacts, and which have lower impacts.

It should also be noted that all four studies make attempts to model future large-scale production of graphene, rather than lab-scale production. Lab-scale production can have very high impacts, which may not become realized at larger production scales. For example, one study showed that the energy requirements for producing carbon nanotubes decreased by >99.9% when going from conceptual and engineering development to small-scale production **[93]**. Scenarios describing future large-scale production are therefore relevant for guiding strategic technology choices towards reduced environmental and resource impacts.

Although some of the reviewed studies considered toxicity impacts, none of them considered emissions and subsequent environmental and health impacts of graphene itself. Such impacts have been reviewed and discussed in a number of papers **[23-25, 94]**. These studies point to the ability of graphene to cause adverse impacts to human health and the environment should it become emitted, but also highlight the considerable lack of data on the matter. One reason for the lack of consideration of toxicity impacts from graphene in LCA studies is that several of the studies report that no emissions of graphene occurred during production. However, future measurements may detect graphene emissions from production, and emissions of graphene could also occur during the use of graphene in products. In order to be able to assess toxicity impacts of graphene emissions in LCA, a CF for graphene is required (Eq. 1). Recently, Deng et al. **[95]** published CFs for freshwater ecotoxicity impacts of graphene oxide, thus enabling the inclusion of this substance along with other ecotoxic emissions occurring in the production system. The modelling was conducted based on two different approaches **[95]**. One approach was based on traditional chemical fate modelling, which is based on chemical substances' tendency to strive for thermodynamic equilibrium, while the other approach was based on particle kinetics. These two modelling approaches gave notably different results. Which of these approaches is most suitable to model the fate of nanomaterials in the environment is being debated **[96, 97]**. In order to establish a CF for graphene emissions, which of the two fate modelling approaches is most appropriate must be investigated. Further development of methods for deriving CFs for nanomaterials in general and for graphene in particular is thus required.

Since only four LCA studies of graphene production exist, there is clearly a need for future studies. Many other production processes in addition to the ones studied so far exist. These include for example micromechanical cleavage with adhesive tape, CVD on other substrates than copper (such as nickel), arc discharge, organic synthesis from smaller polycyclical aromatic compounds and unzipping of carbon nanotubes **[36, 37]**. Although not all of these processes may be feasible for large-scale production, the continuous investigation of novel graphene production processes is essential to provide guidance towards the most environmentally benign production processes.

There is also an increased interest in graphene with other substances covalently bound to it. Such functionalized graphene has many envisioned applications, including electronics **[98]**, biosensors **[99]** and as catalysts **[100]**. In future cradle-to-gate LCA studies, it may thus be interesting to not only consider graphene, but also different types of functionalised graphene. This step has already been taken in LCA studies of fullerene production. In the study by Anctil et al., the life-cycle energy use of fullerenes was calculated **[101]**. In addition, they also calculated the energy use for a functionalized type of fullerenes used in solar cells, called (6,6)-phenyl-C_{61}-butyric acid methyl ester (PCBM).

Conclusion

Considering that graphene is expected to be produced in large amounts in the future, and be used in many different applications, an environmentally benign supply of graphene is important. Although only four LCA studies of graphene production exist yet, these already provide some guidance on how the environmental and resource performance of producing graphene can be improved. For bulk production of graphene in liquid, the studied chemical reduction of graphite oxide and thermal exfoliation seem to have comparatively high impacts. For chemical reduction of graphite oxide, it is mainly the reduction step and the production of the reducing agent hydrazine that cause the high impact **[84]**, and for thermal exfoliation, it is mainly the energy required for heating **[86]**. Ultrasonication exfoliation, on the other hand, seems to have the potential for comparatively low impacts provided that there is reuse of solvents **[84]**. For CVD, the hydrocarbon gas feedstock seems to be largest contribution to the impacts, so reducing or reusing that feedstock is the most important step that can be taken in order to reduce the impacts of CVD-made graphene **[88]**. For epitaxial growth, the production of the silicon carbide wafer is the largest contribution to the impacts of epitaxial graphene. Reducing the input of silicon carbide wafer and producing the wafer with 'green' electricity are thus the most important actions towards lower impacts for this production process **[91]**.

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