Prospective Life Cycle Assessment of Graphene Production by Ultrasonication and Chemical Reduction

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S *Supporting Information*

ABSTRACT: One promising future bulk application of graphene is as composite additive. Therefore, we compare two production routes for in-solution graphene using a cradle-to-gate lifecycle assessment focusing on potential differences in energy use, blue water footprint, human toxicity, and ecotoxicity. The data used for the assessment is based on information in scientific papers and patents. Considering the prospective nature of this study, environmental impacts from background systems such as energy production were not included. The production routes are either based on ultrasonication or chemical reduction. The results show that the ultrasonication route has lower energy and water use, but higher human and ecotoxicity impacts, compared to the chemical reduction route. However, a sensitivity analysis showed that solvent recovery in the ultrasonication process gives lower impacts for all included impact categories. The sensitivity analysis also showed that solvent recovery is important to lower the blue water footprint of the chemical reduction route as well. The results demonstrate the possibility to conduct a life cycle assessment study based mainly on information from patents and scientific articles, enabling prospective life cycle assessment studies of products at early stages of technological development.
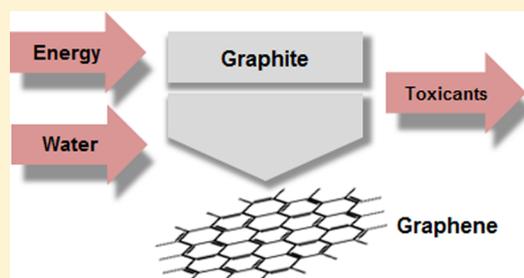
1. INTRODUCTION

Graphene is a newly discovered material with a number of promising technical applications due to its unique properties.[1] These applications include the use of graphene as an additive in composites to increase strength and conductivity,[2] as a replacement of indium tin oxide in liquid crystal displays,[3] as a semiconductor in electronics,[4] and in applications for energy storage and conversion.[5] From an environmental point of view, graphene has potential advantages. Replacing rare metals with graphene could alleviate resource scarcity problems.[6] Improving the feasibility and competitiveness of novel energy technologies could reduce the overall environmental impact of society.[5] However, this new material could also have negative environmental impacts.

Graphene production and use have two primary categories of negative environmental impact. The first is toxic effects from exposure to graphene itself. A number of studies have highlighted the potential toxic effects of nanomaterials in general.[7−11] A review of toxicity impacts related to graphene and its use concluded that although graphene appears to have a notable toxicity to both human cells and other organisms and could become produced in large quantities in the future, it is uncertain whether there will be any release of graphene to the environment.[12]

The second category of negative environmental impact arises from processes along the life cycle of graphene. Life cycle assessment (LCA) is a method used to quantify such environmental impacts, identify products and processes of particular concern, and compare the impacts of different processes and products.[13] LCA has been recommended for environmental assessment of nanomaterials,[10,14] and a number of other nanomaterials have been studied in LCAs.[15−17] Published LCA studies of another carbon nanomaterial, carbon nanotubes, typically show a relative high life cycle energy use compared to both other nanomaterials and traditional materials such as aluminum.[17−19] The aim of this study is to assess the life cycle environmental impact of graphene production for use in composite bulk materials.

A number of graphene production routes for laboratory-scale have been suggested.[20,21] It is not trivial to identify which of those routes are of relevance for industrial-scale production of graphene. Patents should, to a larger extent than scientific articles, disclose production processes that are demonstrated to be technically feasible and considered to have economic value.[22] Sivuvu and Mahajan[23] conducted a patent analysis of graphene production routes for mass production. They concluded that for producing graphene to be used as filler in polymer composites, which is likely to become a major application of graphene,[6] liquid phase exfoliation routes are most promising because they have the advantage of high scalability and low potential costs.[23] The chemical reduction
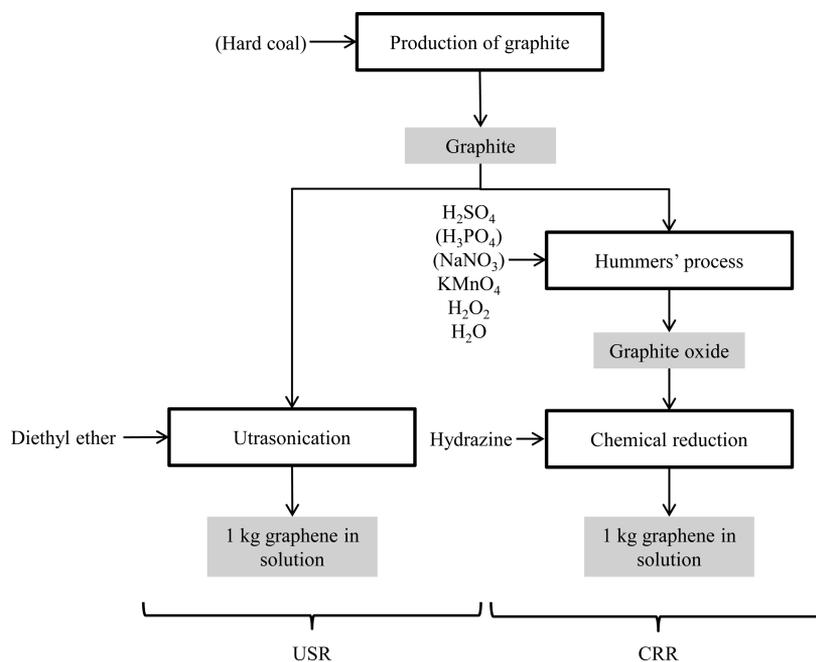
Figure 1. Flowchart describing the cradle-to-gate life cycle of graphene produced via the ultrasonication route (USR) and the chemical reduction route (CRR), respectively. The phosphoric acid and the sodium nitrate are within parentheses as they are only used in some variants of the Hummers' process. Similarly, hard coal is used only when producing graphene through synthesis.

route (CRR)[24] and the ultrasonication route (USR)[25] are two liquid phase exfoliation routes with industrial-scale potential at low costs.[23] The USR has been claimed to be environmentally superior,[25] and this claim is investigated in this study by comparing the USR to the CRR. Thermal exfoliation of graphene, which is a third potential process for liquid exfoliation, is not included due to presumed high energy use because of high temperatures (approximately 2000 °C).[26] Applications of graphene in electronics are not included in this study, since such applications require other production routes such as chemical vapor deposition and epitaxial growth,[23] and may also require other functional units.

2. MATERIALS AND METHODS

LCA is a well-documented method that requires stringent definitions of the functional unit and studied production system.[13,27,28] The functional unit of this study is 1 kg of graphene in solution, which may then subsequently be used as additive in composite materials. Graphene produced from USR and CRR does not have exactly the same physiochemical properties. USR provides thinner graphene sheets (less than 1–10 nm compared to >100 nm[25] for the CRR) with a higher C/O ratio (approximately 1/0 compared to 12.5/1 for the CRR).[25,29] Note that the output of the CRR is considered to be graphene although it has a C/O ratio lower than 1/0.[29] The output of both the CRR and the USR allows the graphene to be used in composites and the material from both processes results in similar composite properties.[24,25]

Figure 1 presents a flowchart of the two production routes. Process data for the graphene production processes was mainly obtained from patents, as patents should disclose production processes that are demonstrated to be technically feasible and considered to have economic value.[22] The patents by Zhamu and Jang[25] and Stankovich et al.[24] were used as the main data sources for USR and CRR, respectively. Data for Hummers' process for production of graphene oxide was taken from

Marcano et al.[30] For all other processes, inventory data was obtained from the Ecoinvent database.[31]

2.1. Graphite Production. Graphite is the baseline raw material of both production routes under investigation.[24,25] Graphite can be either mined or synthesized. The synthesized graphite is typically much purer (>99.9%) than mined graphite (>93%). Neither of the production routes is sensitive to graphite purity. Because of the lower costs of the low purity mined graphite, mining of graphite is assumed to best represent future large-scale production and is therefore applied as baseline case for both routes. The influence of changing to synthesized graphite was tested in the sensitivity analysis. The synthesized graphite is assumed to be made from hard coal coke.[31]

2.2. Graphite Oxide Production. Before graphite can be turned into graphene through CRR, it must first be oxidized to graphite oxide. The so-called Hummers' process[32] was recommended in the considered patent,[24] and is the most common production process for graphite oxide today.[30] Hummers' process thus constitutes our baseline case. In Hummers' process, graphite is oxidized using potassium permanganate, sodium nitrate, and sulfuric acid. However, Marcano et al.[30] describe two modified versions of Hummers' process. The first uses twice the mass of potassium permanganate. The second also uses twice the mass of potassium permanganate, but also adds phosphoric acid and does not use sodium nitrate. Based on the denotations by Marcano et al.,[30] we label the three processes "Hummers'" (the original method and baseline case), "Hummers'+" (twice the potassium permanganate) and "Hummers'++" (twice the potassium permanganate, addition of phosphoric acid, exclusion of sodium nitrate). In addition, some deionized water is needed for washing and dissolution, and some hydrogen peroxide is needed to reduce excess potassium permanganate in all three variants of Hummers' process. Data on inputs for the modifications of Hummers' process were obtained from

Marcano et al.[30] A detailed comparison between the three variants of Hummers' process can be found in Section 2 of the Supporting Information (SI), and the influence of the different variants was tested as part of the sensitivity analysis.

For the sulphuric and phosphoric acid used as solvents in Hummers' process, recovery is an issue. Although not well documented, solvent recovery in industry can range from 0% to 90%. Acid recovery was set to 0% in the baseline case, meaning that all acid was neutralized after Hummers' process. However, since the sulphuric acid is in surplus in Hummers' process, there will be unreacted acid in the output. Recovery was assumed to be in the form of recirculation and reuse of the reaction solution, which has negligible environmental impact. The influence of a 90% recovery rate is assessed in the sensitivity analysis.
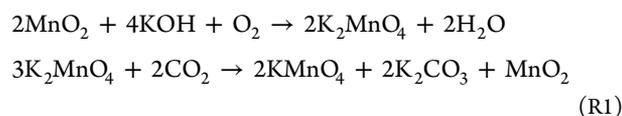
Based on input data from Marcano et al.[30] and tabulated values for heat capacities, the energy use of heating and cooling in Hummers' process was calculated using

$$E = m \times c_p \times \Delta T \tag{E1}$$

where E is the energy, m is the mass of the heated or cooled body, c_p is the specific heat capacity of the body, and ΔT is the change in temperature that the body experiences. Heat losses were calculated using the mechanical insulation design guide provided by the National Institute of Building Services,[33] with temperatures and their duration times obtained from Marcano et al.,[30] see Section 2 in SI for specific values. Only heat losses during operation were considered, and not those occurring during startup and shutdown. No heat recovery was assumed. The influence of variations in heat losses on the total energy use was investigated in the sensitivity analysis.

Deionized water is required for washing and dilution of the graphene oxide, but there is a large uncertainty about how much will be required in future industrial production systems. In order to account for this uncertainty, a wide range of this parameter was tested in the sensitivity analysis to investigate its influence on the blue water footprint and the other impact categories. The baseline case was 1000 L per kg of graphite oxide. The Ecoinvent data represents deionized water produced through ion exchange of tap water.[31]

Ecoinvent data for potassium permanganate is based on production by reacting manganese mineral (MnO_2) with potassium hydroxide (KOH) in the presence of liquid oxygen (O_2), and then boiling with liquid carbon dioxide (CO_2):[31]

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + 2K_2CO_3 + MnO_2 \tag{R1}$$

The process data assumes that manganese is mined, and liquid oxygen is produced from liquefaction of air, whereas the carbon dioxide is extracted from different waste gases and liquefied using electricity.[31] The potassium hydroxide is assumed to be produced through electrolysis of potassium chloride (KCl):[31]

$$2KCL + 2H_2O \rightarrow 2KOH + Cl_2 + H_2 \tag{R2}$$
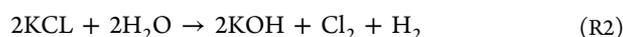
For the sodium nitrate reactant in the Hummers' process, no unit process data was found in the Ecoinvent database or elsewhere. Similar to graphite, it can be mined or synthesized from raw materials. To cover this data gap, we assumed that the emissions and resource use of producing sodium nitrate is the same as that of producing potassium chloride. This analogy is

considered reasonable since most sodium nitrate is mined and processed at similar locations and in a similar manner to potassium chloride, a typical example being via open pit mining and processing in Chile.[34,35]

Data for sulphuric acid represents production of sulfur oxide gas from sulfur-containing raw materials and conversion into sulfur trioxide and then sulphuric acid.[31]

The industrial grade phosphoric acid is assumed produced from fertilizer-grade phosphoric acid according to Ecoinvent.[31] The fertilizer-grade phosphoric acid is in turn produced using the dihydrate process from mined phosphate rock (P_2O_5), sulphuric acid (H_2SO_4), and mined quicklime (CaO).[31] The dihydrate process can be described by the following chemical reaction:[36]

$$Ca_3(PO4)_2 + 3H_2SO_4 + 6H_2O$$
$$\rightarrow 2H_3PO_4 + 3CaSO_4 \bullet 2H_2O \tag{R3}$$
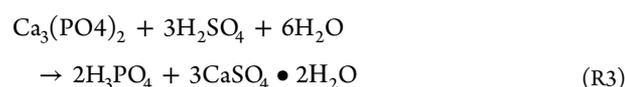
where the $Ca_3(PO_4)_2$ is a reaction product of the quicklime and phosphate rock.[31]

Hydrogen peroxide is according to Ecoinvent produced by the anthraquinone process, which requires liquid oxygen (O_2), and hydrogen (H_2) as inputs:[31]

$$H_2 + O_2 \rightarrow H_2O_2 \tag{R4}$$

2.3. Chemical Reduction Process. In the chemical reduction process, graphite oxide (G-O) is assumed to be reduced to graphene by hydrazine (N_2H_4), which is the currently most used reduction agent for this purpose:[2]

$$G\text{-}(O)_{2n} + nN_2H_4 \rightarrow G + 2nH_2O + nN_2 \tag{R5}$$
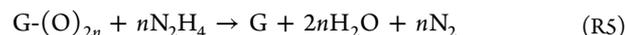
where n is a natural number. The C/O ratio varies in graphite oxide, but was assumed to be 1.5 as obtained by Marcano et al.,[30] see further Section 4 in SI. In addition, energy use for heating and heat losses were calculated based on data from Stankovich et al.[2] in the same manner as for the Hummers' process, see further Section 3 in SI.

No data for hydrazine is available in the Ecoinvent database, and no obvious analog exists. Therefore, detailed modeling of the production of hydrazine has been conducted, see Section 5 in SI.

2.4. Ultrasonication Process. During ultrasonication at frequencies of about 20 kHz, graphite sheets can be separated into graphene.[25] Electricity used to produce the ultrasound was estimated through linearly scaling the input electricity of similar equipment with solvent volume. Although up scaling of sonochemistry is complex, a linear relation between power input and solvent volume is both convenient and established.[37] The power input of the ultrasound device may vary between 150 and 300 W per liter solvent.[25] The parameter was varied in the sensitivity analysis, with 300 W/liter as the baseline case. The sonication time, which is required to calculate the energy use from the power input, was 30 min.[25] The yield of the ultrasonication may vary between 95% and 99%.[25] The rage of 95−99% was tested in a sensitivity analysis, with 95% as baseline. As the reaction takes place at room temperature,[25] there is no energy needed for heating, but the separation of the graphene sheets must be facilitated by proper solvents. Zhamu and Jang provide a list of tested solvents. Among them are some perfluorinated substances and diethyl ether leading to very thin graphene sheets.[25] As diethyl ether is an industrial chemical produced in large volumes, and with data available in the Ecoinvent database, it was assumed to be representative for
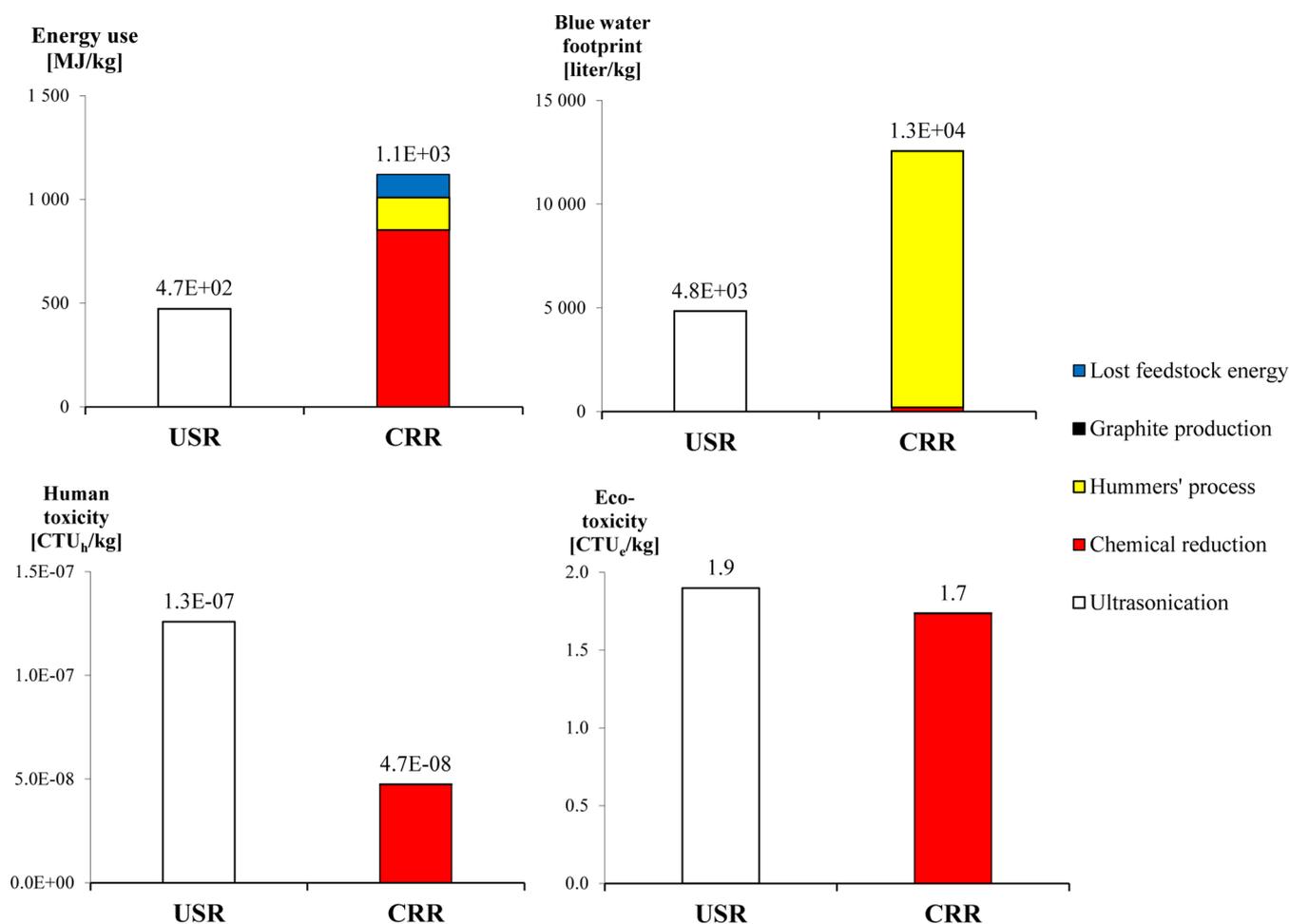
Figure 2. Baseline case energy use, blue water footprint, human toxicity and ecotoxicity for graphene produced via the ultrasonication route (USR) and the chemical reduction route (CRR).

industrial scale USR of graphene. Recovery of the diethyl ether solvent may vary between 0% and 90% through distillation. This variation was tested in a sensitivity analysis, with 0% as the baseline case. In the Ecoinvent database, the diethyl ether ($CH_3CH_3OCH_2CH_3$) is reported to be produced as a byproduct of direct hydration (reaction with water, H_2O) of ethylene (C_2H_2) according to the following reaction:[31]

$$2C_2H_2 + H_2O \rightarrow CH_3CH_2OCH_2CH_3 \qquad (R6)$$
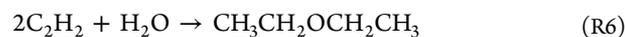
Ecoinvent data for ethylene represents production by cracking of petroleum.[31]

2.5. Foreground and Background Systems. We have previously highlighted the importance of differentiating foreground and background systems in LCAs on immature products.[18,38] The foreground system constitutes the production system under investigation. Background systems include the production of electricity and transport for the various precursors and products. For immature products that may not appear on markets for tens of years, including background systems may be misleading from a technology guidance perspective. During the period over which the immature products become mature, background systems may change radically. Assessing an immature product using current transport fuels and electricity mixes may say more about the environmental impact of the background system than of the actual foreground system under investigation. Therefore, following Kushnir and Sandén,[18] we only consider the

foreground system. Considering this assumption, unit process data rather than cumulative data was obtained from the Ecoinvent database for each process. The only aspect of the background system included is the heat-to-electricity conversion factor, which is varied to account for different future scenarios. In addition, as it is impossible to know future locations of the different processes and thereby also transport distances, as well as future modes of transport, any environmental impact from transports were excluded. The influence of this assumption was tested in a sensitivity analysis with an example.

2.6. Impact Categories and Environmental Indicators. We include four impact categories: energy use, water use, human toxicity and ecotoxicity. The energy use was calculated as heat, meaning that electricity used in the processes was converted to the corresponding heat by multiplying with a conversion factor, which could approximately vary between 0.3 (e.g., for electricity from fossil fuels) and 1 (e.g., for solar electricity).[39] Here, 0.3 was set as baseline, and 1 was tested in a sensitivity analysis. In addition, the lost feedstock energy is included in the energy use, which equals the energy content of the mined raw material (graphite or hard coal) minus the energy content of the graphene.

Blue water footprint, which is the freshwater withdrawn from lakes, rivers, aquifers and similar sources, indicates water use.[40] No rainwater stored in the soil as soil moisture is used along the graphene life cycle, so no green water footprint is

calculated. Similarly no gray water footprint, indicating water required to dilute emissions to legally acceptable concentrations, was included due to redundancy with the toxicity impact categories.[41] In line with previous assumptions, only blue water used in the foreground system is included, excluding blue water embedded in energy supply or transports. The assumption of not including the water use of energy production was tested in a sensitivity analysis.

The human toxicity and ecotoxicity indicators are from the recently established USEtox model.[42,43] These impact categories are measured in comparative toxic units (CTU), with a subscript "h" and "e" to indicate human or ecotoxicity, respectively. Again, only toxic impacts from the foreground system are included, excluding emissions occurring during, for example, electricity production. This assumption was also tested in the sensitivity analysis.

Impacts from emissions of the graphene product itself are not considered, as there are yet no reports of graphene being emitted to the environment.[12]

Some of the more common impact categories in LCA, such as global warming and acidification, are not included here, as those impacts do not mainly arise from the foreground system of graphene. Rather, they arise from background systems such as transport and production of heat and electricity. The future performance of transport and energy production systems regarding, for example, emissions of greenhouse gases and acidic substances, is unknown.

3. RESULTS AND DISCUSSION

3.1. Energy Use. As shown in Figure 2, the energy use of the CRR is approximately twice that of the USR. The main contributor to high energy use in CRR is the chemical reduction process (approximately 75%), due to heating during chemical reduction and high energy use of hydrazine production. Hummers' process and the lost feedstock energy contribute as well, approximately 15% and 10%, respectively, whereas contributions from graphite production are negligible. For the USR, the ultrasonication process contributes approximately 100% of the energy use, due to the production of diethyl ether. Here too, the energy use from production of graphite is negligible. For a more detailed table showing the numerical contributions to the energy use for all main processes, see Section 6 in SI.

Kim and Fthenakis[17] compared the per kg primary energy use of a number of nanomaterials (carbon nanotubes, fullerenes, quantum dots, carbon nanofibres, nanoclay, and titanium dioxide nanomaterials) to that of materials that have been used for long in society (aluminum, polypropylene, and steel). The energy use of the nanomaterials varied considerably, from as high as 100 000 MJ/kg for one case of carbon nanotubes to as low as 1 MJ/kg for one case of nanoclay.

Comparing the numbers from Kim and Fthenakis[17] to the energy use results in Figure 2, it seems that the energy use from graphene production by the USR and the CRR, ranging approximately 500—1000 MJ/kg, ends up close to the middle of a relative ranking of the nanomaterials' energy uses. Notably, most energy use numbers for carbon nanotubes are higher than those obtained for graphene in this study. For some other nanomaterials, such as carbon nanofibers, titanium dioxide nanoparticles, and nanoclay, the energy use of graphene is higher for both investigated production routes. It is also worth noting that both USR- and CRR-made graphene have at least

twice as high energy use as aluminum and almost an order of magnitude higher energy use than polypropylene.[17]

3.2. Blue Water Footprint. Regarding the blue water footprint, the CRR again has approximately twice as high impact as the USR (Figure 2). Hummers' process is the main contributor, mainly due to water use during production of sulphuric acid and water needed for washing and dissolving the graphene oxide, which contribute approximately 70% and 14%, respectively. For the USR, the main contributor is production of ethylene and subsequently diethyl ether for the ultrasonication process, which contribute by approximately 57% and 41%, respectively. For a more detailed table showing the numerical contributions to the blue water footprint for all main processes, see Section 6 in SI.

3.3. Human Toxicity Potential. For human toxicity, the USR has the largest impact, about three times that of the CRR (Figure 1). The ultrasonication process accounts for approximately 100% of the USR human toxicity potential. More precisely, emission of mercury to air during production of ethylene, from which the diethyl ether for the ultrasonication process is produced, is the largest contributor and accounts for approximately 89% of the toxicity. The mercury emitted was contained within fossil resources from which the ethylene is produced during cracking. For the CRR, the chemical reduction process is the largest contributor, representing approximately 100% of the human toxicity potential. Emissions of cadmium, zinc, and lead to air during hydrazine production are the main reason for that. Similarly to mercury for the USR case, these metals were originally contained within fossil resources, in this case those used for production of ammonia, which in turn is used to produce hydrazine. For more detailed results, see Section 6 in SI.

3.4. Ecotoxicity Potential. The results for the ecotoxicity potential are similar for the two production routes (Figure 2). The ultrasonication process accounts for approximately 100% of the ecotoxicity potential of the USR, with the main contributor being ethylene production, where emissions of copper constitute approximately 74% of the ecotoxicity potential. For the CRR, the chemical reduction process is again the main contributor, accounting for approximately 100% of the ecotoxicity potential. This is mainly due to emissions of vanadium during hydrazine production, which contributes more than 95% of the ecotoxicity potential. For more detailed results, see Section 6 in SI.

To conclude the toxicity potential sections, emissions of metals during various processes appear to cause the highest toxicity potential.

3.5. Sensitivity Analysis. A number of input parameters included in the assessment are uncertain in the sense that their values may vary, and the values that might best represent industrial-scale production are unknown. The influence of variations in parameter values on the results of the included impact categories was therefore tested in a sensitivity analysis. The aim was to identify parameters with a large impact on the results. Such sensitive parameters may then be subject to more detailed data gathering in future studies. For parameters with a low influence on the results, further data gathering is not as urgent. Sensitive parameters may also provide opportunities for environmental improvements. If some parameter values result in lower environmental impacts, those values provide important guidance for graphene producers.

The parameters investigated in the sensitivity analysis are the ultrasonication yield (95—99%), the ultrasound effect (150—
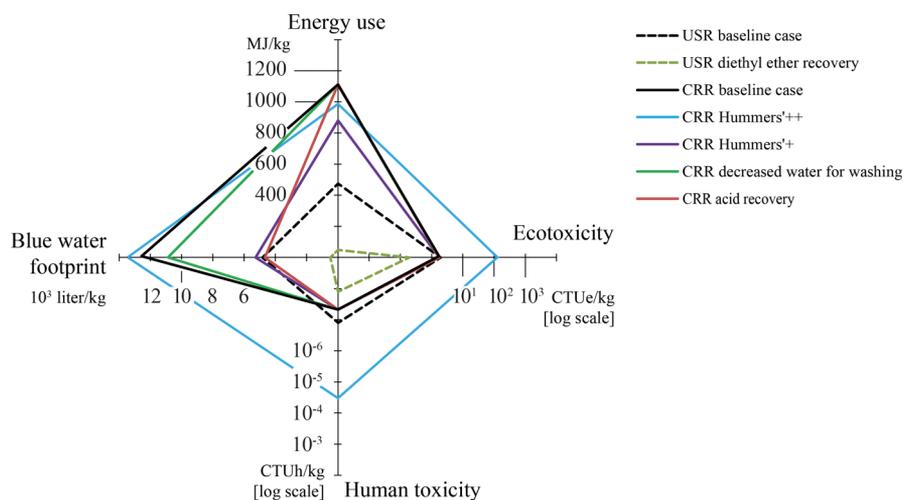
Figure 3. Graphical illustration of the results of the sensitivity analysis, showing the scenarios that considerably differ from the baseline cases.

300 W/liter), diethyl ether solvent recovery (0−90%), acid solvent recovery (0−90%), amount of deionized water used for washing and dissolution of the graphite oxide (100−1000 L/kg), the production method for graphite (mining or synthesis), the exact variant of the Hummers' process (Hummers', Hummers'+, or Hummers'++), and the conversion factor between electricity and heat (0.3−1). Note that the baseline case, shown in Figure 2, is a worst case scenario for most parameters, although not necessarily for the graphite production method and variants of Hummers' process.

Changes in ultrasonication yield had very little effect on the results, as did changes in the ultrasound effect. Increasing the diethyl ether recovery to 90% considerably reduces the environmental impact of the USR. As the use of diethyl ether is the main contributor to all four impact categories, the impact is then reduced by approximately 90% for all impacts, and all impacts then become lower than those of the CRR baseline case.

Acid recovery during the Hummers' process is important as well, since a 90% recovery reduces the blue water footprint by almost two-thirds. The other impacts, however, hardly change. Decreasing the water used for washing and dissolution of the graphite oxide in the Hummers' process to 100 rather than 1000 L/kg graphite oxide has some effect on the blue water footprint of the CRR-made graphene, but it is still approximately twice as high as that of the USR baseline case.

Producing graphite through synthesis instead of mining does increase the environmental impacts for all included impact categories, but only to a minor extent. The largest increase is the human toxicity of the CRR, where the increase would be by almost one-third. This is mostly due to emissions of zinc during production of the hard coal coke. However, the human toxicity of CRR would still be lower than that of the baseline case for USR. For all other impact categories, the increase in environmental impact from changing from mined to synthesized graphite is negligible.

The Hummers'+ process gives similar life cycle energy use, human toxicity, and ecotoxicity as the original Hummers' process. However, the blue water footprint is reduced by more than half compared to the baseline. This is because of the increased yield of the Hummers'++ process compared to the Hummers' original process, which results in less water-demanding sulphuric acid production per kg graphene. The

Hummers'++ process gives similar life cycle energy use and blue water footprint as the baseline case, but a much higher human toxicity and ecotoxicity potential. The human toxicity potential increases by more than 2 orders of magnitude, and the ecotoxicity potential by almost 2 orders of magnitude. The increase is due to the use of phosphoric acid in the Hummers'++ process, and more precisely to emissions of arsenic and zinc during production of the phosphoric acid. This suggests that although Hummers'++ process may be promising in terms of yield,[30] it is less so from an environmental point of view. For the Hummers'++ process then, recovery of phosphoric acid is of great importance to avoid high toxicity impacts.

As heat is the main energy form used, changes in the conversion factor between electricity and heat from 0.3 (e.g., a fossil-based energy system) to 1 (e.g., a wind- and solar-based energy system) is almost negligible for both the USR and CRR. The reduction is also similar for both routes, so the relation between them changes negligibly. This negligible change is because heat is the main energy used throughout the life cycles of both the USR and CRR, so recalculating the fewer MJ of electricity into heat does not make much of a difference.

In addition, different assumptions can be made in the calculation of heat losses.[33] In Section 5 in SI, minimum and maximum heat loss values are shown in addition to the baseline case heat loss values. However, changing to minimum or maximum values only changes the CRR energy use by ±4%, primarily due to heat losses during the chemical reduction process, and the USR changes negligibly.

As it is impossible to know future transport distances and modes of transport of input materials, any environmental impact from transports were excluded. High level estimations of environmental impacts from transports also suggest that the influence of this assumption on the result is negligible. For example, the energy use for sea transport is about 0.2 kJ per kg and km.[13,31] Transporting 1 kg of the graphite 10 000 km (e.g., from China to Europe) would result in 2 MJ/kg, which is less than 1% of the energy use results in Figure 2. Even if transport of all input materials were included, the contribution would be small.

Toxic impacts from energy production were excluded, as the energy sources of the future energy system is unknown. Based on data from Querini et al.[44] the impact of 1 MJ coal electricity can be estimated at 6.4×10^{-9} CTU$_h$/MJ and 4.3×10^{-3}

CTU_e/MJ. As most energy use was heat for both the USR and the CRR, a 0.3 conversion factor can be used to recalculate those numbers to 1.9×10^{-9} CTU_h/MJ and 1.3×10^{-3} CTU_e/MJ for heat. As the energy use varied in a range of approximately 500−1000 MJ/kg graphene depending on production route, the toxicity impacts from energy production can be roughly estimated at $1-2 \times 10^{-6}$ CTU_h/kg and 0.7−1 CTU_e/kg. Although coal-based heat is probably a worst case scenario regarding toxicity impacts, a comparison with the results in Figure 2 indicates that the contribution of energy production to the two toxicity impact categories could be of similar magnitude as the toxicity impacts of the foreground system.

Water use from energy production was excluded as the future status of the energy system is unknown. According to Gerbens-Leenes et al.[45] the water footprint (both blue, green and gray) is negligible for wind power and 0.16 L/MJ for coal. For both these scenarios, the water use from energy production would be minor (<1%) compared to the overall energy use for both the USR and the CRR.

Hence, based on this sensitivity analysis, the following main conclusions can be drawn: (1) Diethyl ether recovery may considerably reduce the environmental impacts of the USR and (2) Hummers'++ process has considerably higher toxicity impacts than the other variants of the Hummers' process, to the extent that it outweighs all other toxicity impacts of all other scenarios. These conclusions are shown graphically in Figure 3 to illustrate the range of environmental impact. Numerical values for the results of the sensitivity analysis can be found in Table S8 in the SI.

In addition, more radical changes in the studied system are possible. For USR, other solvents than diethyl ether may be used, such as perfluorohexane, perfluoroheptane, or perfluorooctane.[25] Other raw materials than graphite may also be used for the ultrasonication process, such as pitch and coke.[25] For the CRR, other graphite oxide production processes exist, for example the Staudenmaier process.[32] Other reduction agents than hydrazine, such as ascorbic acid, may be used in the chemical reduction process.[46] Finally, hydrazine is a rather toxic substance,[25] so any emissions of hydrazine would probably considerably increase the toxicity impact categories. It remains for future studies to investigate whether such changes in the production system would cause major changes in environmental impacts.

3.6. Implications for the Graphene Industry and Researchers. In Figure 2, where the baseline cases are compared, it can be seen that there is no clear "winner" in the sense that no production route performs best for all included impact categories. The CRR has higher energy use and blue water footprint, but the USR has higher human toxicity potential. The statement by Zhamu et al.[25] that the USR is more "environmentally benign" was thus not unequivocally confirmed. However, given a high recovery of diethyl ether, the USR can get considerably lower impacts compared to the CRR for all impact categories (Figure 3). There is thus the potential that USR can be a more environmentally benign production route than CRR. In addition to recovering diethyl ether, our analysis also points to the importance of recovering acid solvents in the Hummers' process to lower the blue water footprint. These results lead to the general recommendation that graphene producers should consider solvent recycling in order to reduce environmental impacts from graphene production.

The considerably higher human toxicity and ecotoxicity of the Hummers'++ process, but similar or higher impacts for the other impact categories, makes us question this process for large-scale production of graphite oxide and graphene.

We have also found in this study that it is possible to conduct an LCA largely based on process information and data in patents and scientific papers. This implies that independent researchers have the ability to assess the life cycle impacts of materials at an early stage of technological development, independent of specific, and often secret, information and data provided by companies. Such studies can thereby provide environmental guidance at a crucial stage in the development of a material or production process. It is possible, however, that more complex production processes would be more challenging to assess using LCA in a prospective manner.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information is available for this article, with the following content: SI Section 1: Input data for the three variants of the Hummers' process (including Table S1); SI Section 2: Description of how heat losses were calculated (including Table S2); SI Section 3: Calculation of hydrazine requirement for the chemical reduction process; SI Section 4: Description of the modeling of hydrazine production; and SI Section 5: Tables with numerical results presented for the baseline cases and the sensitivity analysis (including Table S3−S7). This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

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