Positioning supercritical solvolysis among innovative recycling and current waste management scenarios for carbon fiber reinforced plastics thanks to comparative life cycle assessment

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Baptiste Pillain[1,4], Philippe Loubet[1], Fadri Pestalozzi[5], Joerg Woidasky[3], Arnaud Erriguible[2], Cyril Aymonier[2], Guido Sonnemann[1]

[1] Univ. Bordeaux, CNRS, Bordeaux INP, ISM,UMR 5255, F-33400, Talence, France

[2]CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France

[3]Pforzheim University of Applied Sciences, School of Engineering, 75175 Pforzheim, Baden-Württemberg, Germany

[4]Altran Research, 4 avenue Didier Daurat, Parc Centreda – Bâtiment Synapse, F-31700 Blagnac, France

Abstract

Global consumption of carbon fibers reinforced plastic (CFRP) is rising and the management of waste is an issue of high concern. In order to implement a sustainable carbon fiber recycling sector, there is a need to evaluate the potential environmental impacts of recycling processes.

In this context, we compared current end-of-life scenarios (landfilling and incineration) with recycling technologies: pyrolysis, supercritical solvolysis and electrodynamic fragmentation using life cycle assessment. We conducted two analyses: a comparison between the CFRP end-of-life processes and a comparison including the substituted products from the recycled carbon fibers.

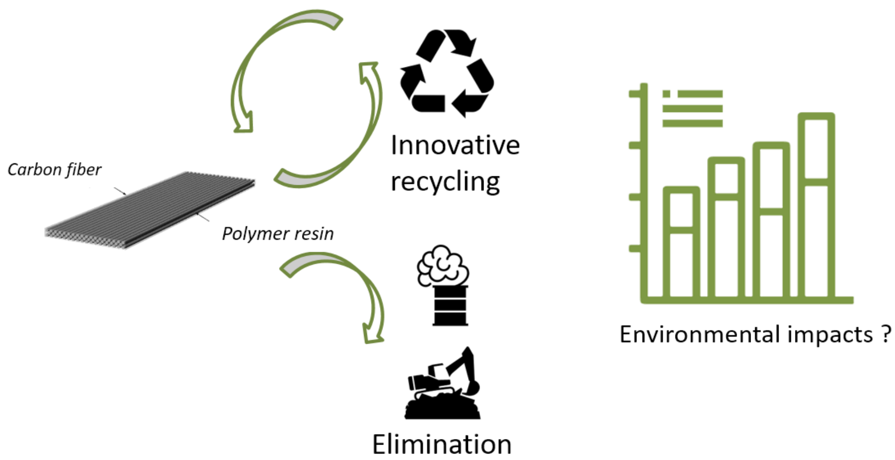
When only considering the end-of-life processes, recycling processes have a higher environmental impact as they require higher energy demand than incineration or landfilling. When considering product substitution, recycling is environmentally beneficial since they replace the production of virgin products.

Results are variable depending on the technology readiness level and the quality of fibers recovered from the recycling processes.

Keywords

Life cycle assessment, Carbon fiber reinforced plastics, recycling process, pyrolysis, supercritical hydrolysis, supercritical water, electrodynamic fragmentation, end of life, incineration, landfilling

Graphical abstract



1. Introduction

The increasing demand of carbon fiber reinforced plastics (CFRP) from automotive, aeronautic, wind energy and sport and leisure [1], combined with the growing interest of new sectors, e.g. pressure vessels [2] increase the production needs in the future, that will theoretically reach 116 000 tons by 2021 [3].

The development of CFRP recycling technologies answers to both the growing availability of CFRP based products at their end of life and the increased demand [4]. It is also driven by the creation of new regulations on waste management such as the end of life vehicles directive [5]. Considering the energy and material consumed during the production of virgin carbon fiber, it is necessary to develop a sustainable recycling sector [6]. Moreover, as of today municipal solid waste (MSW) incineration has proven not to be a technical solution for carbon fiber composites destruction as the residual times in the process are insufficient to both oxidize the resin and the fibers, although oxidation of carbon fiber with oxygen present starts beyond 585°C. Consequently, carbon fibers are found both in the fly ash and the bottom ash of MSW incineration plants [7].

Techniques applied for CFRP recycling can be grouped into three main types: mechanical, thermal and chemical [8]. Only the thermal and chemical treatments allow the entire separation of the fibers from the resin. Pyrolysis is the most developed thermal technology and is already industrialized [9]. Chemical treatment processes are currently under development such as the supercritical solvolysis [10]. A new alternative has been recently developed to recycle CFRP using their electrical properties: the electrodynamic fragmentation technology [11].

The principal aim of recycling technologies is to reduce the financial and environmental cost of CFRP raw material. Also, supply of raw CFRP can be disrupted which is considered as a risk [12]. The evaluation of environmental impacts of CFRP recycling processes have been studied by many authors using the life cycle assessment (LCA) methodology : thermal processes such as fluidized bed [13,14] steam-thermolysis [15,16], microwave pyrolysis [17] ; chemical processes [18,19]; or mechanical processes [20,21]. These studies show that production of recycled carbon fibers generates less environmental impact than production of virgin carbon fibers [22].

However, innovative processes such as supercritical solvolysis and electrodynamic fragmentation have never been benchmarked against conventional recycling processes (such as pyrolysis) or end-of-life waste treatment scenarios (i.e., incineration and landfilling).

In this context, the aim of this paper is to assess the environmental impacts of these recycling scenarios and to compare them with end-of-life waste treatment scenarios. This is done through a comparative LCA. The novelty of this paper relies in (i) analyzing and comparing innovative processes (supercritical solvolysis and electrodynamic fragmentation) at both lab scale and modeled industrial scale with current end of life practices and (ii) including sensitivity analysis depending on the product these recycling processes can substitute.

2. Material and methods

LCA is a multicriteria tool to assess the burdens on the environment of a product or a service over its lifetime, i.e., from the production of the raw materials to the end of life management. LCA is suitable to assess the potential benefits of sustainable chemistry [23].

The LCA methodology is defined by ISO standards (ISO 14040) and is divided in four steps:

- Goal and scope definition phase. The objectives of the study are stated. Then, the functional unit (FU) which is the quantification of the functions of the product, services or processes under study is defined. This aims to compare different products, services or processes on a common basis. Finally, the boundaries of the system are clearly presented.
- Life cycle inventory (LCI) analysis phase. The elementary flows (inputs and outputs) of the product system are collected. The inventory entails the quantification of energy, resources, and emissions to air, soil and water. LCI includes foreground data which are directly related to the studied system and background data which are related to the indirect flows occurring during the supporting activities (production of energy, chemicals, etc.)
- Life cycle impact assessment (LCIA) phase. Based on the LCI, the different flows are converted into environmental impacts (such as climate change impacts in kg CO_2 eq).
- Interpretation phase. The results are interpreted and lead to the identification of the environmental hotspots and to recommendations to improve the environmental performance of the product.

2.1. Goal and scope definition

The goal of this study is to evaluate the environmental impacts of three recycling scenarios (pyrolysis, supercritical solvolysis (named supercritical hydrolysis in the following because water is used as solvent in this study), electrodynamic fragmentation) and to compare them with existing end-of-life scenarios, i.e., landfilling and incineration. The functional unit of this study is defined as **"**Managing the end of life of 1 kilogram of CFRP composed of 60 wt% carbon fibers and 40 wt% resin.**”.** The matrix is considered to be epoxy resin and is named resin hereafter. Two different analyses will be conducted accordingly to the goal of this study, each one having different system boundaries:

(i) “Process oriented” analysis aims to compare the impacts of the end-of-life scenarios listed above (incineration, landfilling, pyrolysis, supercritical hydrolysis and electrodynamic fragmentation) at a process level (Figure 1 (i)).

(ii) "Product oriented" analysis aims to compare the impacts of the 5 end-of-life scenarios considering the recovered products from the recycling processes that substitute virgin materials (Figure 1 (ii)).

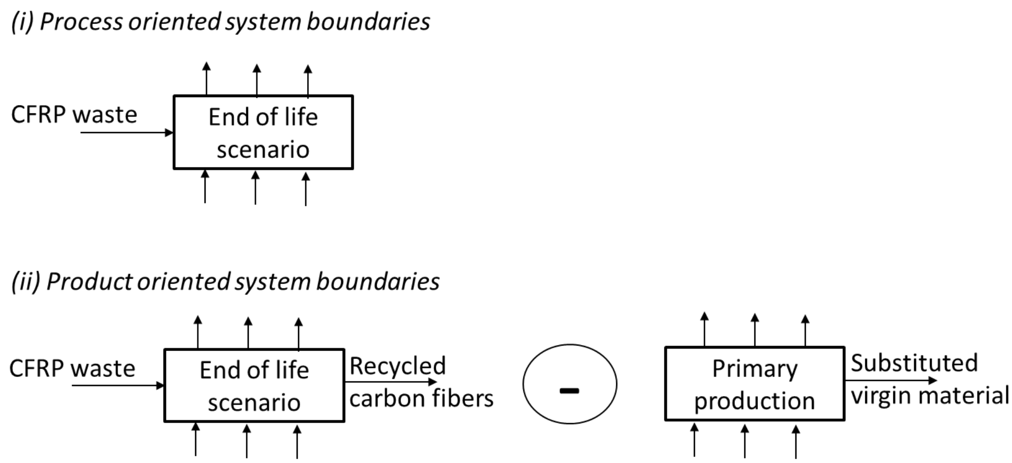


Figure 1. Boundaries for (i) the "process oriented" analysis aiming to compare the impacts of the different process and (ii) the "product oriented" analysis aiming to compare the impacts considering the virgin materials that substitute recycled carbon fibers

2.2. Life cycle inventory related to end-of-life processes

This section describes the different processes for CFRP end-of-life management as well as the foreground data for each scenario (i.e., energy, chemicals, transportation, waste, etc.) and the sources of these data. All background data are taken from the life cycle inventory database ecoinvent 3.3.

2.2.1. Pyrolysis

Pyrolysis (Figure 2) is currently the most developed CFRP recycling process and is already commercialized [24]. In this thermal process, the resin of the CFRP waste decomposes at high temperature.

More precisely, CFRP are shredded through mechanical grinder. The resulting scrap is fed into the pyrolysis reactor to be processed at a temperature between 450°C to 700°C, and in controlled atmosphere in order to avoid oxygen reaction with carbon fibers. During the reaction, resulting gases from resin degradation are recovered using a condenser. This step allows recovering and separating solid, liquid and gas phases. Ash residuals from the process are subsequently discarded to landfilling and liquid and gas phases are recovered and used as fuel for the reactor. The recovered carbon fibers have a small to medium size [24].

LCI foreground data were taken from Witik et al. [9] and are presented in Figure 2. The energy requirement for shredding for pyrolysis and for all following processes has been updated with more realistic data from Howart et al. [21].

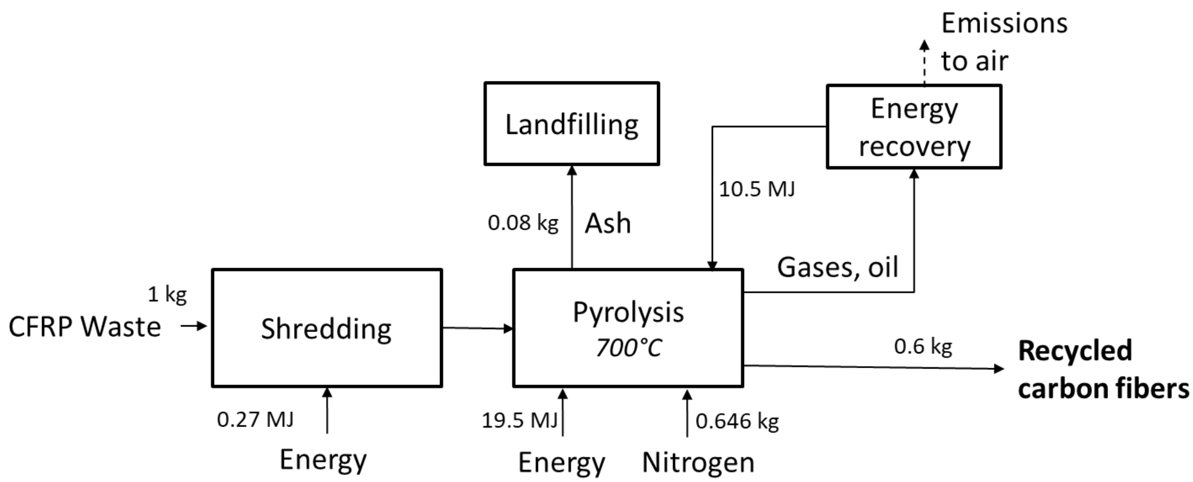


Figure 2: Representation of the pyrolysis process

2.2.2. Supercritical hydrolysis

2.2.2.1. Lab-scale LCI

This recycling process (Figure 3) is under development at the laboratory scale. We assessed the experimental process from a collaboration with the Institute of Condensed Matter Chemistry of Bordeaux (ICMCB, France). We developed a semi-continuous solvolysis process, especially with supercritical water. This is a chemical treatment that uses water as solvent and reagent for the depolymerization of the polymers into monomers in a selective way.

First, either CFRP scrap or full CFRP parts are directly put into the solvolysis reactor without a shredding pre-treatment. This is because the solvolysis reactor is scaled as a function of the length of the recycled fibers to be recovered. Water is pressurized (at about 25 MPa), preheated and injected in the reactor to obtain a temperature above 374°C (i.e., the critical temperature of water). At this point water hydrolyzes the polymer and breaks down the resin into compounds that are released in the water stream at the output [25]. This process leads to the recovery of carbon fibers that are similar to virgin fibers (Figure 6 S-1, S-2 and Figure 7 S-3). Their size only depends on the dimension of the reactor.

The water use data (10L/kg of CFRP) was obtained from direct measurements from the experiment. The energy use was assessed theoretically from the heat capacity of water that is heated, which is dependent of the temperature (see Supplementary Information). The inventory of the treatment of the resulting wastewater was modeled with the EPI Suite v4.11 software and "LCA 2.0 waste water treatment" [26]. Such a modeling was possible from the identification of molecules produced from the resin degradation [25].

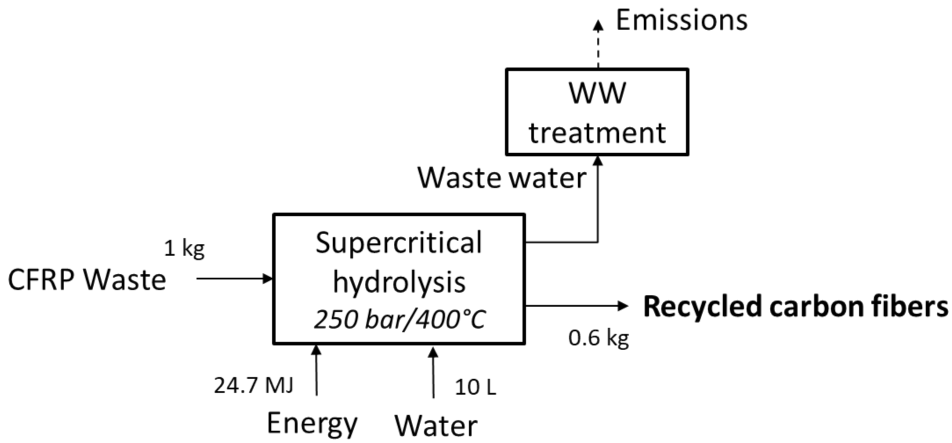


Figure 3: Process flow chart of the supercritical hydrolysis modeled at the lab-scale

2.2.2.2. Industrial scale modeled LCI

Since this process is at the laboratory scale, it is not optimized. We assumed two additional operations in order to model this process at the industrial scale for a fair comparison with pyrolysis: 1) heat recovery from the output water stream via a heat exchanger, and 2) wastewater treatment with combustion of emitted methane for energy recovery into the system (Figure 4).

Energy recovery by heat exchanger

We assume that the installation of a heat exchanger at the industrial scale aiming to recover heat of the water at the output of the hydrolysis process in order to preheat the input water. Our calculation described in Supplementary Information show that 22.2 MJ/kg of CFRP could be recovered.

Methane valorization for energy recovery

The waste water treatment inventory modelling derived from the waste-water LCA 2.0 tool [26] has shown that an amount of methane (0.04 kg CH_4 / 1 kg CFRP) was emitted during the treatment of waste water resulting from the degradation of the resin by hydrolysis in supercritical water. Direct recovery of methane from wastewater is possible and has already been studied [27,28].

Based on the calorific value of 50MJ/kg of methane, we assumed a theoretical energy recovery of 2MJ/kg of CFRP. However, this energetic conversion requires an amount of specific transformation energy of 0.05 KWh/m^3 of methane [28]. This represents a demand of 0.011 MJ/kg of CFRP (from the density of methane, which is 0.656 kg/m^3). Also, the combustion of one mole of CH_4 generates one mole of CO_2, thus 0.11g of CO_2/kg of CFRP is emitted during the combustion of methane.

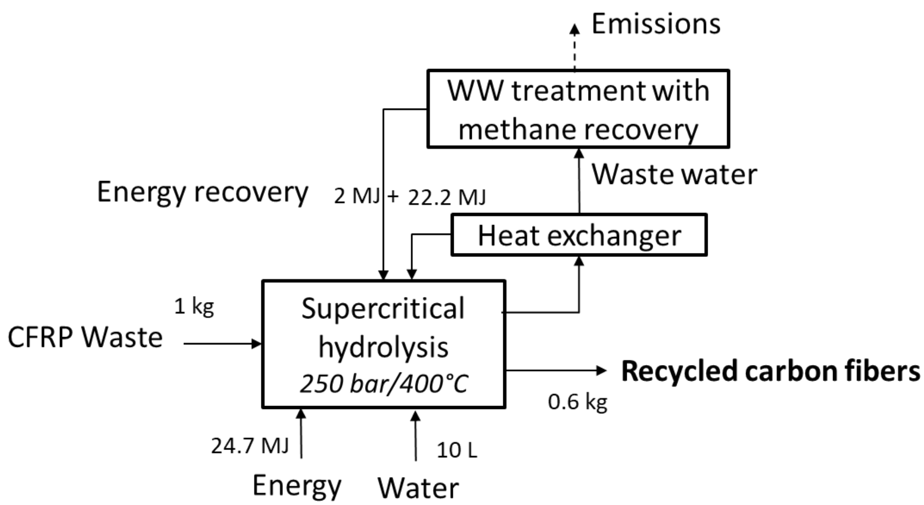


Figure 4: Process flow chart of the optimized supercritical hydrolysis (assumed at the industrial scale) with both heat exchanger and methane valorization

2.2.3. Electrodynamic fragmentation:

2.2.3.1. Lab-scale LCI

Initially this process (Figure 5) was developed to extract rare mineral from rocks. Due to the interfaces' dielectrical properties between resin and fibers, experiments have shown the potential of this method applied to the recycling of composites fibers/polymeric matrices. The studied system Selfrag Lab S2.1 is available in Pforzheim University, Germany, using the SELFRAG® process, that is currently at an applicability validation stage.

First, the CFRP sample is put in a reactor containing two electrodes and filled with deionized water. Then high electric pulses of <0,5 µs each are applied . These pulses induce a strong electric arc and pressure, up to 10^4 MPa and 10000°C and generate a shock wave that breaks up the composite[29] . Matrix and fibers are separated and can be recovered. The resulting product is a mix of fibers, from original length to carbon powder. Also depending on the experimental conditions, the presence of residual resin was observed (Figure 6 EF-1 and EF-2).

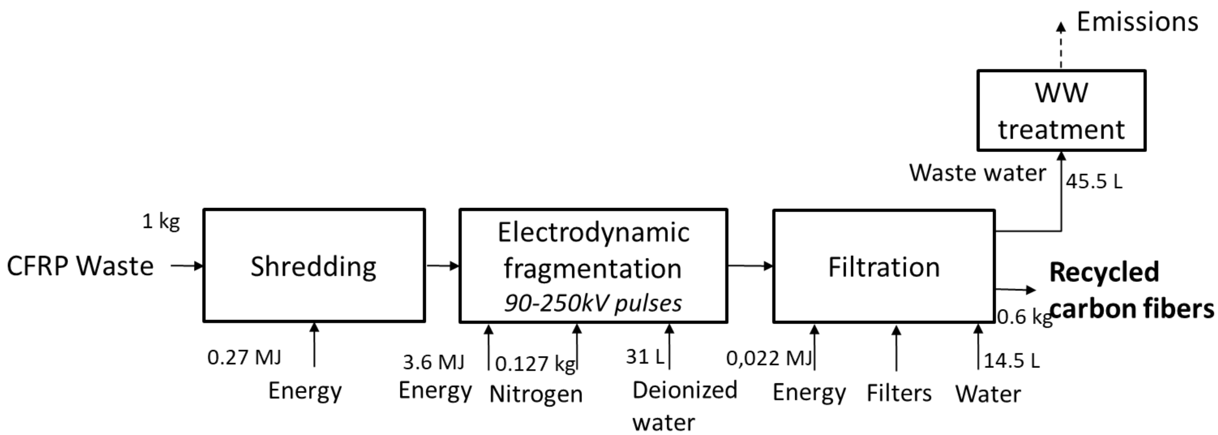


Figure 5: Representation of the electrodynamic fragmentation process

2.2.3.2. Industrial scale LCI

Similar to the solvolysis process, also electrodynamic fragmentation is not optimized since it is at the laboratory scale. We assumed an industrial scale process to enable a fair comparison with the pyrolysis process.

Two process improvement scenarios can be considered for electrodynamic fragmentation. The first scenario corresponds to an evolution of the mechanisms currently observed in the process. These are electrodynamic fragmentation (EF) and electrohydraulic fragmentation (EHF), used for the separation of the resin and the reinforcement. Electrohydraulic fragmentation requires a lower voltage than electrodynamic fragmentation and therefore enables energy use reduction [30].

The second improvement scenario is to operate the flow of waste CFRP continuously rather than a batch process. This principle is currently tested for the building recycling sector on a pilot scale [31].

However, these two options are currently in research and development phase for an application oriented towards the recycling of concrete. This will require additional efforts for a CFRP-oriented use and makes it difficult to translate these improvements possibilities with data derived from physical measurements for calculations. Therefore, we assume that the application of both scenarios would enable to process twice the quantity of material than for the current lab-scale experiments with the same energy (and material such as nitrogen) needs, based on expert judgments. Therefore, for one kg of CFRP processed, the energy use for electrodynamic fragmentation would be divided by 2.

2.2.4. Incineration

Incineration is one of the current end of life scenario of CFRP waste management [32]. Incineration with energy recovery can be considered as an attractive end of life scenario in comparison to landfilling with clear obligations that waste should meet the required heating value to overcome the energy necessary to trigger its combustion. It is also a relevant option when the waste cannot be recycled, or if the organic content of the waste exceeds legal limits for landfilling. Life cycle inventory was obtained through the use of ecoinvent waste disposal modeling tools and is graphically shown in SI (Figure S1) [33]. It is to be noted that energy needed for incineration process (ie., heat to trigger the combustion and electricity for generic devices) is met through the recovered energy of CFRP combustion. There is a surplus of recovered energy that is considered as an environmental credit in the analysis as computed in ecoinvent waste disposal modeling tool (Figure S1).

2.2.5. Landfilling

Disposal on landfills is along with incineration the current process of CFRP waste management. In landfilling, all cumulated substances, processes, and services that have been used to manufacture CFRP are lost. Other relevant effects are not only potential emissions of substances from material degradation leading to potential water pollution, but also land occupation and soil contamination. Life cycle inventory was taken from ecoinvent waste disposal modeling tools and is graphically shown in SI (Figure S2) [33]. The modeling tool considers that the CFRP waste material (composed of of 84.2% of carbon, 6% of oxygen, 4% of hydrogen, 5.8% of nitrogen) is ultimately decomposed in substances emitted to water (carbon substances as chemical oxygen demand, COD, biological oxygen demand, BOD, total organic carbon, TOC, ammonium, nitrogen, nitrates and nitrites).

2.3. Life cycle inventory related to substituted products

2.3.1. Characterization of recycled fibers

In this section, we describe the fibers recovered by the different recycling processes in order to determine which product they can substitute. The LCI related to the substituted products are included in the second analysis of the paper ("product oriented").

We characterize the recycled fibers with their mechanical properties' conservation and their surface aspect. Theoretical information on properties conservation was taken from Pimenta and Pinho (2011) and is described in the processes description [24].

Surface aspect is assessed in a qualitative way from microscopic observations of the carbon fiber samples. Such analysis shows the resin removal and potential damage induced to the fibers. Figure 5 shows recovered fibers from the pyrolysis process using scanning electron microscope as found in the literature, as well as observations of recovered fibers from solvolysis and electrodynamic fragmentation directly undertaken using a scanning electron microscope (ZEISS EVO 50).

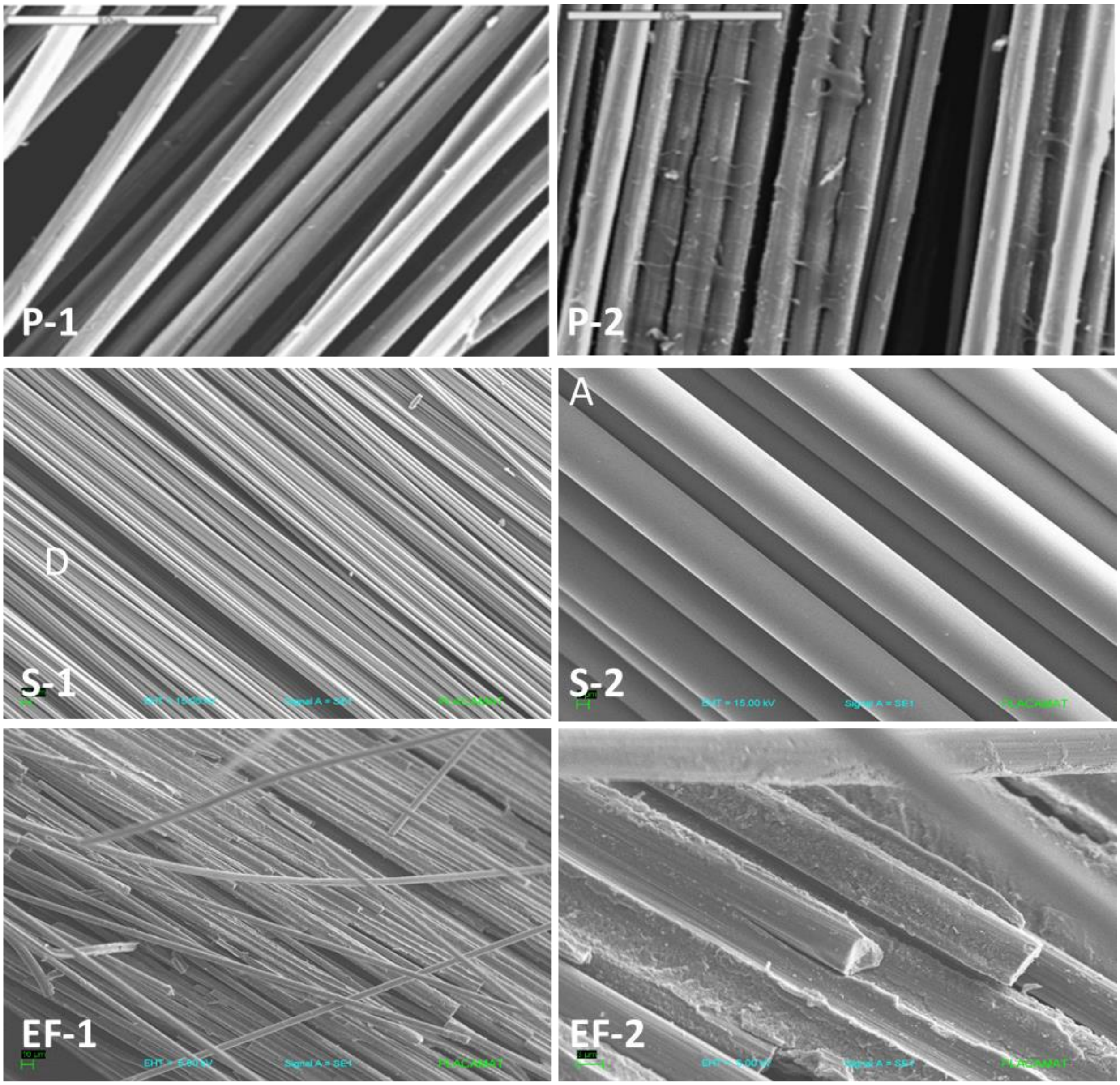


Figure 6: Observation of fibers surface and resin removal after recycling from scanning microscope (P: pyrolysis, images from Pimenta and Pinho (2001) and microscope ZEISS EVO 50 (S: Supercritical hydrolysis, EF: Electrodynamic fragmentation from own observation)

The level of resin removal is different for the three processes. The resin is still observable in pictures P-1, P-2 and EF-2 under the form of unremoved resin that has taken the cylindrical shape of fibers. Pictures S-1 and S-2 show a full resin removal from the carbon fibers recycled with the supercritical hydrolysis process. Moreover, in some point, the fibers seem to be damaged (breaking observable on Figures EF-1 and EF-2). Also, some small inclusion (bright dust) can be observed in P1, EF1 and EF2 that can be the result of the cutting of the CFRP sample or if the quantity is representative, these inclusions could potentially be chars that remains from the resin degradation.

Moreover macro observation of recovered fiber are shown in Figure 7. Pictures were directly taken from lab experiment for S-3 and EF-3 (supercritical hydrolysis and electrodynamic fragmentation, respectively) and taken from Pimenta and Pinho (2011) for P-3 (pyrolysis) [34].

Figure 7: Recycled carbon fibers after processing (P-3: pyrolysis (Wood, 2010); supercritical hydrolysis and EF-3: electrodynamic fragmentation, respectively)

The final output of the recycled CFRP is a “ball” of fibers for the pyrolysis (P-3, Figure 7). Supercritical hydrolysis process results in folds of weaved carbon fibers (S-3). Electrodynamic fragmentation results in carbon powder and dispersed fibers (EF-3) of different lengths from 2µm to 2.8mm (60% of the recovered fibers were between 125-28000 µm and 40% have been measured to be between 2-125 µm).

Literature also gives quantitative information on the mechanical characterization of recycled carbon fibers from the assessed processes:

- Pyrolysis: Many studies have characterized the mechanical properties of recycled carbon fiber from pyrolysis and the results show high diversity in strength and stiffness of the fibers. A review from Oliveux et al. (2015) shows that decrease in tensile strength of recycled CFs compared to virgin ones vary from -4% to -82% depending on the studies [8]. The average loss of tensile strength from all the studied review was -42%.
- Supercritical hydrolysis : A review on carbon fibers recycling processes show that supercritical hydrolysis does not alter the mechanical properties of the fiber [10].
- Electrodynamic fragmentation: few studies have reported mechanical properties of recycled carbon fibers from this process. In their study on the recycling of door hinger with EF, Roux et al. (2017) show that the recycled carbon fiber has a loss in mechanical properties of -17% compared to the virgin material (3.464 kN and 4.164 kN, respectively).

These complementary observations and characterizations from the literature enabled to define as substituted product:

- Glass fibers for pyrolysis due to the medium property conservation of resulting carbon fibers and residual resin remaining after recycling. This is because the loss of mechanical properties is comparable with the difference in properties between carbon and glass fibers.
- Carbon fibers for the supercritical hydrolysis due to high quality of resulting carbon fibers aspect conservation and properties listed previously,
- A mix of clay and short glass fibers due to low quality of resulting carbon fibers and size diversity for the electrodynamic fragmentation. The share of each material is determined depending on the length of the recovered output (40% and 60%, respectively). This is because: (i) 40% of the

recovered fibers could be reused as fibres (with mechanical properties comparable with the ones of glass fibers) and (ii) 60% is not usable as fibers due to their limited length and rather could be used as road backfilling (as a substitute of clay).

The resulting quality of recovered fibers could be improved with the development of the technologies. Therefore we also provide a sensitivity analysis considering that the recovered fibers substitute carbon fibers for all scenario.

LCI related to the primary production of the substitution products is detailed in the following section.

2.3.2. Substituted products LCI

The database ecoinvent does not provide life cycle inventory for the production of carbon fibers. We collected inventory data of carbon fiber production based on the report from Griffing and Overcash (2010) [35], as shown in Supplementary Information (section S2). LCI of glass fibers and clay production are directly taken from the ecoinvent 3 database.

2.4. Life cycle impact assessment

LCA software Simapro 8 is used to assess the environmental impacts of the different scenarios. Even though standard methodologies can be used to conduct life cycle impact assessment, their multitude of indicators can lead to a misunderstanding of the results in the context of life cycle assessment, even more when these indicators are brought together with other indicators used for assessing the complementary sustainability pillars. It is then necessary to assess the most relevant indicators, depending on the importance, the degree of robustness and the correlation with the aim of the studied product. Pillain et al. (2017) identified the most relevant impact indicators to for the sustainability assessment of the potential creation of the CFRP recycling sector [6]:

- acidification using accumulated exceedance (AE) in mol H+ eq.
- global warming potential (GWP100) using IPCC method that assess impacts on climate change in kg CO_2 eq with a 100-year time horizon.
- human toxicity indicators (using USEtox method) that assess cancer and non-cancer effects in CTUh.
- resources depletion using CML-IA method in kg Sb eq.

They also identified other indicators assessing the different sustainability pillars, such as the “GeoPolRisk resource indicator” assessing the geopolitical and strategic point of view along the supply chain [12]. They are not computed in the present publication as we only focus on the environmental point of view.

3. Results

The relative LCIA results for the different scenarios are presented hereafter. The absolute LCIA results are shown in Supplementary Information (Table S1).

3.1. Process oriented LCA of CFRP end of life scenario

We first show the comparison of environmental impacts from lab scale experiments and optimized industrial scale for the supercritical hydrolysis and electrodynamic fragmentation processes. In the following sections we only kept results modeled at the industrial scale for these two processes in order to (i) be comparable with the three other processes that are modeled at the industrial scale, and (ii) improve the clarity of the results.

3.1.1. *Comparison of lab-scale and industrial scale scenarios*

Figure 8 compares the environmental impacts of the supercritical hydrolysis process at the lab scale with different process improvement scenarios at the industrial scale (heat exchanger, methane recovery and both). Heat exchanger allows recovering more energy than methane recovery for 1 kg of CFRP recycled (22.2 and 2 MJ, respectively). Therefore, the heat exchanger scenario generates lower impacts for most impact categories, except for the climate change category. This is because the methane recovery scenario enables to avoid emissions of methane that have a higher global warming potential than carbon dioxide.

Eventually, the industrial optimized scenario leads to a reduction of impacts from 30% to 80% depending on the impact categories. This scenario will be used for the future comparison.

Figure 8 also shows the environmental impacts of processing 1 kg of CFRP waste with the electrodynamic fragmentation process at the laboratory scale and considering an improvement ratio (quantity of energy and materials used for the process divided by 2). Logically, 3 out of 5 impacts are reduced by 50% because they are mostly driven by energy consumption. As for climate change and acidification, impacts are decreased to a smaller extent because the quantity of waste resin to be treated is the same for both scenarios, and related pollutants released in air and water are therefore the same.

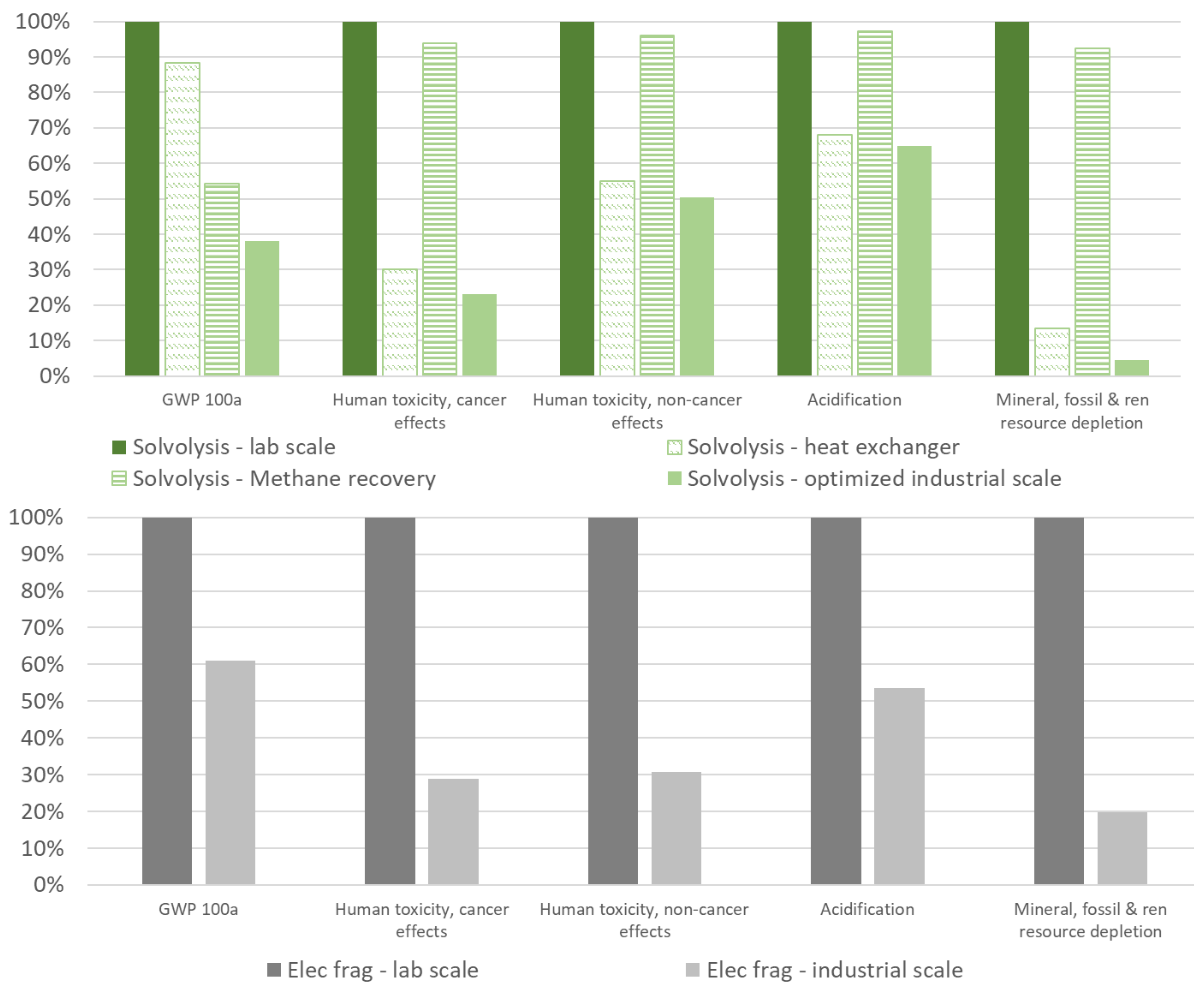


Figure 8: Environmental impact comparison between lab-scale and industrial scale results for the supercritical hydrolysis and electrodynamic fragmentation processes.. FU = managing the end of life of 1 kilogram of CFRP

3.1.2. Comparison of the end-of-life processes

Figure 9 shows the environmental impacts from the five different end of life scenario processes described previously.

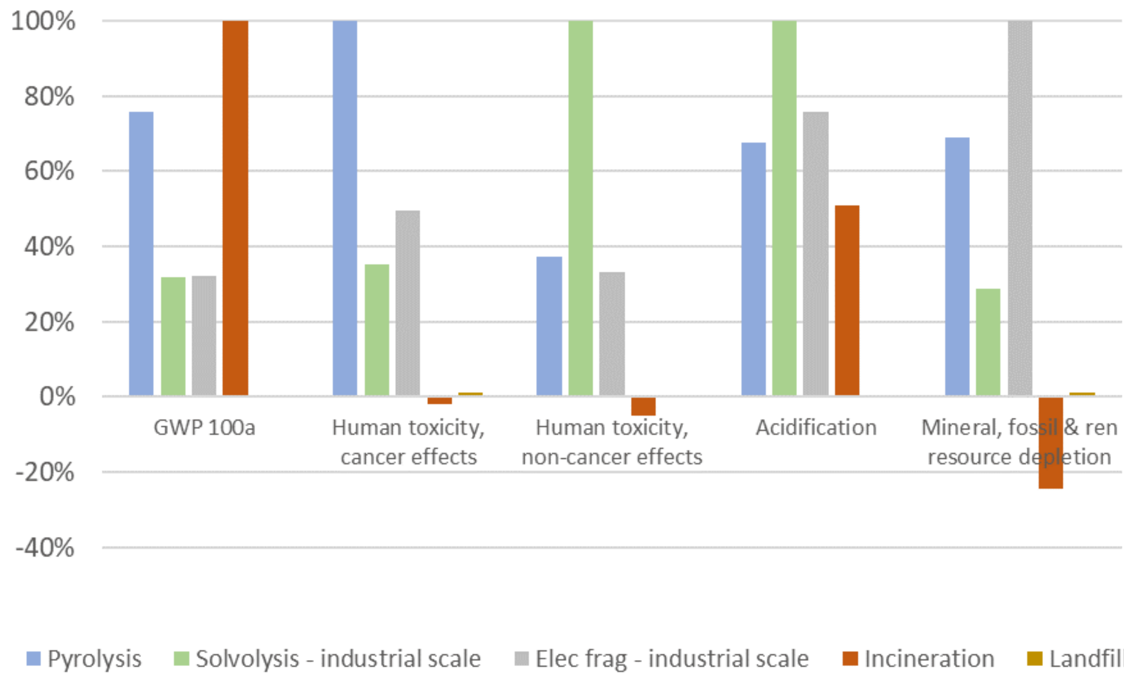


Figure 9. Environmental impacts comparison between Pyrolysis, Supercritical hydrolysis, Electrodynamic fragmentation, Incineration and Landfilling. FU = managing the end of life of 1 kilogram of CFRP

Incineration has the highest impact on climate change due to the amount of carbon dioxide release during the fibers and resin combustion. However, recycling processes generate the highest share of impacts in the other categories.

Pyrolysis generates higher impacts on human toxicity (cancer effects) compared to the other processes due to the release of metals during supporting activities in the background (production of liquid nitrogen and energy, landfilling of residual ashes). It is to be noted that the characterization of metals on human toxicity with the Usetox model has not reached a consensus and it may result in a possible overestimation of the impact in all processes.

As for non cancer effects, supercritical hydrolysis generate the highest share of impacts, mostly due to the direct emissions of organic compounds in water (e.g., aniline generated by the decomposition).

For the acidification potential the only processes with direct release of ammonia is the supercritical hydrolysis process through the wastewater treatment leading to an overall higher impact. In this category the second most contributing substances is sulfur dioxide directly linked to the electricity production in all the processes.

For the resources indicator, electrodynamic fragmentation shows a higher impact, because of the quantity of energy required for the process, and therefore more resources. On the other hand, incineration generates negative impacts since energy demand is met with energy recovery from the combustion of CFRP and there is also a surplus of energy production that lead to environmental credits for this process.

An important fraction of the impact from the supercritical hydrolysis is induced by the waste water treatment and the release of organic compounds (e.g., aniline) which were modeled through a LCI modeling tool. It has to be underlined that the waste water treatment was not specifically modelled for electrodynamic fragmentation because released compounds from this process are not known. Generic process from ecoinvent database (i.e. "*Wastewater treatment, average*") was considered which might underestimate the impacts compared to the supercritical hydrolysis process. The assumption considered was that after the filtration step, the water was cleaned of the potential residual compounds and the "*Wastewater, average*" treatment from ecoinvent 3 was considered. This is also the case for pyrolysis where it was necessary to rely on the LCI data obtained in the literature, but the specific point of waste water is of relatively less importance for this process since water is not in direct contact with the reaction medium.

As the impacts associated with the management of organic compounds from the resin are high in all the recycling processes (either when releasing to the water or to the air), an eco-design solution could be to recover resulting compounds from resin degradation in order to produce new chemicals.

In light to these first results, pyrolysis has an overall higher impact when focusing on the processes, followed by the supercritical hydrolysis and electrodynamic fragmentation. Incineration and landfilling generally generate less impact than the recycling processes.

3.2. LCA of CFRP recycling options considering product substitution

Figure 10 shows the net environmental impacts resulting from the recycling processes (positive values) and the avoided impacts generated by the production of primary materials substituted by recycled materials (negative values). Therefore, environmental impacts of recycling processes create negative values in calculation.

Supercritical hydrolysis substitutes 0.6 kg of carbon fibers manufacturing for 1 kg of processed CFRP waste. It results in a net environmental impact benefit for all impact categories. This is because the environmental impact from manufacturing carbon fibers is remarkably higher than the other products considered for substitution (such as glass fibers). Particularly, virgin carbon fiber production requires more than 10 times energy needs than the solvoysis process.

Pyrolysis presents a net environmental benefit for 4 over 5 impact categories when considering the substitution of glass fibers. The emissions of the pyrolysis affecting climate change are not overcome by the avoided impacts from the glass fibers. Electrodynamic fragmentation has also a net environmental benefit in 4 over 5 impact categories.

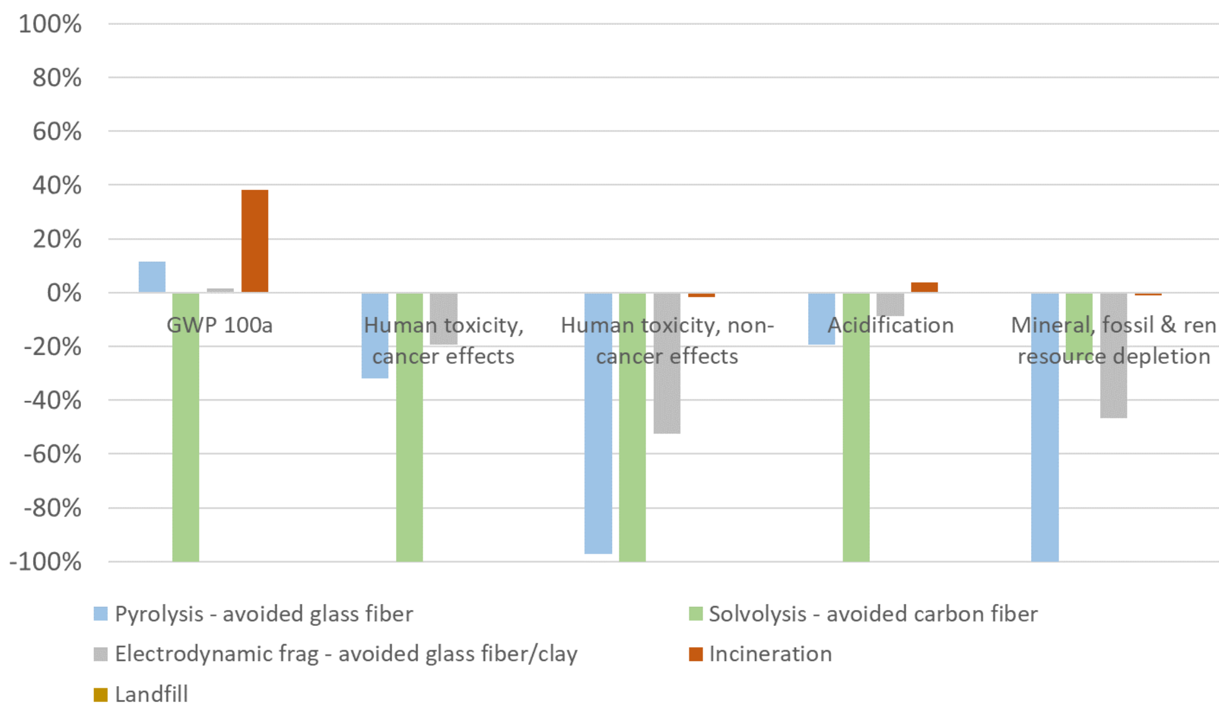


Figure 10. Environmental impacts comparison between Pyrolysis, Supercritical hydrolysis, Electrodynamic fragmentation, Incineration and Landfilling, considering different products of substitution. FU = managing the end of life of 1 kilogram of CFRP

Figure 11 shows the environmental impacts if all processes substitute the same quality of recovered products, i.e., carbon fibers. It shows the potential improvement in environmental benefits for the pyrolysis and electrodynamic fragmentation if these processes reach a high quality of the recovered fibers. Environmental benefits are similar for all recycling scenario if they substitute virgin carbon fibers. This is because the impacts related to manufacture virgin carbon fibers is way higher than the impacts of all recycling scenario.

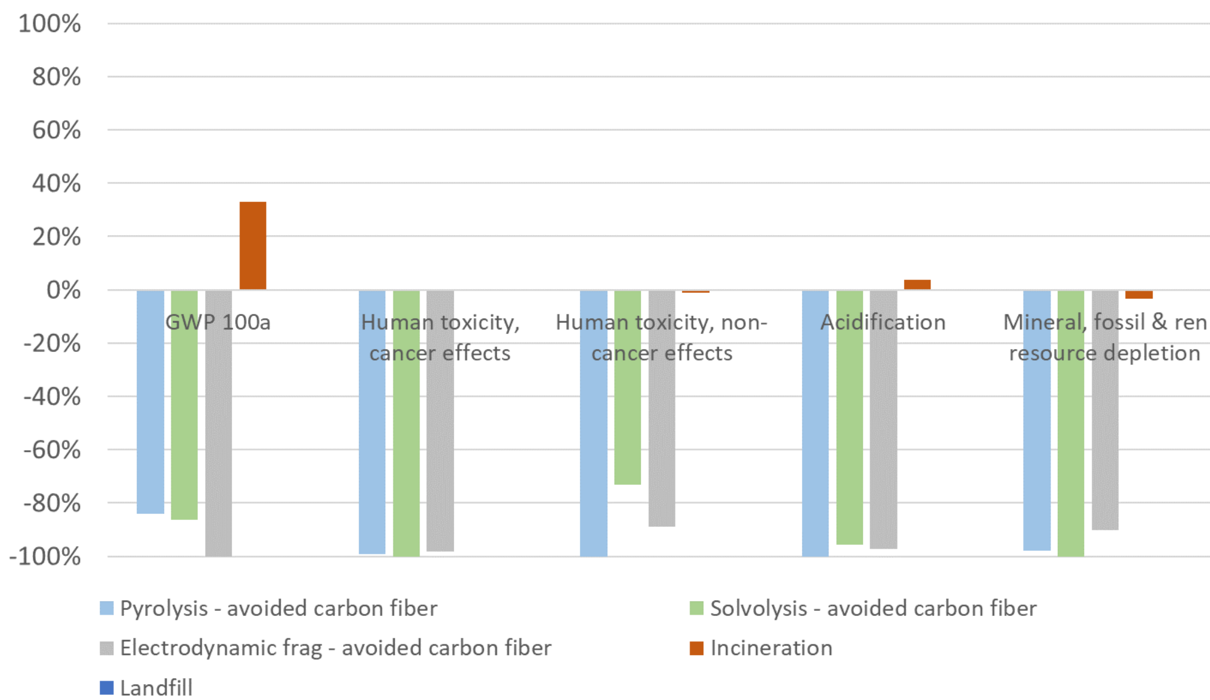


Figure 11. Environmental impacts comparison between Pyrolysis, Supercritical hydrolysis, Electrodynamic fragmentation, Incineration and Landfilling, considering the same product of substitution : carbon fiber. FU = managing the end of life of 1 kilogram of CFRP

A supplementary analysis can be done by comparing the environmental impacts from the production of 1kg of virgin carbon fiber and 1kg of recycled carbon fiber (from supercritical hydrolysis) (Figure 12). It shows that producing carbon fibers from supercritical hydrolysis recycling process generates 70% to 95% less impacts than the virgin production depending on the impact categories.

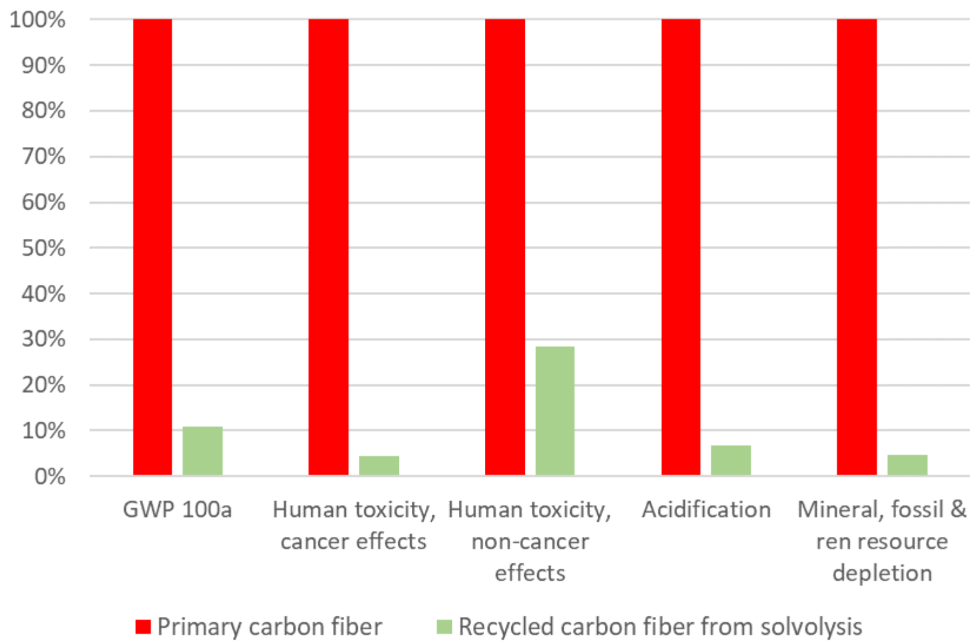


Figure 12. Comparative LCA between primary production of carbon fibers and secondary production of carbon fibers from supercritical hydrolysis. FU = Production of 1kg of carbon fiber

4. Discussion

The three recycling processes presented in this study are currently at different development scales. Indeed, pyrolysis is at a stage of industrialization whereas supercritical hydrolysis is currently in feasibility study stage and electrodynamic fragmentation is at a stage of adaptation of a technology (application from mineral extraction to composites recycling). The processes could be further optimized and potentially evolve from a technological point of view. As shown by the study on improvement of supercritical hydrolysis and electrodynamic fragmentation processes, the environmental impacts are still dependent on the various conditions of implementation and optimization. The industrial scale modelling proposed in this paper is based on simplistic assumptions. However, it enables to show the potential improvement for both processes from lab scale to optimized industrial scale. The LCA results can guide the technical choices for implementing these technologies at the industrial scale in order to decrease environmental impacts. For example, it was shown that the impacts of supercritical hydrolysis is strongly dependent on the energy requirements of the process, and the design of an efficient heat exchanger will be a key point for the environmental performance of this process.

Also, the three recycling technologies currently do not allow to obtain the same output quality of recovered fibers as shown with our experiments and correlated with current literature [24], the conservation of properties trend to get closer to those of the virgin ones with the supercritical hydrolysis [25]. We also provide a sensitivity analysis to assess the environmental benefits in the case where all processes substitute virgin carbon fiber. It shows that the benefits are much higher in this case than in the original scenario of substitution. Therefore, the environmental performance of the recycling processes is related to their capacity to substitute virgin carbon fiber. It would be interesting to carry out the same comparative study of these processes when they will reach the same stage of development.

It is therefore advisable to consider these results as an assessment of the potential environmental impact of these recycling processes characterizing the current state of technology rather than absolute values.

Moreover, life cycle inventories are coming from different sources (either literature, laboratory experiments or modeling). For the processes where it was possible to collect data from direct measurements (supercritical hydrolysis and electrodynamic fragmentation), it should be noted that they are only representative for the recycling of CFRP epoxy resin / carbon fibers and for the chosen fiber-to-resin ratio (60 wt%-40%wt). The use of a resin of different nature will induce, for example, emissions of different organic molecules directly influencing the emissions to the environment and therefore, the resulting impacts. Experimental variation of the fiber-to-resin ratio will have to be part of future works, as the focus of the current experiment was on feasibility questions of the processes only. Nonetheless variation of the fiber share will both affect the electrodynamic fracture process due to increase of the fiber-resin interfacial area, and the overall environmental impact of the recycling processes due to 1) the total recoverable fiber mass potential, 2) the mass of degraded resin that generate emissions to air (for the pyrolysis) or wastewater (for the supercritical hydrolysis and the electrodynamic fragmentation). The fiber-resin-ratio chosen (60 wt%- 40 wt%) lies in the typical fiber share range of CFRP of 20wt%-80wt% [14] to 70wt%-30wt% [36]. The high fiber fraction of 60% was chosen to maximize the recoverable fiber mass potential in the experiment. Additional tradeoff experiments between fiber recovery and recycling effort will have to be conducted in future.

Other ongoing technological researches are currently undertaken on the recycling processes, which have not been considered in this publication: steam-thermolysis [15,16], microwave pyrolysis [17], fluidized bed [13], and chemical recycling using acetic acid [18]. LCA were conducted on some of these processes and they all show environmental benefits of recycling [13,18]. For example, La Rosa shows that acetic chemical recycling of a CFs material of 0.556kg requires 23.5 MJ of primary energy whereas it enables to avoid 523 MJ of primary energy required for virgin CFs manufacturing. Further research should include and compare environmental impacts of all innovative recycling technologies for CFRP using harmonized inventory data and impact assessment methods.

Currently no technically feasibly carbon fiber disposal scenario besides landfilling and incineration exists at a large scale. CF recycling can be regarded as an intermediate solution in a circular economy, but even the most advanced processes (pyrolysis, available in technical/commercial scale) still suffer from low fiber qualities (short fibers, lower strength compared to virgin fibers). Two separate directions of development might be expected in the future: (1) Specific recycling steps for CFRP production waste of known composition and origin, which will apply tailored pyrolysis or supercritical hydrolysis processed and yield near-to-new fiber qualities feasible for high-quality applications such as automotive parts; (2) separation of carbon-fiber containing materials from the general (municipal solid) waste stream in order to control fiber disposal. To this end, either robust recycling processes which at best will produce short carbon fibers or fillers will be applied, or processes for final disposal (oxidation) which still will have to be developed. With regard to the development path (1), this paper aims to present and to assess different routes from the current technical portfolio. It shows that current developments should be environmentally beneficial than current end-of-life scenarios at the industrial scale. However, further work on the implementation of complete end-of-life chain should be assessed, including the collecting and sorting processes.

5. Conclusion

This research provides an initial estimation of the environmental impacts induced by innovative recycling processes applied to epoxy resin / carbon fiber composites (supercritical hydrolysis and electrodynamic fragmentation), and their comparison with typical recycling process (pyrolysis) and typical waste management scenario (incineration and landfilling).

LCA applied to the processes shows that the environmental impacts of supercritical hydrolysis, pyrolysis and electrodynamic fragmentation are higher compared to landfill and incineration. However, when considering recycled products, recycling processes become environmentally beneficial by avoiding the impacts associated with the production of a new product from virgin material. This is not the case for landfill and incineration scenarios, which are "end-of-pipe" waste management scenarios and thus become unfavorable as they do not provide environmental benefits. It is, however, important to consider that the processes studied are at different technological development scales. The quality of the output products is therefore likely to evolve over potential developments.

In addition, studying the supercritical hydrolysis and electrodynamic fragmentation processes improvement capabilities has made possible the evaluation of environmental impacts reduction in the case of upscaling and maturation. It would also be interesting to be able to carry out this study at the same technological readiness level for the three recycling processes in order to determine which process is more advantageous from the environmental preservation point of view, depending on the mechanical properties conservations.

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Bibliography

[1] E. Witten, M. Thomas, K. Michael, T. Kraus, M. Kühnel, Composites Market Report 2015, AVK, carbon composites, 2015.

[2] S. Das, J. Warren, D. West, S.M. Schexnayder, Global Carbon Fiber Composites Supply Chain Competitiveness Analysis, 2016. doi:10.2172/1333049.

[3] E. Witten, T. Kraus, M. Kühnel, Composites Market Report 2016, (2016) 1–46.

[4] A. Lefeuvre, S. Garnier, L. Jacquemin, B. Pillain, G. Sonnemann, Anticipating in-use stocks of carbon fiber reinforced polymers and related waste flows generated by the commercial aeronautical sector until 2050, Resour. Conserv. Recycl. 125 (2017). doi:10.1016/j.resconrec.2017.06.023.

[5] European commission, Directive 2000/53/EC on end-of-life vehicles, Version 1 (2005) 48.

[6] B. Pillain, E. Gemechu, G. Sonnemann, Identification of Key Sustainability Performance Indicators and related assessment methods for the carbon fiber recycling sector, Ecol. Indic. 72 (2017) 833–847. doi:10.1016/j.ecolind.2016.08.056.

[7] M. Limburg, P. Quicker, Entsorgung von Carbonfasern - Probleme des Recyclings und Auswirkungen auf die Abfallverbrennung, Energ. Aus Abfall, Band 13. (2016) 135–144.

[8] G. Oliveux, L.O. Dandy, G.A. Leeke, Current status of recycling of fibre reinforced polymers: {Review} of technologies, reuse and resulting properties, Prog. Mater. Sci. 72 (2015) 61–99. doi:10.1016/j.pmatsci.2015.01.004.

[9] R.A. Witik, R. Teuscher, V. Michaud, C. Ludwig, J.A.E. Månson, Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling, Compos. Part A Appl. Sci. Manuf. 49 (2013) 89–99. doi:10.1016/j.compositesa.2013.02.009.

[10] C. Morin, A. Loppinet-Serani, F. Cansell, C. Aymonier, Near- and supercritical solvolysis of carbon fibre reinforced polymers (CFRPs) for recycling carbon fibers as a valuable resource: State of the art, J. Supercrit. Fluids. 66 (2012) 232–240. doi:10.1016/j.supflu.2012.02.001.

[11] M. Roux, C. Dransfeld, L. Giger, Recycling of high performance thermoplastic composites with high voltage fragmentation, in: 19TH Int. Conf. Compos. Mater., 2013: pp. 1–8.

[12] C. Helbig, E.D. Gemechu, B. Pillain, S.B. Young, A. Thorenz, A. Tuma, G. Sonnemann, Extending the geopolitical supply risk indicator: Application of life cycle sustainability assessment to the petrochemical supply chain of polyacrylonitrile-based carbon fibers, J. Clean. Prod. 137 (2016) 1170–1178. doi:10.1016/j.jclepro.2016.07.214.

[13] F. Meng, J. McKechnie, T.A. Turner, S.J. Pickering, Energy and environmental assessment and reuse of fluidised bed recycled carbon fibres, Compos. Part A Appl. Sci. Manuf. 100 (2017) 206–214. doi:10.1016/j.compositesa.2017.05.008.

[14] S.J. Pickering, T.A. Turner, F. Meng, C.N. Morris, J.P. Heil, K.H. Wong, S. Melendi, Developments in the fluidised bed process for fibre recovery from thermoset composites, CAMX 2015 - Compos. Adv. Mater. Expo. (2015).

[15] A. Oliveira Nunes, Composites renforcés à fibres de carbone: récupération des fibres par vapo-thermolyse, optimisation du procédé, (2015).

[16] M. Boulanghien, F. Berthet, G. Bernhart, Y. Soudais, Using steam thermolysis to recycle carbon fibres from Composite waste, Jec Compos. (2015) 99–101.

[17] R. Emmerich, J. Kuppinger, Recovering carbon fibers, Kunststoffe Int. 2014 (2014) 62–65.

[18] A.D. La Rosa, D.R. Banatao, S.J. Pastine, A. Latteri, G. Cicala, Recycling treatment of carbon fibre/epoxy composites: Materials recovery and characterization and environmental impacts through life cycle assessment, Compos. Part B Eng. 104 (2016) 17–25. doi:10.1016/j.compositesb.2016.08.015.

[19] M. Prinçaud, C. Aymonier, A. Loppinet-Serani, N. Perry, G. Sonnemann, Environmental Feasibility of the Recycling of Carbon Fibers from CFRPs by Solvolysis Using Supercritical Water, ACS Sustain. Chem. Eng. 2 (2014) 1498–1502. doi:10.1021/sc500174m.

[20] N.A. Shuaib, P.T. Mativenga, Energy demand in mechanical recycling of glass fibre reinforced thermoset plastic composites, J. Clean. Prod. 120 (2015) 198–206. doi:10.1016/j.jclepro.2016.01.070.

[21] J. Howarth, S.S.R. Mareddy, P.T. Mativenga, Energy intensity and environmental analysis of mechanical recycling of carbon fibre composite, J. Clean. Prod. 81 (2014) 46–50. doi:10.1016/j.jclepro.2014.06.023.

[22] S. Das, Life cycle assessment of carbon fiber-reinforced polymer composites, Int. J. Life Cycle

Assess. 16 (2011) 268–282. doi:10.1007/s11367-011-0264-z.

[23] L.M. Tufvesson, P. Tufvesson, J.M. Woodley, P. Börjesson, Life cycle assessment in green chemistry: overview of key parameters and methodological concerns, Int. J. Life Cycle Assess. (2012) 431–444. doi:10.1007/s11367-012-0500-1.

[24] S. Pimenta, S.T. Pinho, Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook, Waste Manag. 31 (2011) 378–392. doi:10.1016/j.wasman.2010.09.019.

[25] L. Henry, A. Schneller, J. Doerfler, W.M. Mueller, C. Aymonier, S. Horn, Semi-continuous flow recycling method for carbon fibre reinforced thermoset polymers by near- and supercritical solvolysis, Polym. Degrad. Stab. 133 (2016) 264–274. doi:10.1016/j.polymdegradstab.2016.09.002.

[26] I. Muñoz, N. Otte, G. Van Hoof, G. Rigarlsford, A model and tool to calculate life cycle inventories of chemicals discharged down the drain, Int. J. Life Cycle Assess. 22 (2017) 986–1004. doi:10.1007/s11367-016-1189-3.

[27] F.Y. Cakir, M.K. Stenstrom, Greenhouse gas production: A comparison between aerobic and anaerobic wastewater treatment technology, Water Res. 39 (2005) 4197–4203. doi:10.1016/j.watres.2005.07.042.

[28] P.L. McCarty, J. Bae, J. Kim, Domestic wastewater treatment as a net energy producer - can this be achieved?, Environ. Sci. Technol. 45 (2011) 7100–6. doi:10.1021/es2014264.

[29] M. Roux, N. Eguémann, C. Dransfeld, F. Thiébaud, D. Perreux, Thermoplastic carbon fibre-reinforced polymer recycling with electrodynamical fragmentation: From cradle to cradle, J. Thermoplast. Compos. Mater. 30 (2017) 381–403. doi:10.1177/0892705715599431.

[30] A. Küchler, Hochspannungstechnik, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009. doi:10.1007/978-3-540-78413-5.

[31] R. Pomberger, J. Adam, A. Aldrian, S. Hiden, D. Höllen, L. Kranzinger, K.E. Lorber, S. Neuhold, T. Nigl, K. Pfandl, R. Sarc, T. Schwarz, P. Sedlazeck, Recycling & Abfallverwertung Abfallwirtschaft & Ressourcenmanagement Deponietechnik & Altlasten Sondersession, (2016).

[32] A. Jacob, Composites can be recycled, Reinf. Plast. 55 (2011) 45–46. doi:10.1016/S0034-3617(11)70079-0.

[33] G. Doka, Life Cycle Inventories of Waste Treatment Services. ecoinvent report No. 13, Zyw. Czlowieka I Metab. (2003) 97. doi:10.1002/0470012668.ch5.

[34] K. Wood, Carbon fiber reclamation: Going commercial, High-Performance Compos. 18 (2010).

[35] E. Griffing, M. Overcash, Carbon fiber HS from PAN [UIDCarbFibHS], (2010).

[36] M. Dauguet, O. Mantaux, N. Perry, Y.F. Zhao, Recycling of CFRP for high value applications: Effect of sizing removal and environmental analysis of the Super Critical Fluid Solvolysis, Procedia CIRP. 29 (2015) 734–739. doi:10.1016/j.procir.2015.02.064.