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Comparative environmental and human health evaluations of thermolysis and solvolysis recycling technologies of carbon fiber reinforced polymer waste

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ABSTRACT

This quantitative research aims to compare environmental and human health impacts associated with two recycling technologies of CFRP waste. The '*baseline*' recycling technology is the conventional thermolysis process via pyrolysis and the '*alternative*' recycling technology is an emerging chemical treatment via solvolysis using supercritical water (SCW) to digest the thermoset matrix. Two Gate-to-Gate recycling models are developed using GaBi LCA platform. The selected functional unit (FU) is 1 kg CFRP waste and the geographical boundary of this comparative LCIA is defined to be within the U.S. The results of this comparative assessment brought to light new insights about the environmental and human health impacts of CFRP waste recycling via solvolysis using SCW and, therefore, helped close a gap in the current state of knowledge about sustainability of SCW-based solvolysis as compared to pyrolysis. Two research questions are posed to identify whether solvolysis recycling offers more environmental and human health gains relative to the conventional pyrolysis recycling. These research questions lay the basis for formulating two null hypotheses ($H_{0,1}$ and $H_{0,2}$) and their associated research hypotheses ($H_{1,1}$ and $H_{1,2}$). LCIA results interpretation included '*base case*' scenarios, '*sensitivity studies*,' and '*scenarios analysis*.' The results revealed that: (a) recycling via solvolysis using SCW exhibits no gains in environmental and human health impacts relative to those impacts associated with recycling via pyrolysis and (b) use of natural gas in lieu of electricity for pyrolyzer's heating reduces the environmental and human health impacts by 37% (lowest) and up to 95.7% (highest). It is recommended that on-going experimental efforts that focus only on identifying the best solvent for solvolysis-based recycling should also consider quantification of the energy intensity as well as environmental and human health impacts of the proposed solvents.

1. Introduction

1.1. Background

Global consumption of carbon fiber reinforced polymer (CFRP) continues to increase and is estimated to reach ≈209,800 tons by 2020 (Yuyan et al., 2009; Witik et al., 2013; La Rosa et al. 2016; Das et al., 2016; Li et al., 2016; Pillain et al., 2017; Meng et al., 2017). This lightweight structural material has many industrial applications including commercial and military aircraft, automotive, electronics, construction, sporting goods, etc. (Khalil, 2017). Another CFRP application is manufacturing CF-based Type-III and Type-IV tanks (Khalil et al., 2009, 2010) for on-board vehicular hydrogen storage (whether H2 is stored as compressed gas or in solids-state forms such as metal hydrides, chemical hydrides, or adsorbed on activated carbon). For the commercial aircraft industry, good cases in point which demonstrate use of CFRP are Airbus A350XWB and Boeing 787 Dreamliner (Pimenta and Pinho, 2011; Yang et al., 2012; Shuaib et al., 2015), where ≈50% of the aircraft weight is composite. Use CFRP in unmanned aerial vehicles (UAV) is an example of how the military leverages this lightweight structural material. Demand for carbon fiber (CF) in the aerospace defense sector is forecasted to reach 18,462 tons by 2020 compared to 7694 tons in 2011 (Robert, 2017).

Abbreviations: CF, carbon fibers; CFRP, carbon fiber reinforced polymer; CTUe, comparative toxic unit for ecotoxicity impacts such freshwater toxicity; CTUh, comparative toxic unit for human toxicity impacts; EOL, end of life; EP, epoxy resin; FU, functional unit; LCA, life cycle assessment; LCI, life cycle inventory; LCIA, life cycle impact assessment; nCF, neat carbon fibers; NG, natural gas; PAN, polyacrylonitrile; rCF, recycled carbon fibers; RQ, research question; SCF, supercritical fluids; SCW, supercritical water; TRACI 2.1, tool for reduction and assessment of chemicals and other environmental impacts; TRL, technology readiness level; vCF, virgin carbon fibers.

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Current estimates show that ≈3000 tons of CFRP waste are generated annually in Europe and the U.S. (Vicki, 2010; Ye et al., 2013; Shuaib et al., 2015). Sources of this waste include tows cuttings during manufacturing, expired prepregs during storage, and EOL CFRP components. Literature data (Lester et al., 2004) shows that waste from tows cutting could be as high as 40%.[1] Moreover worldwide, ≈8500 commercial aircraft are expected to retire and dismantled by 2025 (Carberry, 2008). In this regard, Yang et al. (2012) noted that the aerospace industry alone is estimated to reclaim between 4.5 and 6.8 million kg of rCF (both from manufacturing and EOL) by 2029.

The forecasted rise in CFRP waste generation signals an urgent need for identification of sustainable technologies to process the anticipated thousands of tons of CFRP waste. Section 1.2 summarizes current and emergent methods for managing CFRP waste.

1.2. Literature review

The published literature covers numerous studies on waste management of CFRP manufacturing waste and EOL components. The reported waste management approaches include landfilling, incineration (with and without heat recovery) and recycling (Shuaib et al., 2015; Khalil, 2017). Historically, CFRP waste has been disposed of in landfills but since 2004 both the U.S. Environmental Protection Agency (EPA), Land Disposal Restrictions (LDR), and European regulation (EU Directive 99/31/EC) continued to impose constraints on disposal of organic materials (like CFRP) in landfills (Shuaib et al., 2015; La Rosa et al., 2016; Meng et al., 2017). Aircraft manufacturers are anticipating future regulations on aircraft EOL composite waste disposal in a manner similar to current regulatory restrictions on CFRP waste from scrapped vehicles. Incineration of composite waste has its own environmental problems and, thus, is viewed as an unsustainable solution. Additionally, high cost and high energy intensity of CF production from the Pan-based precursor (Shuaib et al., 2015; Khalil, 2017) has driven the need for recycling of CFRP waste. In this regard, numerous studies have reported on CF recycling technologies including microwave heating (Lester et al., 2004; Shuaib et al., 2015; Khalil, 2017), pyrolysis (Cunliffe et al., 2003), hydro-thermolysis (Pinero-Hernanz et al., 2008), chemical solvolysis (Pinero-Hernanz et al., 2008; Goto, 2009). Those studies among others reached the same conclusion that recycling CF from manufacturing waste and EOL CFRP components has environmental and economic benefits.

The CFRP waste recycling approach includes mechanical recycling, thermolysis, and solvolysis using supercritical fluids (SCFs)[2] like water, alcohols (*e.g.*, methanol, ethanol, n-propanol, etc.), and other organic solvents (such as acetone and acetic acid) under different operating temperatures and pressures (Pimenta and Pinho, 2011; Khalil, 2017).

Mechanical recycling involves CFRP waste grinding and sieving to separate CF from the resin matrix (Oliveux et al., 2015; Shuaib et al., 2015). The associated source of environmental and human health burdens comes from the electrical energy (MJ/kg CFRP waste) expended in the grinding and sieving processes. Because mechanical recycling is out of scope of the current research, it will not be further discussed in the remainder of this section in order to focus only on recycling via thermolysis and solvolysis using supercritical water (SCW).

Thermolysis involves thermal decomposition of the thermoset resin matrix to recover CF (Cunliffe et al., 2003; Pickering, 2006; Song et al., 2009; Pompidou et al., 2012; Yang et al., 2012; Greco et al., 2012; Morin et al., 2012; López et al., 2013; Witik et al., 2013). Song et al. (2009), for example, reported that ≈2.8 MJ of energy would be needed to pyrolize 1 kg of CFRP waste and that ≈19 MJ/kg CFRP waste could be recovered from pyrolysis's recyclate byproducts. Witik et al. (2013) reported that use of pyrolysis to recover CF from CFRP waste would consume ≈5–10% of the energy required to produce neat CF (nCF). Applying this insight to Khalil's (2017) estimated energy consumption of 301.3 MJ to produce 1 kg CFRP (60 wt% CF), the energy required to produce 1 kg rCF via pyrolysis would range from 15 to 30 MJ/kg rCF. Moreover, studies on microwave heating of CFRP (Lester et al., 2004; Shuaib et al., 2015). Obunai et al. (2015) reported this emerging technology is technically feasible, more energy efficient, and faster compared to the conventional thermolysis. Lester et al. (2004) reported that microwave heating would require about 10 MJ/kg of CFRP which less than the energy required for conventional pyrolysis (without heat recovery) by about 33% less that the energy required for conventional pyrolysis (Shuaib et al., 2015). However, neither Lester et al. (2004) nor Shuaib et al. (2015) have commented on the cost of the microwave recycling technology. With respect to the tensile strength of rCF, microwave heating can retain about 79% of the fiber's original tensile strength compared to about 96% for conventional pyrolysis technology (Shuaib et al., 2015).

Thermolysis via Pyrolysis is done by heating the CFRP waste in an inert environment such as nitrogen (N_2) at temperatures between 400 °C and up to 800 °C (Pickering, 2006). Pyrolysis also produces byproduct recyclates, namely, gases (such hydrogen, methane, and other non-condensable hydrocarbons), oils and wax (the condensable byproduct), and carbonaceous solid residue (char). The liquid byproduct has a relatively high caloric value (embodied energy) similar to fuel oil (≈30–40 MJ/kg) and the gaseous byproduct has a relatively lower calorific value ≈15–20 MJ/kg (Pickering, 2006). Nunes et al. (2017) examined CFRP waste recycling via thermolysis using steam and nitrogen gas by a process developed in France. They used 1.4 kg N_2 gas and 1.6 kg water (steam) to treat 1 kg of CFRP waste. The total electric energy consumption in this process was 71.64 MJ (≈20 kWh) per kg CFRP waste. Their LCIA results showed environmental advantages compared to waste landfilling.

Recycling CFRP using the gasification technology involves using superheated steam at about 600 °C at atmospheric pressure. The authors reported that this technology is efficient in removing the epoxy resin used in CFRP. Their observation was based on a bench-scale experimental investigation. As a mild ocident, superheated steam decomposes the polymer matrix into low molecular weight hydrocarbons with emission of gases including CO, CO_2, H_2 and CH_4. The authors judged, based on their experimental observations, that this technology could be technically and economically feasible. However, they arrived at this conclusion without providing a rigorous scaling-up study from their bench-scale results to a typical industrial setting.

Researchers like Pinero-Hernanz et al. (2008), Yuyan et al. (2009), Morin et al. (2012), Knight (2013), Pinçaud et al. (2014), Yildirir et al. (2014), Dauguet et al. (2015), Henry et al. (2016), La Rosa et al. (2016), Keith et al. (2016), and Okajima and Sako (2017) had experimentally examined CFRP waste solvolysis using SCFs as solvents to digest the thermoset resin into liquid-phase depolymerized monomers. The removal efficiency of the resin matrix could be ≥98% (Pinero-Hernanz et al., 2008) and Yuyan et al. (2009) reported 100% decomposition efficiency of the thermset resin using SCW. The operating temperature and pressure of this chemical treatment are above the critical temperature (T_C) and critical pressure (P_C) of the solvent. For example, water has

[1] Vartega Carbon Fiber Recycling, December 2016.

[2] A supercritical fluid (SCF) is a substance at temperatures and pressures above its critical point, where distinct liquid and gas phases do not exist and where the liquid and gas phases disappear to become a single supercritical phase. SCFs effuse through solids just like a gas, dissolve materials just like a liquid, and have characteristics that are useful in many industrial applications including digesting the polymeric resin matrix in CFRP waste.

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