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## Modelling pyrolysis process for CFRP recycling in a closed-loop supply chain approach

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### Abstract

Several pathways have been investigated to recycle Carbon Fibre Reinforced Polymers (CFRP), that have been increasingly used in a wide range of applications such as automotive, aerospace and renewable energy. Pyrolysis is currently considered to be the only process that is available on an industrial scale. Yet to our knowledge, no study based on process systems engineering concepts has been performed in order to evaluate the environmental gain that can be obtained from the production of the very energy-intensive production of virgin carbon fibres. In this work, a pyrolysis recycling process of a capacity of 1500 tonnes/year has been modelled by using Aspen Hysys v8.6 simulation software to evaluate the avoided environmental impacts using a Life Cycle Assessment approach, and in particular, those related to Global Warming Potential (expressed in kg CO<sub>2</sub> eq.). A functional unit based on the recycling of 1 kg of carbon fibre reinforced polymers has been considered. An economic evaluation has also been carried. The objective is to use these results in order to build the process echelon of the CFRP recycling supply chain based on reliable data.

**Keywords:** Pyrolysis, Recycling, Carbon Fibre Reinforced Polymers, Life Cycle Assessment

### 1. Introduction

In the last 30 years, Carbon Fibre Reinforced Polymers (CFRP) have been increasingly used in a wide range of applications (Pimenta and Pinho, 2011) such as automotive, aerospace and renewable energy due to their high mechanical properties, stiffness to weight ratio and damage tolerance. In that context, CFRP disposing will become a big issue as today's low-weight CFRP structures reach the end of their service lives. Under upcoming economic, environmental and regulatory pressure, the development of viable CFRP waste recycling pathways is thus a strategic issue. Among CFRP recycling processes, pyrolysis appears as a rather mature process available on an industrial scale due to several advantages such as a high retention of mechanical potential, a recovery potential of chemical feedstock from the resin, and no use of chemical solvents. Despite these advantages, the pyrolysis process has only been developed from an empirical approach and a global modelling of the process based on process flowsheeting concepts has not been reported in the dedicated literature. The lack or imprecise nature of economic and environmental information about CFRP recycling processes at industrial

scale may thus hamper the development of reliable recycling strategies for the deployment of CFRP recycling supply chains that are particularly relevant to promote the concepts of circular economy.

The aim of this study is to use the well-known potential of process flowsheeting to evaluate design parameters of the pyrolysis process that can be further used for the design of closed-loop supply chain networks and for the determination of the best recycling strategies. For this purpose, a process model for CFRP pyrolysis that captures the essence of a plant to scale up the technology at various scales has been developed based on Aspen Hysys v8.6 simulation software (AspenTech: Optimizing Process Manufacturing 2017). The estimation of capital and operating costs as well as the evaluation of environmental impact is an integral component of such assessment. This study highlights the link between process flowsheeting tools and LCA tools as well as the interest of modelling some specific steps such as pyrolysis in global process modelling.

## 2. Modelling methodology

Pyrolysis is a thermal recycling process of FRP that decomposes the matrix at around 400 to 750 °C (Oliveux, Dandy, and Leeke 2015) depending on the thermal properties of resin in order to recover fibres. The main characteristic of this process is the thermal decomposition in an inert environment or in a controlled atmosphere with a low proportion of oxygen to avoid the oxidation of fibres. Classically, the procedures for process simulation mainly involve defining chemical components, selecting a thermodynamic model, determining plant capacity, choosing, proper operating units and setting up input conditions (flowrate, temperature, pressure, and other conditions). The studied pyrolysis plant involves a thermoset epoxy resin matrix (40% vol) reinforced with polyacrylonitrile-based carbon fibre (60% vol). A capacity of 1500 t/y of recycled CFRP waste has been considered for design. Pyrolysis conditions have been set in Aspen Hysys v8.6 according to the results reported in the literature. Temperature, pressure, atmospheric composition are the three important parameters governing the pyrolysis process. Recently, Yang et al. (2015) have studied the impact of various oxygen concentrations in nitrogen-oxygen atmosphere and temperature reaction on the recycling carbon fibre (rCF) mechanical properties. It has been shown that rCF mechanical properties decrease with the increase in oxygen concentration and temperature.

From these results, the pyrolysis process has been modelled according to the following conditions. The operating conditions in a fixed-bed reactor have been set at 550°C under N<sub>2</sub> atmosphere, to achieve full fibre/matrix separation and prevent fibre degradation. Then, the proportion of gases and liquids coming from the pyrolysis reaction has been determined from the work of (Cunliffe et al., 2003). The product yields of oil, gas and solid residue have been determined together with a detailed composition of the derived gases from the degradation of the epoxy resin in relation to final pyrolysis temperature (400°C to 800°C). Moreover, the thermodynamic model chosen for the simulations is the NRTL activity coefficient model (Fakhrhoseini and Dastanian, 2013).

Figure 1 shows the flowsheet of the pyrolysis process developed with Aspen Hysys v8.6. First, CFRP waste, gaseous nitrogen and propane, respectively, streams 1, 13 and 14 are introduced into the pyrolysis reactor modelled by a boiler and a reactor (FH-100 and CRV-100). The CFRP waste is modelled by carbon and Diglycidyl Ether of Bisphenol A (DGEBA) in relation with the proportion of carbon fibres and epoxy



Table 1: Aggregation of components for life cycle inventory design

Inputs	Outputs
Stream 13 : Nitrogen (0.667 kg/kg CFRP recycled)	Stream 20 : Methanol {GLO} (0.025 kg/kg CFRP recycled)
Stream 14 : Propane {GLO} (0.994 kg/kg CFRP recycled)	Stream 17 : Ethyl acetate {GLO} (0.164 kg/kg CFRP recycled)
Steam, in chemical industry {GLO} (0.228 kg/kg CFRP recycled)	Stream 7 : PAN carbon fibre (Das 2011) (0.602 kg/kg CFRP recycled)
Water, process and cooling (3.675 l/kg CFRP recycled)	Stream 16 : Hazardous waste, for incineration {RoW} (0.189 kg/kg CFRP recycled)
Electricity, low voltage {FR} (0.552 kWh/kg CFRP recycled)	

In this study, the rCF has been modelled in Simapro by virgin glass fibre (vGF) to take into account a possible decrease in their capacity to reinforced polymers due to a contamination of their surface, and a decrease in their mechanical properties, and their length. Consequently, the recycling of carbon fibre avoids the manufacturing of virgin glass fibre, thus leading to a negative environmental impact with a calculated total GWP for 1 kg of recycled CFRP waste being equal to -0.53 kg CO<sub>2</sub> eq. (Figure 2). A negative impact is also calculated due to the recovery of both Methanol (-0.015 kg CO<sub>2</sub> eq) and Ethyl acetate (-0.431 kg CO<sub>2</sub> eq) that has been taken into account in a similar way since their recovery avoids their production in an extended boundary of the system. This result thus confirms the benefit to recycle CFRP waste. A substantial gain is also obtained for the other categories of impacts as highlighted in Figure 2.

These results are in agreement with those obtained from a literature analysis: pyrolysis can be simply modelled as a combustion process of the matrix (35wt% of CFRP waste) (see Figure 3).

No energy recovery from thermal decomposition of matrix has been assumed. The total energy used in pyrolysis has been estimated at about 30 MJ/kg composite (Witik et al. 2013). The environmental impact of virgin glass fibre has been calculated by Das (2011): the manufacturing of 1 kg of vGF leads to a GWP value equal to 2.6 kg CO<sub>2</sub> eq. Under these conditions, a total GWP equal to -0.08 kg CO<sub>2</sub> eq has been obtained.

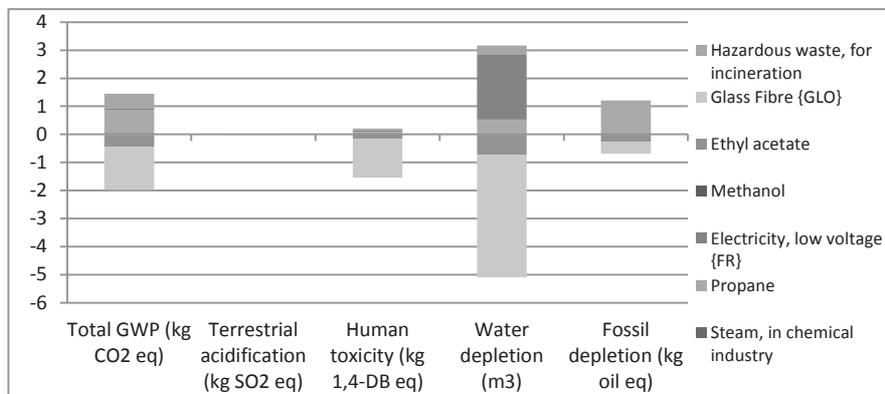


Figure 2: Environmental impact of the recycling of 1 kg of CFRP by pyrolysis calculated from SimaPro

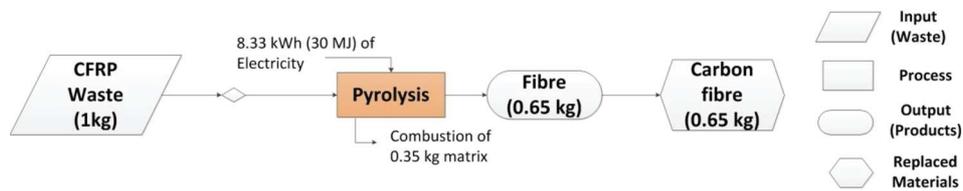


Figure 3: Simplified modelling of the CFRP pyrolysis recycling process

### 3.2. Economic evaluation

Table 2 presents the results concerning both capital and operational expenditures computed from Aspen Hysys v8.6. An order of magnitude obtained from the review of (Krawczak, 2011) after actualization and capacity extrapolation is also mentioned. The comparison is yet difficult since only the pyrolysis pilot (without mentioning the separation train) is considered, thus justifying the use of process systems engineering approach to a more accurate evaluation.

Table 2: Cost calculated by Aspen Hysys v8.6 and comparison with literature data (Krawczak, 2011)

	Aspen Hysys v8.6	Literature
CAPEX	4,282,000 USD	1,284,000 USD
Equipment cost	103200 USD	
Total installed cost	637000 USD	
OPEX	1,677,220 USD/year	1,197 USD/year
CFRP waste transport cost to the recycling plant	625,849 USD/year	
Electricity cost	7.31 USD/h	
Water cost	0.02 USD/h	
Steam cost	0.70 USD/h	
Taxes	71,798 USD/year	

## 4. Conclusions

In this study, the modelling of the pyrolysis recycling process has been carried out by using Aspen Hysys v8.6 simulation software. The environmental assessment has been implemented via SimaPro. The results obtained from flowsheeting simulation have thus been used to build the Life Cycle Inventory data using Ecoinvent database. The focus on Global Warming Potential has shown that an environmental gain is obtained from the production of virgin fibres with a functional unit involving the recycling of 1 kg of Carbon Fibre Reinforced Polymers (CFRP) waste. An economic evaluation has also been carried. The objective is to use these results in order to build the corresponding pyrolysis process echelon of the CRFP recycling supply chain with the appropriate precision level at this step of project development. The perspective is to extend the approach to the other pathways of CFRP recycling that gain increasing attention (supercritical water process, microwave for instance). For this purpose, PSE concepts are of tremendous importance to generalize the link between process simulation and LCA software tools (Morales-Mendoza et al., 2012) and to optimise the recycling strategy taking into multiple criteria at earlier design stage of the supply chain.

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