



Recovery of carbon fibres and production of high quality fuel gas from the chemical recycling of carbon fibre reinforced plastic wastes



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ABSTRACT

A solvolysis process to depolymerize the resin fraction of carbon fibre reinforced plastic waste to recover carbon fibre, followed by hydrothermal gasification of the liquid residual product to produce fuel gas was investigated using batch reactors. The depolymerisation reactions were carried out in ethylene glycol and ethylene glycol/water mixtures at near-critical conditions of the two solvents. With ethylene glycol alone the highest resin removal of 92.1% was achieved at 400 °C. The addition of water to ethylene glycol led to higher resin removals compared to ethylene glycol alone. With an ethylene glycol/water ratio of 5, at 400 °C, resin removal was 97.6%, whereas it was 95.2% when this ratio was 3, at the same temperature. The mechanical properties of the recovered carbon fibre were tested and showed minimal difference in strength compared to the virgin carbon fibre. The product liquid, containing organic resin degradation products was then subjected to catalytic supercritical water gasification at 500 °C and 24 MPa in the presence of NaOH and Ru/Al₂O₃ as catalysts, respectively. Up to 60 mol.% of H₂ gas was produced with NaOH as catalyst, and 53.7 mol.% CH₄ gas was produced in the presence of Ru/Al₂O₃.

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1. Introduction

Since the beginning of the 1960s, carbon fibres have become one of the most important engineering materials, as they offer excellent physical and chemical properties. For example, they are a good replacement for steels and aluminium composite materials due to their high tensile strength, low density, high resistance to temperature and corrosion, and low thermal expansion [1,2]. Carbon fibres have been used widely as reinforcements in composite materials such as carbon fibre reinforced plastics (polymers), carbon–carbon composite and carbon fibre reinforced cement in many applications such as automobiles, housing, sport and leisure industries as well as airplane and space applications [2,3].

In the USA and Europe, 3000 tons of carbon fibre reinforced plastics (CFRP) waste is generated every year, and this number is expected to rise dramatically as it is predicted that between 6000 and 8000 airplanes containing large quantities of carbon fibre materials will reach their end-of-service life by 2030 [4]. With the widening of the usage area of CFRP, the production rate of carbon fibre has also increased with market projections suggesting that production is expected to rise to 140,000 tons by 2020 [5]. As the

carbon fibre industry grows rapidly, the need for effective recycling of carbon fibre reinforced plastic waste is gaining attention due to environmental and economic factors.

Currently, various mechanical, thermochemical and chemical recycling processes of CFRP waste are proposed. Mechanical recycling processes consist of reducing the size of waste materials into small pieces by crushing, milling etc. and segregation of these pieces into powdered products (mainly resin) and fibre products. Due to dramatic reduction in the mechanical properties, limited applications can be found for the mechanically recycled CFRP e.g. as reinforcement materials in cement industry as recycled CFRP reinforced concrete [6]. Thermochemical recycling methods such as pyrolysis and gasification are designed to separate the carbon fibre reinforcement from the resin fraction. For example, pyrolysis converts the polymeric organic resin into an oil and gas product which can be used as fuel or as a chemical feedstock [7]. These processes have some challenges, notably formation and deposition of char on the recovered carbon fibre during pyrolysis or over-oxidation during gasification. The main disadvantage is that after pyrolysis, an oxidation process is needed in order to remove the char deposited on the fibre surface [8], which adds to process cost and may inadvertently affect their mechanical properties. To overcome those disadvantages, chemical separation of the resin from the carbon fibre via depolymerisation in a solvent reaction medium can be a solution as it is possible to recover carbon fibre with excellent

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mechanical properties coupled with recycling of the resin fraction into useful chemicals or energy. Subcritical and supercritical fluids such as glycols, simple alcohols and water are excellent solvents for this process [9].

Recent studies on solvo-thermal recycling of CFRP have shown promising results; as the waste can be decomposed into smaller molecules and fibre material. Piñero-Hernanz et al. [10,11] studied the chemical recycling of CFRP in sub- and supercritical water and alcohols (methanol, ethanol, 1-propanol and acetone). They investigated the effect of temperature, reaction time, addition of oxidant (H_2O_2), and catalyst concentration on resin removal efficiency. They reported that in supercritical water, resin removal efficiency reached 79.3 wt% and was further improved to 95.3 wt% by using KOH as a catalyst. Liu et al. [12] used subcritical water for the decomposition of CFRP at temperatures between 250 °C and 290 °C. The resin fractions totally decomposed at 260 °C after 105 min and at 290 °C after 75 min with 1.5 g/mL feedstock concentration. The recovered carbon fibre showed 98.2% of the tensile strength compared to the virgin fibre. They also concluded that addition of 1 M sulphuric acid as a catalyst could increase the rate of degradation of the epoxy resin reinforcement. Bai et al. [13] investigated the effect of O_2 in the chemical recycling of carbon fibre reinforced epoxy resin composites in supercritical water at 30 MPa and 440 °C for 30 min reaction time. They reported the recovery of clean carbon fibre recovered with higher tensile strength relative to a sample of virgin carbon fibre. Further, the resin removal was between 85% and 96%, but the tensile strength of recovered fibre decreased rapidly when resin removal exceeded 96%.

Glycolysis has been generally proposed for depolymerisation of polyethylene terephthalate (PET) and polyurethane (PU). For example, waste PET and PU has been subjected to depolymerisation in ethylene glycol (EG) at low to moderate temperatures (around 200 °C) and atmospheric pressure [14]. However, to achieve complete reaction, long reaction times of up to 8 h may be required, which can contribute to increased process costs when ethylene glycol is used at those conditions [15]. In the studies with PET, 100% conversion has been achieved after 1.5 h in the presence of a cobalt acetate catalyst [16]. However, reducing the reaction time further will enhance the viability of the process.

The supercritical water gasification process to produce energy and fuels from renewable sources and organic wastes has been investigated since the early 1980s. Many studies with model compounds such as cellulose, lignin, methanol, glucose and with real biomass and organic wastes have been carried out by different research groups to understand the reaction mechanism, kinetics and thermodynamics of the process [17,18]. With the help of catalysts, and depending on the reaction conditions, high yields of CO , H_2 and/or CH_4 can be achieved [19]. In this paper, degradation of carbon fibre reinforced plastic waste with ethylene glycol and ethylene glycol/water mixtures has been carried out at sub- and supercritical conditions. Detailed analyses of all the reaction products including gas, liquid and solid have been carried out for better understanding of the process. Also in this study, two processes were investigated to determine an appropriate use for the liquid products after carbon fibre recovery; (1) isolation of the reaction products by liquid-liquid extraction and (2) catalytic supercritical water gasification of the liquid products to produce a syngas rich in hydrogen or methane.

2. Experimental

2.1. Materials

The waste carbon fibre reinforced composite plastic sample consisted of a polybenzoxazine resin backbone (a phenolic-type

thermoset). The composite consisted of approximately 61.5 wt% carbon fibre and 38.5 wt% resin. The elemental (CHNOS) composition of the carbon fibre reinforced plastics was, 80.3% carbon, 2.05% hydrogen, 5.9% oxygen, 4.15% nitrogen and 1.65% sulphur. In addition, proximate analysis of the sample showed 33% volatile matter, 66.6% fixed carbon and 0.4% ash. Sodium hydroxide (pellets), dichloromethane and ethylene glycol were purchased from Sigma-Aldrich, UK. The details of the 500 mL stainless steel reactor which was used for degradation of CFRP [16,20], and the details of 75 ml stainless steel reactor obtained from Parr Instruments Co. USA, have been provided in previous publications [21].

2.2. Procedure

The carbon fibre reinforced plastic sample was cut into strips of approximately 1 cm × 3 cm to fit into the 500 mL stainless steel reactor. Approximately 2.5 g of the CFRP strips was loaded into the reactor along with a known volume of liquid made up to 60 mL with either ethylene glycol or ethylene glycol and distilled water. The reactor was then purged with N_2 , sealed and heated to the designated temperature and corresponding pressure. The heating rate was kept constant throughout the experiments ($\sim 10^\circ C min^{-1}$) and the reactor was quickly withdrawn from the heater as soon as the designated conditions were reached. Zero residence time here indicates that the reactor was withdrawn from the heater as soon as the pre-set temperature was reached. The reactor was then cooled to room temperature and the gaseous effluent sampled for analysis.

2.3. Analyses of reaction products

The gas samples were immediately analyzed off-line by means of two Varian 3380 gas chromatographs for permanent gases and hydrocarbons, respectively [16]. A Varian 3380GC with dual packed columns and dual thermal conductivity detectors (GC/TCD) was used to analyze for H_2 , CO , O_2 , N_2 and CO_2 . The column for CO_2 analysis was 2 m length by 2 mm diameter with Haysep 80–100 mesh packing material. Analysis for H_2 , CO , O_2 and N_2 was carried out in a second column of 2 m length by 2 mm diameter packed with 60–80 mesh molecular sieve. A second Varian 3380 GC with a flame ionization detector (GC/FID) was used to analyze and determine the hydrocarbons (C_1 – C_4) with nitrogen carrier gas. The column was 2 m length by 2 mm diameter, packed with Haysep 80–100 mesh.

The reactor contents, including liquid and solid residues were emptied into a holding beaker and separated by filtration washing several times with distilled water. The solid residue was dried to a constant weight in an oven at 105 °C to determine its weight. Percentage resin removal was calculated on a solid residue dry-weight basis by the formula:

$$\frac{\text{Weight of CFRP feed} - \text{Weight of Solid residue}}{\text{Weight of Resin in CFRP feed}} \times 100$$

A portion of each liquid effluent obtained after each experiment was extracted with dichloromethane. The dichloromethane extract was acidified with hydrochloric acid to a pH of 2–3 to enable quantitative analysis of phenols. Thereafter, the same sample was made alkaline with aqueous potassium hydroxide solution to pH 10 in order to extract the anilines. The extracts were separately analyzed with a Varian 3800 GC fitted with a Saturn 2200 ion trap MS/MS for qualitative identification of the dichloromethane-extractable organics in the liquid residual [21].

2.4. Supercritical water gasification (SCWG) of residual liquid product

The samples of residual liquid product were treated by catalytic supercritical water gasification in a different, higher pressure

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