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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/Al_2O_3 as catalysts, respectively. Up to 60 mol.% of H_2 gas was produced with NaOH as catalyst, and 53.7 mol.% CH_4 gas was produced in the presence of Ru/Al_2O_3.

Keywords: Materials; Composites; Carbon fibre; Catalyst; Hydrogen; Methane

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1.0 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 tonnes 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 oxidization 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 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. Pinero-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 minutes and at 290 °C after 75 minutes 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 minutes 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 ^{o}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.

2.0 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 1cm x 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 (~10 °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 analysed 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 analyse 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 2m 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 analyse and determine the hydrocarbons (C_1 – C_4) with nitrogen carrier gas. The column was 2 m length by 2mm 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;

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

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 analysed 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 rated batch reactor to generate a syngas rich in hydrogen and/or methane. The reactor was a 75 ml Inconel batch reactor obtained from Parr Instruments Co. USA. For the gasification of the liquid product, 15 ml of sample was fed into the 75 mL reactor and heated at an average rate of 12 ^{o}C min^{-1} to the designated temperature. After reaching the set point, the temperature was held constant for the desired reaction time. At the end of experiment, the reactor was cooled rapidly to below 100 °C within 8 min with the help of a cooling fan, and a further 30 min to reach room temperature. The gas products were sampled for analysis by gas chromatography as described previously. The experimental conditions and procedure used for the gasification of the liquid residuals has been reported before [22] and found to favour the production of consistently high yields of both hydrogen and methane from algal biomass slurries.

2.4. Analysis of recovered carbon fibre

The breaking force, tensile strength, elongation and Young’s modulus of virgin and recovered individual carbon fibres were determined using an adaptation of the ISO BS EN ISO 5079 test method for textile fibres. The tests were carried out using an Instron 1123 which was calibrated by means of a 100 g mass. Single fibres were glued to both ends of a hollow square piece of cardboard 2 cm long, located in the middle and parallel to either side for the strongest position. For each result, a total of 50 individual fibres were tested in order to obtain the mean value for the recovered fibres.

The recovered carbon fibres and virgin carbon fibres were analysed using a high resolution LEO 1530 FEG scanning electron microscope to investigate the changes in the fibre surface structure.

3.0 Results and Discussion

3.1. Influence of Reaction Conditions on Carbon Fibre Recovery

The resin removal efficiencies with respect to reaction temperature and time are shown in Table 1 for depolymerisation of the carbon fibre reinforced plastic waste in ethylene glycol and Table 2 for that of the ethylene glycol/water mixture. The experiments of decomposition of waste carbon fibre reinforced plastic in ethylene glycol were carried out at four different temperatures and at zero and ten minutes of reaction times to monitor the effect of time on resin removal. At temperatures of 300 and 360 °C, the resin removal was not significant, however as the temperature was increased, removal increased to 92.1 % at 400 °C. The influence of time on the degree of depolymerisation of the resin was investigated at 380 °C. At this temperature, resin removal increased from 79.3 % to 89.7 %, when the residence time was increased from zero to 10 minutes. In reported studies with thermoplastics, the main drawback to depolymerisation in ethylene glycol was the very long reaction times of up to 8 hours [23]. In our experiments with ethylene glycol at a temperature of 380 °C, the corresponding pressure was recorded as 4.2 MPa, therefore the reaction was conducted near the critical point of ethylene glycol (T_c = 447 ^oC, P_c = 8.2 MPa). Therefore, operating near the supercritical conditions of ethylene glycol enabled more resin to be depolymerised in very short reaction times even for a thermosetting (phenolic) plastic. The solubility of ethylene glycol in water and its decomposition during the reaction meant that it was impossible to measure separately the carbon of the resin degradation products in the liquid and gaseous products. Hence, it was difficult to construct a carbon balance for the carbon fibre reinforced plastics degradation in this work.

The effect of water addition as a modifier to the process was investigated at a temperature range of 380 to 420 °C and at zero residence time. Resin removal increased with increasing ethylene glycol/water ratio (up to ethylene glycol/water ratio of 5:1). In the present study, the highest resin removal of 97.6% was reached when the ethylene glycol/water ratio was 5 at 400 °C. However, when the temperature was increased to 420 °C, resin removal decreased significantly to 90.4 % at the same ethylene glycol/water ratio. The same decrease was observed when the ethylene glycol/water ratio was 3. This might have been due to an increase in the weight of recovered fibre due to char deposition at the higher temperature of 420 °C, resulting in an erroneous decrease in resin removal. It has been reported in the literature that at higher depolymerisation temperatures, repolymerization of degradation products could occur leading to char formation. According to the studies on cellulose by Kruse and Dinjus [24], the decomposition path in supercritical water is from phenols to different short chain polymers due to poly-condensation reactions. From these intermediates, gases and coke formation occurs [24]. The same reaction pathway has been suggested even for very short residence times (0-100 s) by Yong and Matsumura, under sub and supercritical conditions. They stated that phenol reacts with water at near critical conditions to produce gas and char, the char formation was doubled with a 30 ^oC increase in temperature as the reaction conditions approached the supercritical conditions [25]. The carbon fibre reinforced plastic waste sample used in this study has a phenolic resin, repolymerization of phenolic degradation products could produce char that remained on the recovered carbon fibre surface after cooling. Since, the extent of carbon fibre recovery is obtained by gravimetric measurements of solids; it is difficult to distinguish between char and carbon fibre. However, this problem could be addressed by carefully controlling the reaction conditions of temperature and time to minimize char formation. Char deposition on the recovered carbon fibre can be removed by moderate temperature oxidation; however, as mentioned earlier this can add to process cost as well as cause a decline in the mechanical properties of recovered carbon fibre.

The mechanical properties of the recovered carbon fibre were also tested, and the results are shown in Table 3. The results suggest that overall there was no decrease in the tensile strength compared to that of virgin carbon fibre. In our previous work [20], carbon fibre from waste CFRP was recovered with supercritical water with the addition of hydrogen peroxide as an oxidant agent. Although high resin removal efficiencies were achieved, there was a significant decrease in the mechanical properties of the recovered fibres, apparently due to oxidation of carbon fibre surface. Compared to our previous study with supercritical water, EG enabled us to remove almost all the resin from the waste, without using any other catalyst or reactive agent, thus preserving the mechanical properties of carbon fibre. When alcohols such as ethanol, methanol and 1-propanol used, even at higher temperatures than 400^{o}C, high resin removal could not be achieved, the addition of catalysts was required, as reported by Pinero-Hernanz et al. [11]. They used alkalis (KOH and CsOH) as catalyst and achieved 85% of resin removal when 1-propanol was used as solvent, in 15 minutes of reaction time. Also EG successfully depolymerised the resin at zero residence times, which is a further advantage in comparison to the alcohols. The recovered carbon fibres were analysed by a scanning electron microscopy to compare the surface properties with the virgin carbon fibre (Figure 1). In Figure 1(a), the virgin carbon fibre sample is shown and the image of the carbon fibre recovered from the treatment with ethylene glycol only at 400 °C, in Figure 1(b), shows that the surface of the fibre is very similar to virgin fibre. The surface is almost resin free, and no cracks or fissures are observed on the recovered carbon fibre surface. When the reaction temperature was decreased to 380 °C, there was a decrease in resin removal as shown by some resin remaining on the carbon fibre surface seen in Figure 1(c). At the same temperature, when the reaction time was increased to ten minutes, more resin was removed from the carbon fibre surface but still, it can be seen from Figure 1(d) that on the recovered carbon fibre surface, some resin debris remained. The FTIR analysis of the recovered carbon fibre at 400^{o}C in EG/water mixture (EG/water ratio=5) and the virgin fibre also show that the recovered carbon fibre surface has a similar structure, as given in Figure 2.

In the Figures 1(e) and 1(f), the images of carbon fibre reclaimed from the depolymerisation with the ethylene glycol/water mixture are shown. When the ethylene glycol/water ratio was 5, the recovered carbon fibre surface looked similar to that recovered with ethylene glycol alone at 400 °C. The mechanical properties of both reclaimed fibres are similar, with a slight decrease when the ethylene glycol/water mixture was used.

3.2. Processing of the Residual Liquid Product

3.2.1. Liquid-liquid extraction results

The residual liquid product was analysed to determine whether the liquid could be used as a source of chemicals, either to recover the resin monomer or other high concentration/high value compounds. Therefore, liquid products obtained from the depolymerisation of the carbon fibre reinforced plastics were analysed to determine their composition using GCMS/MS analysis. For the GC/MS/MS analyses, extraction with dichloromethane was applied to separate the water fraction from the organic fraction. In our previous work, the extraction was achieved successfully by making pH adjustments during the extraction to separate phenol and aniline compounds [20]. The GC/MS/MS chromatograms obtained from the analysis of the alkaline and acidic extracts of the residual liquid products using water only as solvent at 400 °C, are shown in Figures 3(a) and 3(b), respectively. The alkaline extract contained aniline, methyl aniline, quinoline and phenyloxazole, apparently from the decomposition of the polybenzoxazine-based resin, whereas the acidic extract showed mainly the presence of phenol and methyl phenols.

However, when ethylene glycol was used, it was a significant challenge to separate the organic compounds from the water soluble products with liquid-liquid extraction by using the same method; due to the miscibility of ethylene glycol and water; as well as the solubility of phenols and anilines, the main degradation products of the resin in both solvents. In the presence of ethylene glycol, the decomposition and polymerization of the ethylene glycol solvent occurred during the depolymerisation process as confirmed by the GC/MS/MS chromatograms shown in Fig. 4a and 4b. Although the same acid and alkaline extraction method was applied, total recovery of the organic compounds could not be achieved, as only a small peak corresponding to phenol was found in the acidic extraction while no aniline was detected in the alkaline extract. Instead, products due to the reaction (including polymerization) of the ethylene glycol were obtained. Table 5 presents a list of compounds detected from the chromatograms in Figures 3 and 4. From this table it can clearly be seen that compounds from ethylene glycol dominated the DCM extracts of the residual liquid product from ethylene glycol-treated carbon fibre reinforced plastics. While dioxolanes, dioxanes and diacetates were detected, which are the main organics produced from the cyclization and poly-condensation reactions of EG, phenols and anilines were the major products when only water was introduced into the reaction. The apparent increased solubility of phenols and anilines in ethylene glycol meant that only a small proportion of phenol was extracted into DCM, while no anilines could be extracted.

In addition, there was experimental evidence of the decomposition of ethylene glycol into gas as determined from the product gas analysis results. There was an increase in the yield of ethene in the gas products from ethylene glycol treatment compared to the experiments with water. For instance, the yield of ethene in the gas when the water alone was used for the depolymerisation, was only 0.4 mol%; while in the experiment with ethylene glycol and water mixture at a ratio of 5, it was 48.3 mol%.

3.2.2. Catalytic SCWG of liquid products

As shown above, the use of ethylene glycol as a solvent for the removal of resin from carbon fibre reinforced plastic waste resulted in high resin removal and the recovery of clean, mechanically well-preserved carbon fibres. However, the reaction of ethylene glycol resulted in many organic compounds in the residual liquid product, and recovery of the resin monomers proved extremely difficult. Therefore, designing a process to use the liquid residual product as a source of chemical feedstock may not be cost-effective. In addition, disposal of the liquid residuals as a waste stream, will have both cost and environmental implications for the process. Also, due to its physical properties such as viscosity, and equal C/H/O ratio, EG was considered as a model substance for pyrolysis oil yielded from biomass [26]. Vlieger et al. stated that supercritical water gasification of EG is a promising technique to produce H_2 rich gas from EG with the help of Pt as catalyst [27]. Therefore, the conversion of the residual liquid product into a useable form of energy for the process through hydrothermal gasification to produce hydrogen- and methane-rich fuel gas was investigated.

The liquid products were subjected to non-catalytic supercritical water gasification and also gasification in the presence of two different catalysts, sodium hydroxide and ruthenium on an α-alumina support. For the experiments, the residual liquid product produced from the experiment which gave the highest resin removal was used, i.e., the 5:1 mixture of ethylene glycol/water. This sample was reacted in the presence of no catalysts and also with either NaOH or Ru/Al_2O_3 in the 75 ml reactor at 500 °C for a hold time of 30 min. The product distribution after gasification is shown in Figure 5 and gas compositions are shown in Figure 6. When no catalyst was present, 41 mol.% of H_2 yield was achieved. The remaining species in the gas were CO_2, CO and CH_4 with compositions 17 mol.%, 23.7 mol.%, 11 mol.% respectively. The other hydrocarbon gases, which are defined in Figure 6 as C_2-C_4 had a total of 7.40 mol.%. The high H_2 and CO content in the gas agrees with the work of de Vlieger et al. [22] who achieved 42 % H_2 and 20 % CO yield in the gas produced from 15 wt % pure ethylene glycol and water at supercritical conditions with the help of a Pt catalyst.

With the addition of 1.0 g of NaOH as catalyst at the same reaction conditions, the carbon in the feed was captured as Na_2CO_3, so that the CO formation decreased to yield 1.77 mol.% in the gas. This is suggested to be due to the enhancement of the water-gas shift reaction, converting CO to hydrogen and CO_2, which is captured as sodium carbonate [16]. Correspondingly, there is a large increase in the yield of hydrogen to nearly 60 mol% in the presence of the NaOH. The corresponding compositions of CO_2, CH_4 and C_2-C_4 hydrocarbons in the gas were 23.5 mol.%, 6.95 mol.% and 8.44 mol.%, respectively.

The effect of the presence of the Ru/Al_2O_3 catalyst on gasification of the residual liquid product was also investigated. The results (Figures 5 and 6) showed that the total gas yield was markedly increased in the presence of the Ru/Al_2O_3 catalyst and that the CH_4 yield increased to 53.7 mol.% while that of CO and H_2 decreased dramatically. This could be the result of methanation reactions, promoted by the addition of Ru/Al_2O_3 [28]. So if the aim is to produce CH_4 rich gas, Ru/Al_2O_3 can be a good preference. In the cases where no catalyst and addition Ru/Al_2O_3, there was no char/solid formation, while in the presence of NaOH, because of the Na_2CO_3 formation, there was solid formation.

In Table 4, yields of the product gases in moles per kg feed and the higher heating value of the gas produced are given. The highest HHV was obtained when Ru/Al_2O_3 was used as a catalyst. The average HHV of gases produced from those experiments are similar to that of a typical gas produced from biomass via supercritical water gasification, which is around 20 MJ/Nm^3 [29].

4.0 Conclusions

Depolymerisation of waste carbon fibre reinforced plastics in ethylene glycol at subcritical conditions achieved 92.1 % resin removal at 400 ^oC and also recovered the carbon fibres with similar mechanical properties to virgin carbon fibre. In the presence of water only, to achieve higher resin removal ratios, H_2O_2 was introduced to the reaction at supercritical conditions, which resulted in a dramatic decrease in mechanical properties of the recovered fibre, whereas when EG used with water, the mechanical properties were preserved. Higher resin removal was achieved compared to our previous work with only water; at zero residence time, when mixtures of ethylene glycol and water were used as solvents without any addition of a catalyst, at high ethylene glycol/water ratios. However, increasing the reaction temperature to 420 °C, resulted in char formation, which led to an apparent increase in the solid residue (char and carbon fibre) obtained. In addition, resin removal also decreased at lower ethylene glycol/water ratios. It was difficult to extract carbon fibre reinforced plastics degradation products from the liquid residuals during ethylene glycol treatments, due to their solubility and conversion of some of the ethylene glycol. An alternative treatment of the residual liquid product was via hydrothermal gasification at supercritical water conditions. It was shown that the residual liquid product could be gasified to produce either a hydrogen-rich fuel gas (60 mol.% of H_2) or a methane-rich fuel gas (53.7 mol.% CH_4), depending on whether a NaOH catalyst or Ru/Al_2O_3 catalyst was used respectively.

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Figure Captions

Figure 1: SEM images of virgin and recovered carbon fibre samples in relation to treatment in ethylene glycol (EG) and EG/water mixtures.

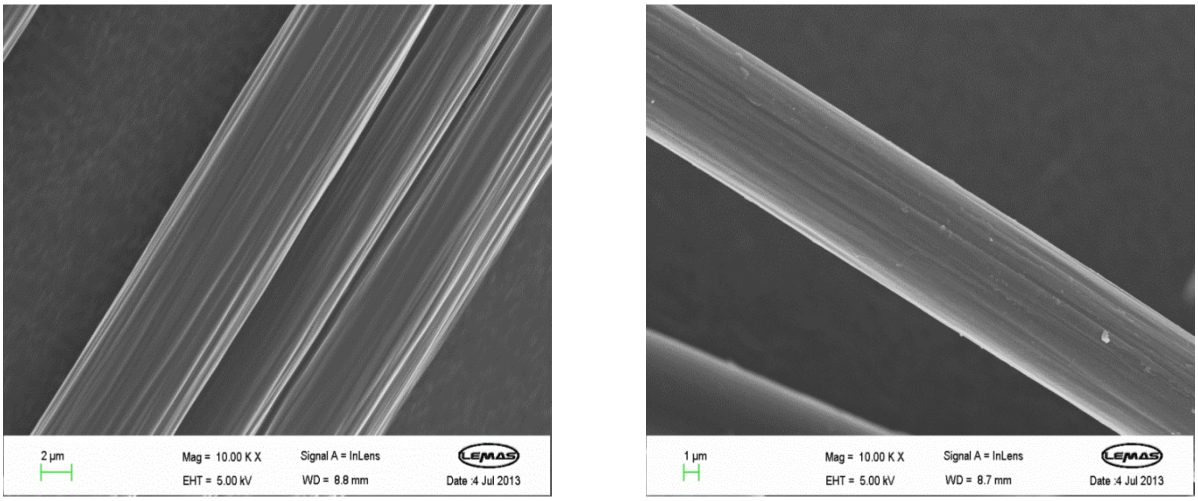
Figure 2: FTIR results (a) recovered carbon fibre at 400°C in EG/water mixture (EG/water ratio=5) (b) Virgin carbon fibre

Figure 3: GC/MS/MS chromatograms of extracts from the residual liquid products obtained during carbon fibre reinforced plastics depolymerisation at 400 °C with water only; (a) alkaline extraction (b) acidic extraction.

Figure 4. GC/MS/MS chromatograms of extracts from liquid residuals obtained during carbon fibre reinforced plastics depolymerisation at 400 °C with ethylene glycol only; (a) alkaline extraction (b) acidic extraction.

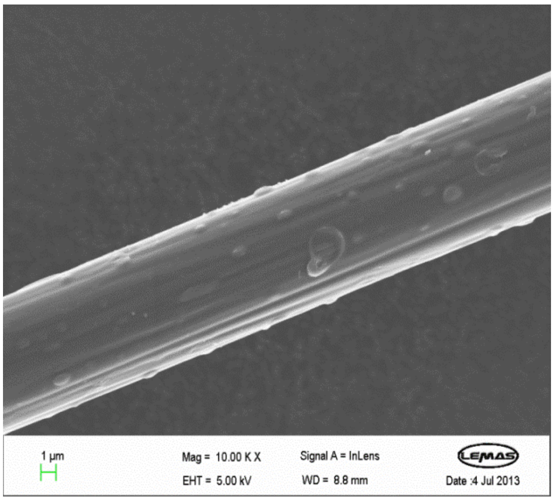
Figure 5. Product distribution after gasification of a sample of the residual liquid product.

Figure 6. **Gas composition after gasification of a sample of the residual liquid product.Figure 1**

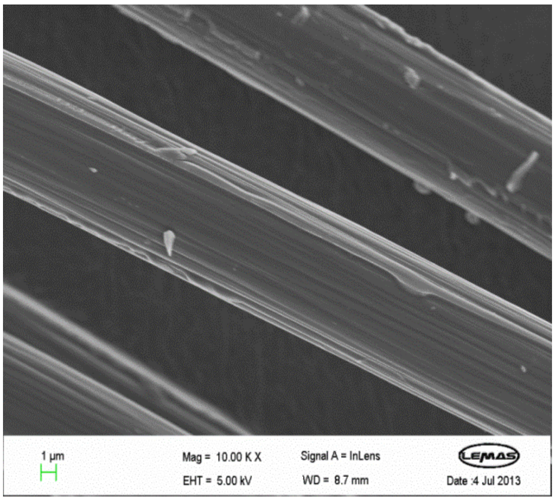


1(a): Virgin

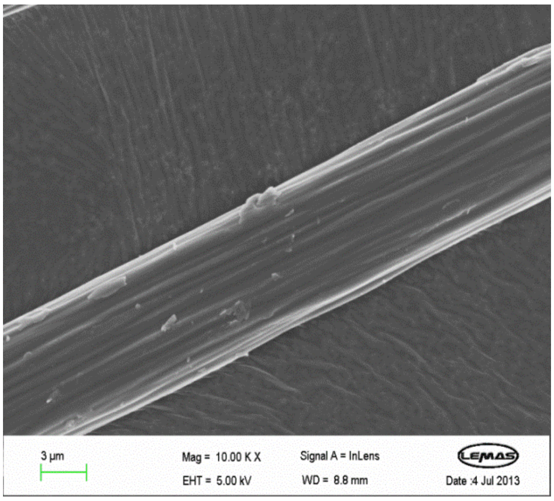
1(b): Recovered at 400 °C, in EG



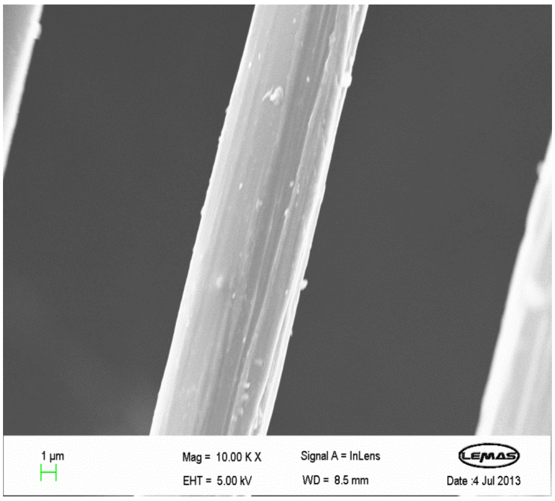
1(c): Recovered at 400 ^{o}C, in EG/water (ratio 5:1)



1(d): Recovered at 400 ^{o}C in EG/water (ratio 3:1)

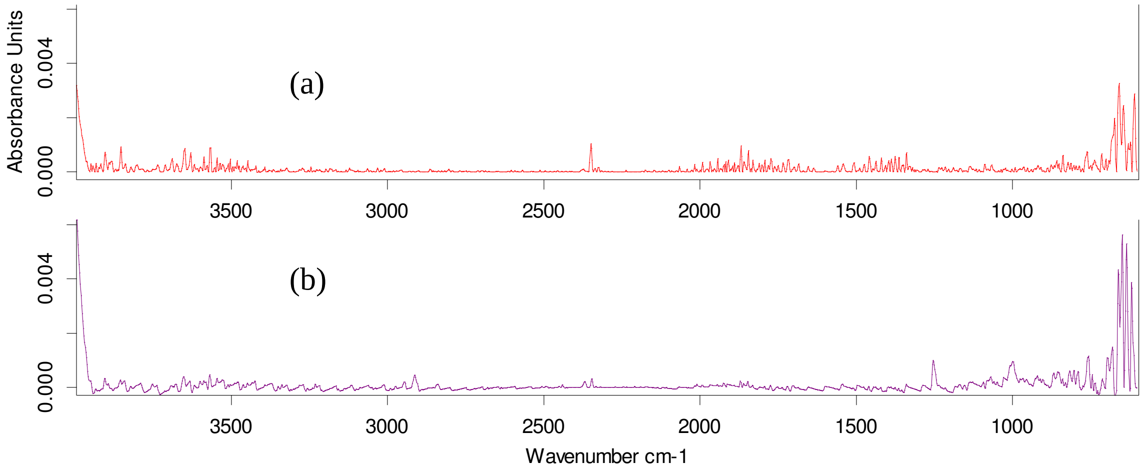


1(e): Recovered at 380 ^{o}C, in EG (t = 0 min)



1(f): Recovered at 380 ^{o}C, in EG (t = 10)

Figure 2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0.004
(a)
3500
3000
2500
2000
1500
1000
0.000
0.004
(b)
3500
3000
2500
2000
1500
1000
Wavenumber cm-1

Figure 3

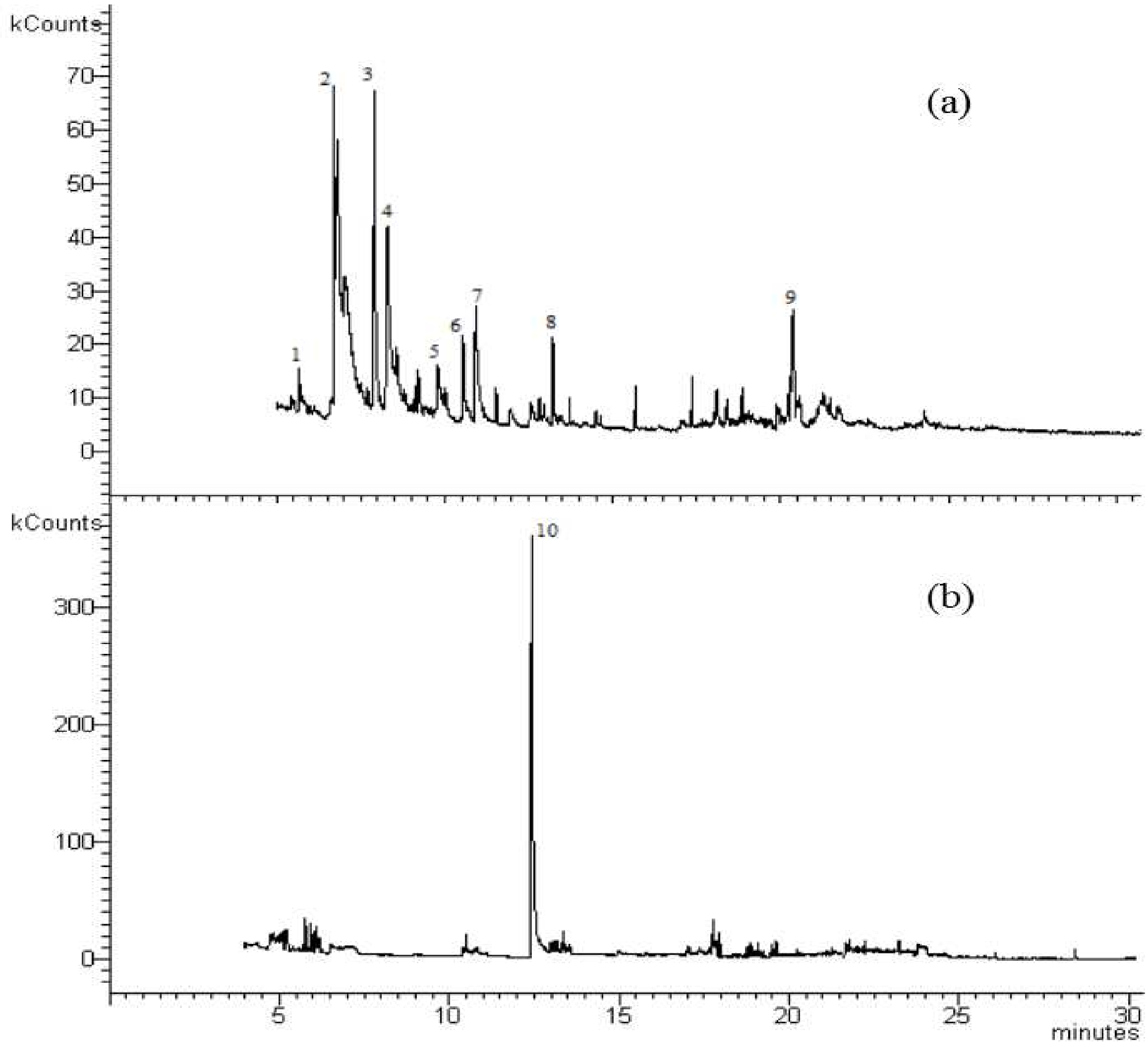
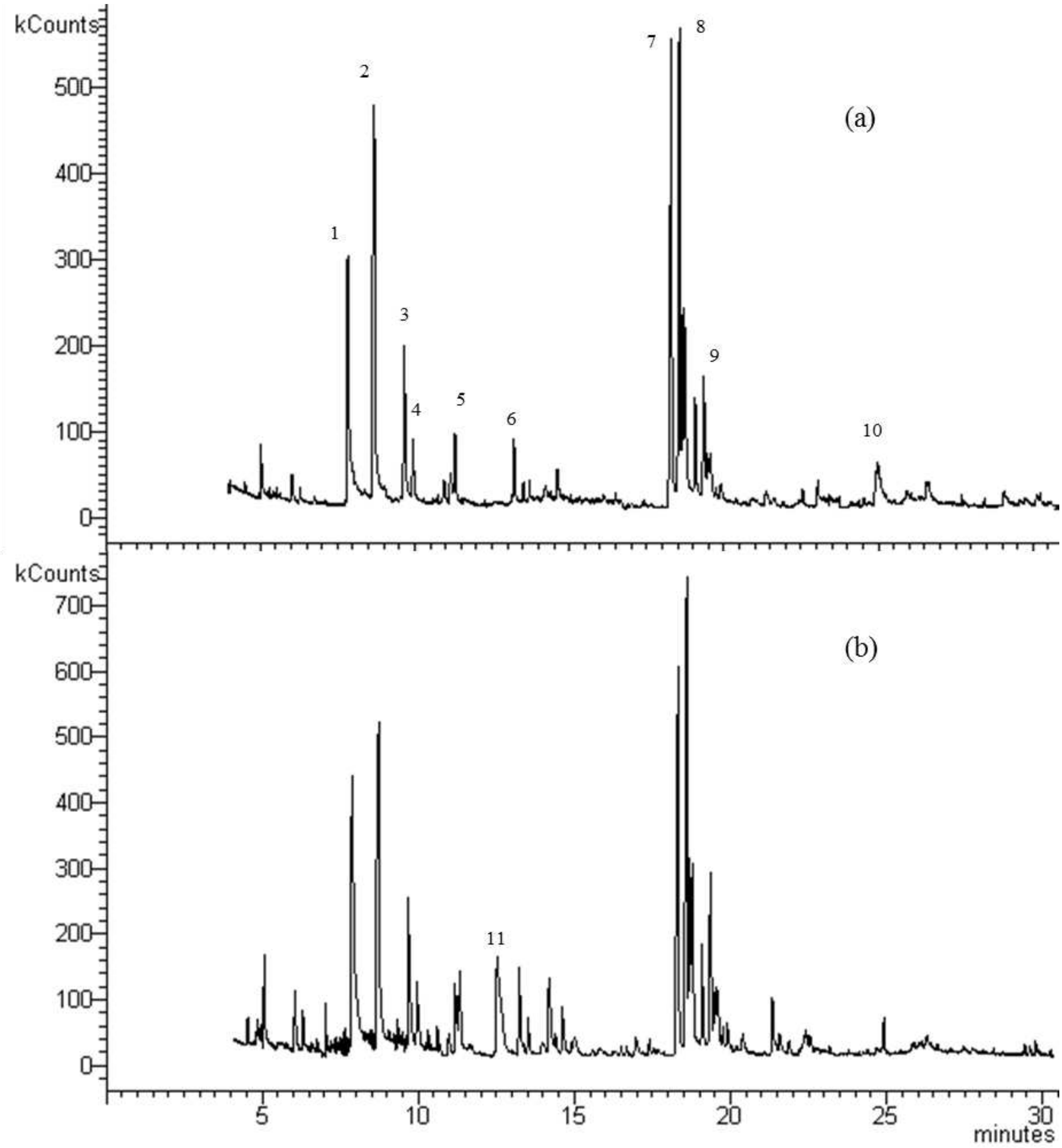

kCounts
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
(a)
kCounts
300
200
100
0
10
(b)
5
10
15
20
25
30
minutes

Figure 4


kCounts
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400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
(a)
kCounts
700
600
500
400
300
200
100
0
11
(b)
5
10
15
20
25
30
minutes

Figure 5

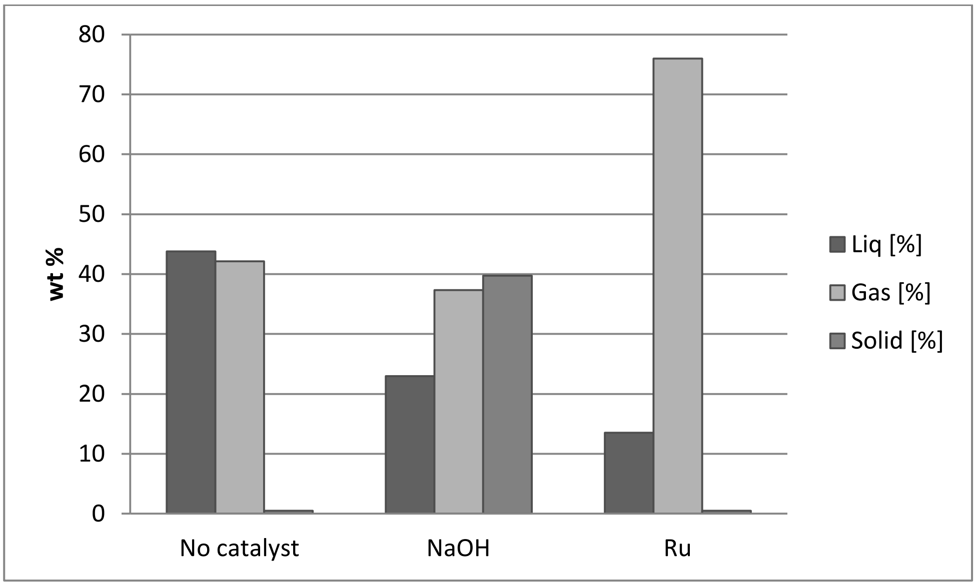


Figure 6

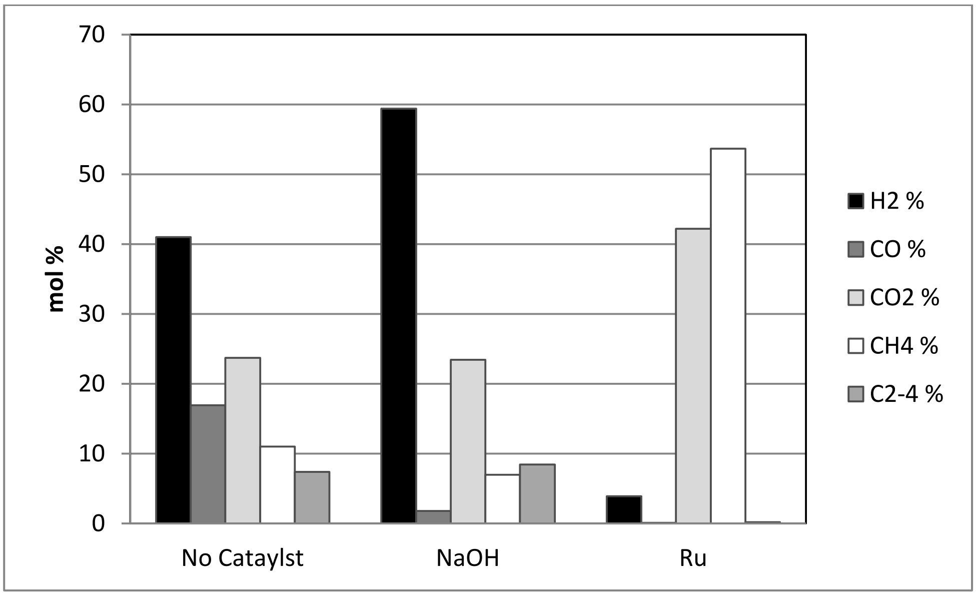


Table 1. The product distribution during depolymerisation of carbon fibre reinforced plastics waste in ethylene glycol

V_{EG} [ml]	T [^{o}C]	Time [min]	Resin Removal [%]
60	300	0	13.2
60	360	0	26.6
60	380	0	79.3
60	400	0	92.1
60	380	10	89.7

Table 2. The product distribution during depolymerisation of carbon fibre reinforced plastics waste in ethylene glycol (EG) /Water mixture

Sample No	EG/Water [ml/ml]	T [ºC]	Time [min]	Resin Removal [%]
1	5	380	0	94.2
2	5	400	0	97.6
3	5	420	0	90.4
4	3	400	0	95.2
5	3	420	0	90.4
6	1	400	0	73.8
7	1	420	0	75.2
8	0.33	420	0	66.5
9	0.2	420	0	67.3

Table 3. The mechanical properties of virgin and recovered carbon fibre

	Virgin Fibre	Recovered Fibre	
		1*	2**
Breaking Force [N]	0.135	0.138	0.131
Elongation [mm]	0.3	0.282	0.427
Tensile Strength [GPa]	3.5	3.56	3.4
Youngs Modulus	233	254.32	159.44

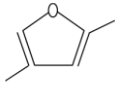
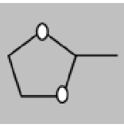
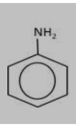
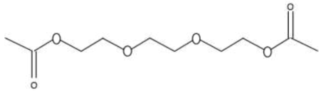
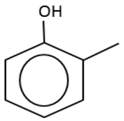
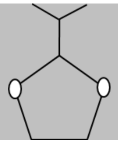
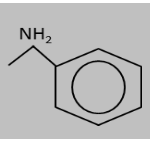
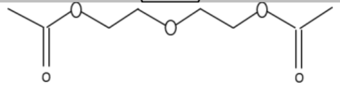
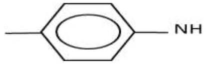
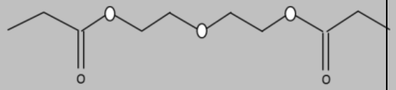
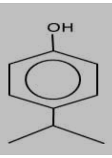
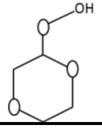
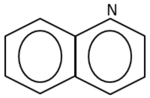
* Carbon fibre recovered during experiments at 400 °C in ethylene glycol

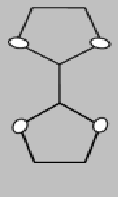
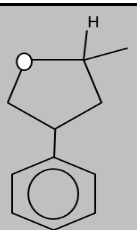
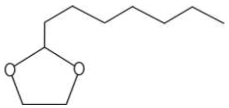
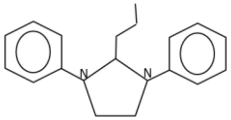
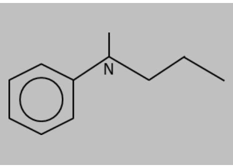
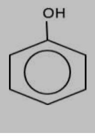
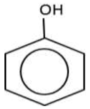
** Carbon fibre recovered during experiments at 400 °C in ethylene glycol/water (ratio = 5)

Table 4. The produced mol gas per kg CFRP waste from the gasification experiments

Sample No	Catalyst	H_2 mol/kg	CO mol/kg	CO_2 mol/kg	CH_4 mol/kg	$C_{2\text{-}4}$ mol/kg	HHV MJ/Nm^3
1	-	150.7	62.2	87.1	40.5	27.1	18.0
2	NaOH	250.3	7.5	98.8	29.3	35.6	17.3
3	Ru/Al_2O_3	18.8	0.5	203.8	259.4	0.8	22.0

Table 5. Main organic compounds detected in the liquid obtained from carbon fibre reinforced plastics depolymerisation at 400 °C, using ethylene glycol and water as separate solvents

	Organic compounds detected with ethylene glycol as solvent		**Organic compounds detected with water as solvent**	
S/N	Compound	Structure	Compound	Structure
1	1,1-Ethanediol diacetate		2,4-Dimethylfuran	
2	2-Methyl-1,3-Dioxolane		Aniline	
3	Ethanol, 2,2’-[1,2-ethanediylbis(oxy)] bis, diacetate		2-Methyl phenol,	
4	2-(1-Methylethyl)-1,3-Dioxolane,		N-Methyl, aniline	
5	Ethanol, 2,2’-oxybis-, diacetate		N,4-Dimethyl Benzenamine,	
6	Ethanol, 2,2’-oxybis-, dipropanoate		4-(1-Methylethyl) phenol,	
7	Hydroperoxide, 1,4-dioxan-2-yl		Quinoline	

8	2,2’-Bi -1,3-dixolane		5-Methyl-3-phenyl-1,3oxazolidine	
9	2-Heptyl -1,3-dioxolane,		1,3-Diphenyl-2-propyl Imidazolidine,	
10	N-(2-Hydroxyethyl)-N-methyl aniline		Phenol	
11	Phenol		-	-