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## Products obtained from decomposition of glass fiber-reinforced composites using microwave pyrolysis

**Summary** — The possibility to obtain useful products from used glass fiber-reinforced composites using microwave pyrolysis were examined. A scrap of blade from a wind turbine was fragmented and microwave-pyrolysed. The oil and gas formed during the pyrolysis were characterized by gas chromatography-mass spectrometry (GC-MS). The oil from pyrolysis consisted mainly of various aromatic compounds and had an energy content of about 36 MJ/kg. The main component of the gaseous products was methane. The glass fiber recovered after pyrolysis represented 70 % of the initial mass of glass fiber-reinforced plastic.

**Keywords:** microwave pyrolysis, recycling, glass fiber-reinforced composites.

PRODUKTY ROZKŁADU KOMPOZYTÓW WZMACNIANYCH WŁÓKNEM SZKLANYM OTRZYMANE ZA POMOCĄ PIROLIZY Z WYKORZYSTANIEM MIKROFAL

**Streszczenie** — Zbadano możliwości uzyskania użytecznych produktów z rozkładu odpadowych kompozytów wzmacnianych włóknem szklanym z wykorzystaniem pirolizy mikrofalowej. Pirolizie mikrofalowej poddano kawałki śmigieł elektrowni wiatrowej. Powstające podczas pirolizy gazowe i olejowe produkty scharakteryzowano za pomocą chromatografii gazowej sprzężonej ze spektrometrem masowym (GC-MS). Frakcja olejowa zawiera głównie różne związki aromatyczne i charakteryzuje się wartością opałową ok. 36 MJ/kg, co stwarza możliwość jej wykorzystania jako paliwa alternatywnego. Składnikiem tej frakcji jest również ftalan dimetylu o potencjalnej możliwości wykorzystania w syntezie poliestrów. Głównym składnikiem frakcji gazowej jest metan. Odzyskane podczas pirolizy włókno szklane stanowi 70 % początkowej masy kompozytu.

**Słowa kluczowe:** piroliza z wykorzystaniem mikrofal, recykling, kompozyty wzmacniane włóknem szklanym.

### INTRODUCTION

Glass fiber-reinforced plastics (GFRPs) are very versatile and offer a very good compromise between price and properties. Glass fiber-reinforced composites are therefore used in a wide range of different applications such as wind turbine blades, automotive applications, and boats. It has been estimated that the annual production of GFRP products in Europe amounts to 1.2 million tons [1].

Even though several attempts to recycle composites have been made, no commercial method of GFRPs recycling has been established. Between 2003 and 2005, the REACT project — with the participation of the Polish Industrial Chemistry Research Institute (ICRI) — was

established for the mechanical recycling of GFRPs, including wind turbine blades, whereby the material was ground and then re-used. After shredding, the fiber was upgraded with a reactivation method specially developed by ICRI [2].

From the environmental point of view, glass fibers are known to consume relatively high amounts of energy when produced. Thus, when composites are disposed of to land-fill sites after their lifetime, a large amount of energy is lost — related to both fiber manufacture and the matrix of organic polymer. Thus, it is desirable to develop methods for the recycling of GFRP composites. However, recycling of glass fiber composites is not very straightforward. When producing GFRP composites, thermoset resins are often used. The composites cannot therefore be re-melted, and it is more or less impossible to separate the matrix from the reinforcement. Several different methods to recycle GFRP composites have been evaluated. One possible way of recycling thermoset composites is energy recovery, and various methods have been evaluated [3–5]. This will recover the energy from the polymer matrix. However, despite many attempts to find a use for

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the glass fibers obtained after incineration, at the industrial level the remaining glass waste is often disposed of. Furthermore, some composites such as sheet-molding composites (SMCs) and bulk-molding composites (BMCs) often have an organic content of 25–30 wt. %, or even less than this [6, 7]. Energy recovery for such composites is therefore not an ideal solution. Another possibility is to pyrolyse the polymer matrix. Pyrolysis is a process whereby an organic material is heated in an inert environment and then decomposed chemically. The polymer matrix degrades into a hydrocarbon mixture. Recycling of composites by pyrolysis has already been examined in a number of studies [8–11].

As an alternative to conventional pyrolysis, the organic material can be heated and pyrolysed by means of plasma [12] or microwaves. Microwave pyrolysis [13] is a relatively new method that has not been studied in depth for composites. Heating by microwave radiation has the advantage that the composite is heated throughout the bulk of the material. Previously, studies on microwave pyrolysis have dealt with the pyrolysis of plastic waste [14], carbon fiber-reinforced composites [15], used engine oil from cars [16], and even biomass [17].

In the present study, we evaluated the possibility to recover the organic fraction from a glass fiber-reinforced composite with microwave pyrolysis. A wind turbine blade was used as a test example for assessment of the technique. There are an increasing number of used blades that ought to be recycled when smaller wind turbines are replaced with bigger ones [18]. It is therefore of considerable interest to develop recycling methods for wind turbine blades to meet this demand in the future.

In the present study, we fragmented a used wind turbine blade and pyrolysed it using microwaves. The hydrocarbon pyrolysis products were analyzed for chemical composition and energy content. Characterization and use of the glass fiber recovered has been discussed in a separate article [19].

## EXPERIMENTAL

### Materials

A scraped blade from a windcraft mill was used as a test object for microwave pyrolysis. The composite material in the blade was composed of glass fibers and an unsaturated polyester resin with balsa wood as a core material. Its inorganic content was about 70 wt. %. The blade was fragmented at the Stena Metall AB facility in Malmö, Sweden. This is a hammer mill, normally used to shred automobiles. In total, 8 tons of material were fragmented and the total processing time was 1.5 h. The material was sieved into three fractions of different fiber length: 0–7 mm, 7–30 mm, and more than 30 mm. The medium-length fraction of glass fiber recovered (7–30 mm) was used in this study.

### Microwave pyrolysis

Pyrolysis of the fragmented composites was carried out at temperatures ranging from 300 to 600 °C under a nitrogen atmosphere. All characterizations presented in this study were done for the products obtained from the pyrolysis carried out at 440 °C. The microwave-pyrolysis equipment is shown in Figure 1. A jar made of glimmer, transparent to microwaves, was placed inside the equipment. The temperature in the reactor was measured with a 3 cm-long temperature sensor. The temperature was controlled by adjusting the effect of the magnetrons. The process was controlled by a computer.

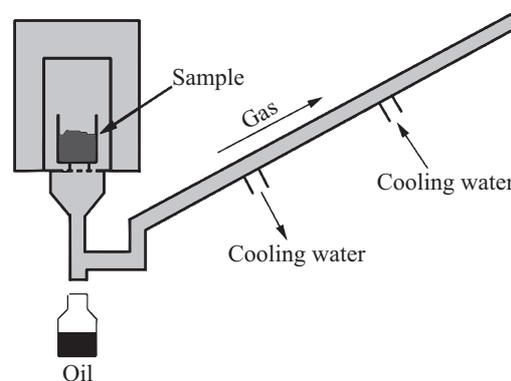


Fig. 1. Schematic outline of the experimental set-up for microwave pyrolysis

The equipment had a capacity of 10 dm<sup>3</sup> and a typical pyrolysis was carried on a 3 kg sample of composite. The microwaves were generated by means of three magnetrons, each giving an effect of 1 kW. The temperature in the reactor was monitored. The pyrolysis was interrupted after about 90 min, when the temperature in the reactor had started to decrease. The resulting oily residue from the pyrolysis was collected at the bottom of the reactor.

### Characterization of pyrolysis products

The residual pyrolysis oil was characterized by gas chromatography-mass spectrometry (GC-MS). The oil was dissolved in dichloromethane and injected into the GC-MS equipment. The compounds identified were quantified by an external calibration. The gas formed during the pyrolysis was sampled in a plastic bag and analyzed in a gas chromatograph equipped with a flame ionization detector.

Fractional distillation was performed using standard distillation set in the temperature range from 65 to 270 °C. 100 cm<sup>3</sup> of the post-pyrolysis oil was heated, followed by collection of a 10 cm<sup>3</sup> portion with the recording of characteristic end-of-fraction temperatures.

The energy content of the pyrolysis oil was determined by bomb calorimetry according to ASTM D4809. The

GC-MS analysis and the bomb calorimetry were done at an external research institute.

## RESULTS AND DISCUSSION

### The pyrolysis oil

Pyrolysis of 3 kg of composite yielded 0.5 kg of pyrolysis oil, 2.1 kg of solid residue, and 0.4 kg of gas. The pyrolysis oil was analyzed by bomb calorimetry and this test showed that the pyrolysis oil had a calorific value of 36.10 MJ/kg. This is a relatively high energy content, and one possible application for the oil is therefore to use it as a fuel. For comparison, the calorific value of diesel is roughly 44 MJ/kg [20] and most thermoset polymers have the calorific value of about 30 MJ/kg [21]. De Marco *et al.* pyrolysed an SMC composite and got the calorific value of about 37 MJ/kg [10]. Cunliffe and Williams [11] pyrolysed an unsaturated polyester resin reinforced with glass fiber. They obtained the calorific value of 33.6 MJ/kg. The microwave pyrolysis used in this study can therefore be said to give a roughly comparable result. The pyrolysis oil was also analyzed by GC-MS. The chromatogram is shown in Figure 2 and the components identified are listed in Table 1.

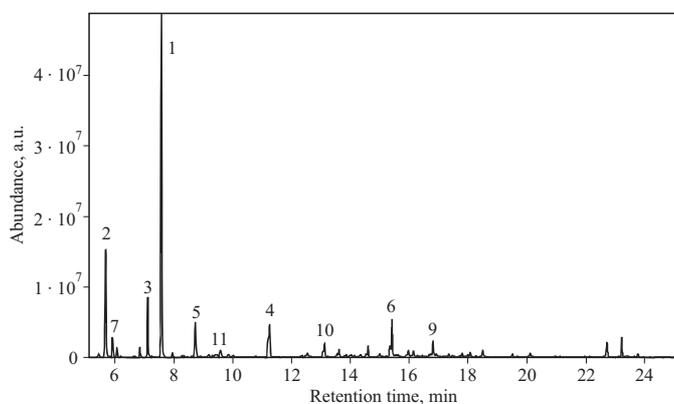


Fig. 2. Results of GC-MS analysis for the pyrolysis oil

The pyrolysis oil consisted mainly of various aromatic compounds. This is to be expected, since commercial resins such as unsaturated polyester resins and epoxy resins usually consist of aromatic compounds. These results are consistent with what other authors have found. For example, Cunliffe and Williams pyrolysed a glass fiber composite and found aromatic compounds in the pyrolysis oil such as styrene and  $\alpha$ -methylstyrene [11]. Torres *et al.* pyrolysed SMC composites at temperatures ranging from 300 to 700 °C, and the pyrolysis oils obtained were analyzed with GC-MS [22]. They found that the pyrolysis oils contained 64–68 % aromatic compounds. As can be seen from Table 1, no more than 34 wt. % was measured in the present study.

One possible explanation is that the oil contained compounds either with a lower or a higher boiling point than seen with the test method used. Possible uses of pyrolysis oils are to use them as a fuel or fuel components, to distil the oil in order to isolate valuable components, or conversion of the oil into synthesis gas.

Table 1. Chemical compounds identified in the pyrolysis oil using GC-MS analysis

Number in the chromatogram (according to Fig. 2)	Compound	Amount mg/g
1	styrene	150
2	toluene	60
3	ethyl benzene	30
4	naphthalene	25
5	$\alpha$ -methylstyrene	20
6	1,1'-(1,3-propanediyl)bis-benzene	15
7	2-ethyl-4-methyl-1,3-dioxolane	10
8	unidentified	10
9	phenanthrene	10
10	biphenyl	5
11	inden	5

In order to characterize components of different molecular mass fractional distillation was performed by collecting successive fractions, each of which constituted 10 vol. % of oil used for distillation (Table 2). Starting at 65 °C, the first 10 vol. % fraction ended at 95 °C. The second 10 vol. % fraction ended at 128 °C. Next came two narrow fractions at 140 °C followed by 143 °C. A total of 50 % of the volume of the oil distilled at 161 °C. Next came three higher-boiling fractions at 231 °C, 240 °C, and 270 °C. The remaining 20 % of the volume was left as tar. The results of GS-MS analysis of the different fractions from fractional distillation showed that the main products were aromatic compounds. The first fraction consisted mainly of benzene, *o*-xylene, and 1,1'-(1,3-propanediyl)bis-benzene. The latter two compounds were the main components of the second fraction. Next, there was *o*-xylene and [2.2]paracyclophane. The fourth and fifth fractions contained mainly [2.2]paracyclophane but also toluene, ethylbenzene,  $\alpha$ -methylstyrene, and naphthalene. An important finding was that in the sixth fraction between naphthalene derivatives, one of the main products was dimethyl phthalate. The last two fractions contained a mixture of high molecular weight aromatic compounds.

An alternative to incineration of the oil would be to convert it into syngas (synthesis gas), consisting of hydrogen gas and carbon monoxide. Syngas is widely used in the chemical industry and has many applications [23].

**Table 2. Main components of individual fractions of post-pyrolysis oil obtained by fractional distillation**

Fraction number	Temperature range, °C	Main components of fraction	Content of the main component in given fraction, vol. %
1	65–95	benzene	10
		1,1'-(1,3-propanediyl)bis-benzene	26
		<i>o</i> -xylene	20
2	96–128	<i>o</i> -xylene	33
		1,1'-(1,3-propanediyl)bis-benzene	10
3	129–140	<i>o</i> -xylene	20
		[2.2]paracyclophane	60
4	140–143	[2.2]paracyclophane	50
		toluene ethylbenzene	10
		$\alpha$ -methylstyrene	20
		naphthalene	9
5	144–161	[2.2]paracyclophane	43
		ethylbenzene	10
		$\alpha$ -methylstyrene	8
		naphthalene	6
6	162–231	naphthalene	14
		naphthalenes derivatives	15
		dimethyl phthalate	32
7	232–240	high molecular aromatic compounds	
8	241–270	high molecular aromatic compounds	
X	tar residue		

### The gaseous products

The gas formed during the pyrolysis was sampled and analyzed by GC-MS. It was analyzed for its content of hydrocarbons up to the chain length of five carbon atoms. The results are given in Table 3. Methane was the predominant hydrocarbon. The test method used in this study detects hydrocarbons up to C<sub>5</sub>. Other gaseous products, which constitute about 85 vol. %, such as carbon monoxide, carbon dioxide, and nitrogen are not seen with this method but they would be expected to be present. Earlier studies have shown that pyrolysis of unsaturated polyesters can give a relatively low gross calorific

**Table 3. Composition of the pyrolysis gas (taking into account only hydrocarbons up to C<sub>5</sub>) determined using the GC-MS method**

Compound	Content
methane	10.0 vol. %
ethylene	3.5 vol. %
propene	0.8 vol. %
ethane	0.5 vol. %
acetylene	600 ppm
butenes	600 ppm
butane + isobutane	120 ppm
pentenes + pentanes	<50 ppm

value (GCV). Torres *et al.* pyrolysed SMC and found GCV value of between 13.9 and 16.4 MJ Nm<sup>-3</sup> [22]. The reason for the relatively low calorific values for the gases obtained from pyrolysis of unsaturated polyesters is that these gases usually contain high amounts of CO and CO<sub>2</sub>, where the high content of oxygen comes from the -COO- groups of the polyester.

### CONCLUSIONS

Microwave pyrolysis was used to recover organic materials from glass fiber-reinforced composites originating from used blades of a wind turbine. The pyrolysis will generate gas, oil, and recovered glass fibers. The gas was analyzed for hydrocarbons up to C<sub>5</sub>, and it consisted mainly of methane gas. The pyrolysis oil had relatively high energy content and consisted mainly of aromatic compounds. Some of them, such as dimethyl phthalate, could be easily separated by low-temperature crystallization and used as starting material for polyester synthesis. The glass fibers recovered could possibly be used to prepare new composites [19]. The future applicability of microwave pyrolysis will depend on whether useful products can be developed from the residual hydrocarbon oil from pyrolysis — and from the recovered fibers — at a reasonable cost. The pyrolysis oil can probably be used as a fuel in some industrial processes. The future use of microwave pyrolysis will also depend on its energy con-

sumption. Pyrolysis of 3 kg of composite consumed about 15 MJ of energy. This is a relatively high energy consumption. It is, however, difficult to draw any conclusions from these laboratory-scale trials, as the energy loss in such equipment is very high. A larger, continuous pilot plant is currently being constructed by Stena Metall AB in Sweden. When this pilot plant is ready, it will be possible to predict more accurately whether this technique for recycling of glass fiber-reinforced composites is economically feasible.

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