

CHARACTERISATION OF PHENOLIC RESIN FOR THE LARGE SCALE PRODUCTION OF STRUCTURED PHENOLIC RESIN DERIVED CARBONS.

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1. Introduction

Activated carbon monoliths have been developed into a number of new technologies including volatile organic chemical (VOC) recovery [1] and heated canisters for automotive fuel systems [2]. The process of creating these structured carbons has been well established [3]. Part of the production process is the carbonisation of phenolic resin, which typically sees weight losses in the region of 55%. This has implications for the large scale production of phenolic resin monoliths as large quantities of pyrolysis waste needs to be safely dealt with. A cost effective method of dealing with this waste is via condensation, which can capture up to 50% of the waste. Therefore, accurate characterisation of this condensate is necessary for safe disposal. Extensive work has been carried out into the characterisation of the products of pyrolysis of phenolic resin. It has been reported that these products typically include a range phenols and their derivatives [4]. This work was carried out using a phenol formaldehyde resin with a ratio of 1:5:1[3]. The formation of amines has not previously been reported as samples with nitrogen containing cross linking agents were not studied. Hexamethylene tetramine (HMT) is used as a curing agent during the production of activated carbon monoliths. The addition of HMT introduces nitrogen cross linking between the Novolak polymers [3].

2. Experimental

2.1 Materials

The materials under study were monolithic phenolic resins produced by MAST Carbon International Ltd. Each sample had an outer diameter of 30mm, CPI 700, wall thickness of 375 μ m and channel length of 750 μ m. These samples were extruded from a mixture of cured phenol formaldehyde resin 1:3:1 with hexamine as a cross linking agent. A spaghetti form of phenolic resin was also analysed, known as extrudate. This sample was formed using hexamine cured phenolic resin with the same precursor as above.

2.2 Procedures

The pyrolysis of each monolithic sample was carried out in a Carbolite tube furnace at 3 $^{\circ}$ Cmin $^{-1}$, under a carbon dioxide atmosphere with a flow rate of 0.5Lmin $^{-1}$. A B34 finger trap was used as the collection vessel with dry ice providing

cooling. The process flow diagram for the experiment is shown in fig 2.2.1.

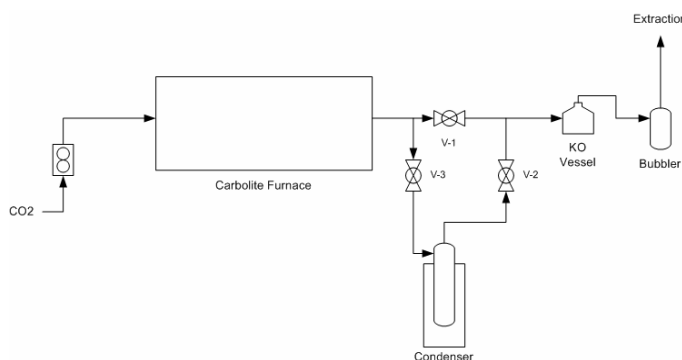


Fig 2.2.1 Process flow diagram

Valves 1, 2 and 3 were operated to direct the furnace off gas during processing. This allowed for the collection of pyrolysis products over a range of different temperatures.

Table 2.1 List of analysed samples

Sample No	Material	Temperature range of pyrolysis ($^{\circ}$ C)	Starting Weight (g)	Weight loss (%)
S1	Extrudate	0-800	25.1	55%
S2	Monolith	0-800	30.2	55%
S3	Monolith	200-300	27.8	6%
S4	Monolith	300-400	29.9	26%
S5	Monolith	400-500	30.1	38%
S6	Monolith	500-600	26.4	48%
S7	Monolith	600-700	28.8	54%
S8	Monolith	700-800	27.3	56%

2.3 Instrumentation

Gas chromatography–mass spectrometry (GC–MS) working in full scan mode (60-650 m/z) was used to analyze pyrolysis products in sample S1. A Trace GC 2000 Series gas chromatograph (ThermoFinnigan) equipped with an AS2000 autosampler coupled with a GCQ/Polaris ion trap mass spectrometer (ThermoFinnigan) was used. The separation was carried out in a BPX-Vol (cyanopropyl-phenyl polysilphenylene–siloxane) column (60 m \times 0.25 mm I.D., 1.4 μ m film thickness; SGE). The oven temperature program was 40 $^{\circ}$ C (held for 2 min) to 250 $^{\circ}$ C at 5 $^{\circ}$ C min $^{-1}$ and to 290 $^{\circ}$ C at 10 $^{\circ}$ C min $^{-1}$ (held for 10 min). Helium was the carrier gas at 1.2 ml min $^{-1}$. The transfer line and ion source temperatures were kept at 280 and 200 $^{\circ}$ C, respectively. The electron energy and the emission current were 70 eV and 250 μ A, in that order. Prior to injection, the analytes were extracted from the sample into hexane (5:1 v/v, respectively), and the organic phase was further diluted with hexane (1:20 v/v) prior to injection. Diluted sample (1 μ L) was injected in splitless mode for 1 min. The injector temperature was kept at 275 $^{\circ}$ C.

An ion trap (IT) and a time of flight (TOF) (Bruker Daltonics) equipped with syringe pumps were used to analyse samples S2 to S8. Electrospray was the ionization source in both instruments. The polarity of the electrospray was negative to detect phenol compounds, and positive when determining amines. Electrospray parameters were nebulizer gas 55 psi; dry gas 12 Lmin⁻¹; 360 °C. The acquisition mode was full scan between 15 and 500 m/z. Each sample was diluted with methanol (1/100) and infused together with methanol:water (50:50) in the MS at a total flow rate of 0.1 mLmin⁻¹, the proportion of sample and methanol:water solution being 1:5, respectively

3. Results and Discussion

Table 3.1 Compounds identified in sample S1 using GC-MS

Compounds	Identified with standard/retention time (min)	Library Search (NIST)	Peak Number
Toluene	16.6	+	1
m-xylene	20.6	+	2
Phenol	27.9	+	3
o-cresol	29.8	+	4-5
p-cresol	30.7	+	4-5
2,6-dimethylphenol	31.3	+	6-7
2,4 dimethylphenol	32.3	+	6-7
2,4,6-trimethylphenol	34.0	89%	8

Tentative identification of phenols was carried out infusing diluted samples into the MS systems. The identification was supported by the accurate mass acquisition performed with the TOF instrument. Additional evidence of their identity has not been obtained due to the lack of the fragmentation of the small-size phenols by tandem mass spectrometry. Separation of the phenols prior to the MS detection was not attempted. However, the tentatively identified compounds, listed in Table 3.2, are in agreement with the identification carried out with GC-MS. Moreover, dimers of trimethylphenol and trimers and tetramers of methylphenol have been detected.

Table 3.2 Phenols tentatively identified in sample S2 using LG-MS IT instrument

Compound	m/z ratio [M-H]-
Phenol	93
Methylphenol	107
Dimethylphenol	121
Trimethylphenol	135

LC-MS IT has tentatively identified a number of amino compounds listed in Table 3.3. These compounds are believed to be present in the pyrolysis gas due the presence of the hexamine curing agent.

Table 3.3 Amino compounds tentatively identified in sample S2 using LC-MS IT instrument

Compound	m/z ratio [M+H] ⁺
Ethylamine	46
Propylamine or 1-methylethylamine	60
Butylamine or 2-methylpropylamine	74

The compounds listed in table 3.2 and 3.3 have been found in samples 2-8 with different abundances, indicating different reaction kinetics and volatility. An example of this is shown in Fig 3.1 that records the evolution of three known species.

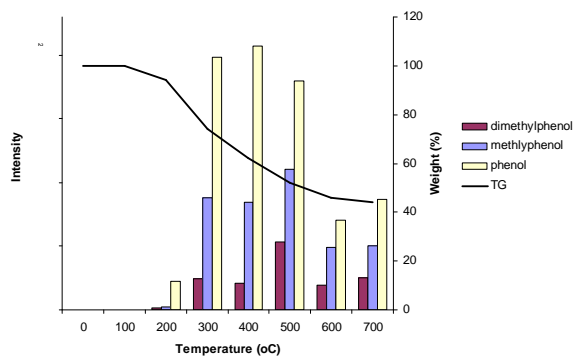


Fig 3.1 TG curve of sample with evolution of some known species

4. Conclusion

In this work, different phenolic compounds have been identified in the pyrolysis of phenolic resins and were found to be in agreement with previous work. In addition, short chain aliphatic amines have been tentatively identified in the pyrolysates by LC-MS, and further work will be carried out for their full identification. A condensation process can recover up to 50% of the waste generated during pyrolysis which in turn reduces the size of any subsequent effluent treatment equipment. All of the products identified in the condensate are listed in the Hazardous Waste (England and Wales) regulations 2005. Therefore, a large scale process must consider the safe management of waste streams.

References

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