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Pyrolytic and Elemental Analysis of Decomposition Products from a Phenolic Resin

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Summary: Research into elucidation of the decomposition mechanism of phenolic resin is being undertaken at the United Kingdom Defence Science and Technology Laboratory. In spite of the widespread use of phenolic resins the underlying decomposition mechanism is not yet fully understood. Central to understanding the mechanism is knowledge of the chemical products formed during the decomposition process and their respective quantities. Pyrolysis-gas chromatography-mass spectrometry and pyrolysis-Fourier transform infrared spectroscopy techniques have been developed to quantify the volatile organic compounds (VOCs), the permanent gases and water generated from the thermal decomposition of a phenolic resin. The VOCs and permanent gases that are produced during pyrolysis of phenolic resin have been identified. Quantitative analysis of the pyrolysis products has been undertaken and the initial results indicate that heating rate affects the composition of the products. Elemental analysis of the residue has been performed.

Keywords: FTIR; GC-MS; phenolic resin; pyrolysis

Introduction

Phenol formaldehyde resins are widely used in industrial applications and commercial products, however the underlying decomposition mechanism is not yet fully understood.[1,2] The decomposition products from phenolic resins are numerous and the mechanism complex. Consequently, analysis of the products is complicated and relating the evolution of products to events in the decomposition process even more so.

Studies of the effect of heating rate on the thermal decomposition of phenolic resin have been performed using thermogravimetric analysis (TGA).[3–10] TGA experiments on phenolic resin suggest that the residual weight percentage associated with the upper temperature of decomposition can be taken as a nominal 50%.[3] A limitation of TGA is the precise interpretation of the events on a TGA curve and their relationship with the chemical mechanism of solid state decomposition.[11] As a result complementary techniques are normally required to understand the mechanism and kinetics of solid state decomposition.

Research at the UK Defence Science and Technology Laboratory (Dstl) in collaboration with Imperial College London has therefore been initiated to develop understanding of the thermal decomposition mechanism of phenol formaldehyde resins using pyrolysis based experiments to complement TGA.

Fast pyrolysis techniques offer one possible way of obtaining information about the products formed during decomposition because breakdown of organic polymers produces lower molecular weight fragments that are more volatile and easier to analyse.[12,13] Exposure of a small sample of resin to a very high heating rate causes scission of the bonds. The high heating rates

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Published with the permission of the Controller of Her Majesty's Stationery Office used reduce the likelihood of secondary reactions and therefore the pyrolysis products are more likely to reflect the original structure of the polymer. The technique of analytical pyrolysis combined with gas chromatography and mass spectrometry is well established for the fingerprinting of cross-linked polymers as well as a tool for the investigation of the underlying chemical structure.[14] Part of the experimental programme also considered the effect of heating rate on the product composition and the associated elemental composition.

Pyrolysis of phenolic resins produces three classes of product: char, volatile organic compounds (VOCs) and permanent gases.[15,16] Three analytical techniques were selected to analyse the complex mixture of products. In one experiment the pyroprobe was coupled to a gas chromatograph and mass spectrometer (PY-GC/MS) to identify and quantify the VOCs. In another experiment the pyroprobe was coupled to a Fourier transform infrared spectrometer (PY-FTIR), which was used to identify and quantify the permanent gaseous products and water. The third experimental technique determined the elemental composition of the char following pyrolysis by elemental analysis for carbon, hydrogen and nitrogen (CHN) content with the oxygen content calculated by difference.

The three analytical methods were applied to the pyrolysis of a phenolic resin to identify and quantify the gaseous and condensable (VOC) products. The elemental composition of the charred residue was also investigated.

Experimental Part

Materials

SC1008 resole phenolic resin was procured from Momentive Specialty Chemicals Inc. (Louisville, KY, USA). Quartz boats (25 mm × 2 mm) and quartz tubes (25 mm × 2 mm) were purchased from Analytix Ltd. (Boldon, Tyne and Wear, UK). The following chemical reference standards were purchased from Sigma Aldrich Ltd. (Gillingham, Dorset, UK): benzene, o-cresol, p-cresol, 2,4-dimethylphenol, 2,6-dimethylphenol, phenanthrene, phenol, toluene, 1,3,5-trimethylbenzene, 2,4,6-trimethylphenol, 9*H*-xanthene, p-xylene and o-xylene. Methanol used for preparing analytical standards was purchased from VWR International Ltd. (Lutterworth, Leicestershire, UK). Dichloromethane used for preparing analytical standards was purchased from Fisher Scientific UK Ltd. (Loughborough, Leicestershire, UK). Acetanilide, benzoic acid, nickel sleeves (7 mm × 5 mm) and tin sample capsules (6 mm × 2.9 mm) were purchased from Exeter Analytical Inc. (Chelmsford, Massachusetts, USA).

Methods

A CDS 5200 pyrolyser (Analytix Ltd, Boldon, Tyne and Wear, UK) was used in trap mode with a Tenax TA^{TM} sorbent trap. The rest temperatures for the interface and trap were set at 50 °C. The trap desorb temperature was set to 280 °C for 2 min and the valve oven and transfer line held at 310 °C. Two standard methods were used: one for pyrolysis of resin (100 °C intervals from 100 °C to 800 °C; see Table 1 for pyroprobe and interface settings) and the other for analysis of the VOC standards. The latter method heated the pyroprobe to 250 °C at 20000 $°C \cdot s^{-1}$ and held it at this temperature for 15 s and the interface was heated to 310 °C and held at this temperature for 4.0 min. For resin heat treatment the pyroprobe was heated to 250 °C at 20000 $°C \cdot s^{-1}$ and held for 240 min. The interface was heated to 260 °C and held for 242 min.

Four types of experiment, detailed below, were performed for both PY-GC/MS and PY-FTIR. In each case the resin sample was pyrolysed at 100 °C intervals from 100 °C to 800 °C in a helium atmosphere. Analysis of the pyrolytic products (VOCs or permanent gases) was performed following pyrolysis at each temperature. Untreated resin refers to the as received cured phenolic resin.

(i) Untreated resin; heating rate = 20000 $°C \cdot s^{-1}$

Table 1.
Pyroprobe and interface parameters for pyrolysis of resin.

Pyroprobe final temperature, °C	Pyroprobe heating rate	Interface final temperature, °C	Interface hold time, min
100	$20000\,°C \cdot s^{-1}$	110	2.0
	$20\,°C \cdot min^{-1}$		7.0
200	$20000\,°C \cdot s^{-1}$	210	2.0
	$20\,°C \cdot min^{-1}$		12.0
300	$20000\,°C \cdot s^{-1}$	310	2.0
	$20\,°C \cdot min^{-1}$		17.0
400	$20000\,°C \cdot s^{-1}$	310	2.0
	$20\,°C \cdot min^{-1}$		22.0
500	$20000\,°C \cdot s^{-1}$	310	2.0
	$20\,°C \cdot min^{-1}$		27.0
600	$20000\,°C \cdot s^{-1}$	310	2.0
	$20\,°C \cdot min^{-1}$		32.0
700	$20000\,°C \cdot s^{-1}$	310	2.0
	$20\,°C \cdot min^{-1}$		37.0
800	$20000\,°C \cdot s^{-1}$	310	2.0
	$20\,°C \cdot min^{-1}$		42.0

(ii) Untreated resin; heating rate = $20\,°C \cdot min^{-1}$
(iii) Resin heat treated in helium at 250 °C for 4 h prior to an experiment; heating rate = $20000\,°C \cdot s^{-1}$
(iv) Resin heat treated in helium at 250 °C for 4 h prior to an experiment; heating rate = $20\,°C \cdot min^{-1}$

The heating rates indicated are those for the platinum coil in the CDS5200 pyroprobe and represent a maximum heating rate for a sample under the specified conditions.

Pyrolysis-Gas Chromatography-Mass Spectrometry (PY-GC/MS)

Resin was prepared by shaving pieces from a puck using a micro-plane. Samples were weighed in a quartz pyrolysis boat before analysis and after the final pyrolysis event. Sample mass (100–600 μg) was chosen such that products could be identified without overloading the analytical system. A microbalance (Mettler Toledo XP2U) was used to weigh samples. Pyrolysis of the resin was carried out using a CDS 5200 pyroprobe directly connected to the GC/MS system via a heated transfer line.

GC/MS analysis of VOCs was performed on a PerkinElmer AutoSystem XL gas chromatograph coupled to a PerkinElmer Clarus 560S mass spectrometer (PerkinElmer, Seer Green, Buckinghamshire, UK). Separation was performed on a Zebron ZB-1701 chromatographic column (dimensions 30 m × 0.25 mm ID × 0.25 μm film thickness). The carrier gas was helium and a constant pressure of 8 psi was applied. Split mode was used with an injector temperature of 310 °C. The oven temperature program was 45 °C for 4.5 min, $10\,°C \cdot min^{-1}$ to 130 °C, hold for 3.0 min, $10\,°C \cdot min^{-1}$ to 280 °C, hold for 2.0 min. The total run time was 33.0 min. Mass spectrometric detection was performed with electron impact (EI) ionisation at 70 eV in full scan mode (m/z 34-450) with a solvent delay of 2.0 min. The source temperature was 230 °C and the inlet line temperature was 280 °C. Analysis of the pyrolytic products was performed following pyrolysis at each 100 °C interval (100 °C to 800 °C).

Quantification was performed against two composite standards of compounds identified as VOC products from the pyrolysis of SC1008 resin (Table 2). Benzene and toluene were prepared as a separate standard due to lower sensitivity in the mass spectrometer compared to the other compounds. Stock solutions of each component were prepared in methanol at a concentration of $50\,mg \cdot mL^{-1}$ with the exception of benzene, toluene, 9*H*-xanthene and phenanthrene which were

Table 2.
Compounds in Mixed Standards 1 and 2 for VOC quantitation.

Mixed Standard 1	Mixed Standard 2
p-Xylene	Benzene
o-Xylene	Toluene
1,3,5-Trimethylbenzene	
Phenol	
o-Cresol	
p-Cresol	
2,6-Dimethylphenol	
2,4-Dimethylphenol	
2,4,6-Trimethylphenol	
9*H*-Xanthene	
Phenanthrene	

prepared in dichloromethane. Working solutions of Mixed Standard 1 in methanol were prepared at 0.1, 0.5 and 2.5 mg · mL^{-1} from the stock solutions. Mixed Standard 2 solutions in dichloromethane were prepared at 0.5, 2.5 and 10 mg · mL^{-1}.

Calibration curves were generated by dispensing aliquots of the mixed standards (Table 3) into a quartz pyrolysis boat and analysing by PY-GC/MS. Peak areas for each compound were plotted against mass loading (μg). Quantities for each of the VOC products produced by pyrolysis of SC1008 resin were calculated by comparison of peak area for an observed component to the respective calibration curve.

Pyrolysis-Fourier Transform Infrared Spectroscopy (PY-FTIR)

Resin was prepared by crushing with a pestle and mortar. Fragments of resin were placed inside a quartz pyrolysis tube and held in place by plugs of quartz wool. Pyrolysis of the phenolic resin was carried out using a CDS Analytical Brill Cell^{TM} controlled by a CDS 5200 pyroprobe (Analytix Ltd, Boldon, Tyne and Wear, UK). The Brill Cell was held at 250 °C with the exception of the analyses involving pyrolysis to lower temperatures, where the Cell was held at an appropriate lower temperature. Analysis of the volatiles of interest: water, methane, carbon dioxide and carbon monoxide was performed using a Thermo-Nicolet 5700 FTIR spectrometer (Fisher Scientific UK Ltd, Loughborough, Leicestershire, UK). It should be noted that hydrogen is also produced during decomposition of phenolic resin[15], but as it is not detectable by infrared spectroscopy this is not included in the analysis reported here. FTIR spectra were produced using a mercury cadmium telluride (MCT/A) detector, cooled by liquid nitrogen. For experiments in which the pyroprobe heating rate was 20000 °C · s^{-1} a single FTIR spectrum was acquired from 32 individual scans with a resolution of 4.0 after each pyrolysis event (100 °C intervals from 100 °C to 800 °C). At the slow heating rate (20 °C · min^{-1}) FTIR spectra of the pyrolysis products were collected in a continuous fashion, each one produced by 16 individual scans, producing a series of spectra, each approximately 8 s and 2.7 °C apart.

Calibration curves for water and carbon dioxide were produced by thermally decomposing known masses of sodium hydrogen carbonate in the Brill Cell and recording the IR spectra. For carbon monoxide and methane known volumes of methane and carbon monoxide at atmospheric pressure were injected directly into the Brill Cell through a septum using a gastight syringe. The absorption bands for each of the gases were quantified and absorbance plotted against mass (mg). Quantities for each of the permanent gas products produced by pyrolysis of SC1008 resin were calculated by comparison of

Table 3.
Aliquot volumes for calibration of mixed standards 1 and 2.

		Standard concentration, mg · mL^{-1}		
		0.1	0.5	2.5
Aliquot volume, μL	Mixed Standard 1	1, 3, 6	1, 3, 6	1, 3, 5
	Mixed Standard 2	–	1, 3, 6	1, 3, 6, 9

absorbance for an observed component to the respective calibration curve.

Elemental Analysis

Elemental analysis (carbon, hydrogen, nitrogen) was performed using a CE-440 Elemental Analyser (Exeter Analytical Inc., Chelmsford, Massachusetts, USA). Elemental analysis was performed on samples of mass 1.6–1.8 mg in a helium atmosphere with a combustion oven temperature of 975 °C and reduction oven temperature of 620 °C. The purge time and combustion time were both set to 60 s. The combustion standard was acetanilide. Benzoic acid was used to calibrate the background nitrogen value.

Samples analysed were residues from each of the four experiments, as received cured resin, and heat treated resin (250 °C for 4 h in helium).

Results and Discussion

Initial qualitative studies identified the principal VOCs (Figure 1), permanent gases (carbon monoxide, carbon dioxide and methane) and water (Figure 2), produced during the pyrolytic decomposition of the phenolic resin.

The identified VOC products are consistent with the polymeric subunit of a phenolic resin and the observed products from previous research on pyrolysis of phenolic resin.[7,9,16]

PY-GC/MS Analysis of VOC Products

Quantitative data for the decomposition products observed by PY-GC/MS are shown in Table 4. The major VOC product observed for all experiments was phenol although phenol detected at temperatures below 300 °C is considered to be residual starting material present in the resin matrix following the resin curing process rather than from the decomposition process. Lower yields of each of the products detected at >0.2 Wt % were observed at the slower heating rate ($20\,^{\circ}C \cdot min^{-1}$) compared to the fast heating rate ($20000\,^{\circ}C \cdot s^{-1}$) for both the untreated and treated resin samples. This trend is also reflected in the total Wt % of VOCs. However, the total mass loss for the four experiments is comparable and this suggests that the formation of other decomposition products, either permanent gases or char, increase at the slower heating rate.

PY-FTIR Analysis of the Permanent Gases and Water

Quantitative data for the permanent gas products and water detected by PY-FTIR are shown in Table 5. The major product observed in each experiment was water although water detected at temperatures below 300 °C is considered to be sorbed atmospheric moisture and water produced during the resin curing process rather than from the decomposition process. This observation is consistent with the evolution of phenol detected during the PY-GC/MS experiments.

Table 5 shows the yield of the permanent gases and water are higher at the slower heating rate compared to the fast heating rate for both the untreated and treated resin samples. This is opposite to, and therefore consistent with, the data trend observed for the VOCs. However, the total mass loss for the four experiments is variable.

Comparison of VOCs and Permanent Gases

Comparison of the data in Table 4 and Table 5 for the VOCs and permanent gases reveals that the relative proportion of VOCs, the total evolved products and total mass losses are not consistent. Despite there being consistent trends between the PY-GC/MS and PY-FTIR data in relation to the proportions of VOCs and gases produced at slow and fast heating rates there are differences between the experiments that have an impact on the pyrolysis beyond the type of analytical instrumentation coupled to the pyroprobe as discussed below.

(i) Sample mass. PY-GC/MS requires a sample mass less than 1 mg compared to PY-FTIR which uses approximately 10 mg. The relative sensitivity

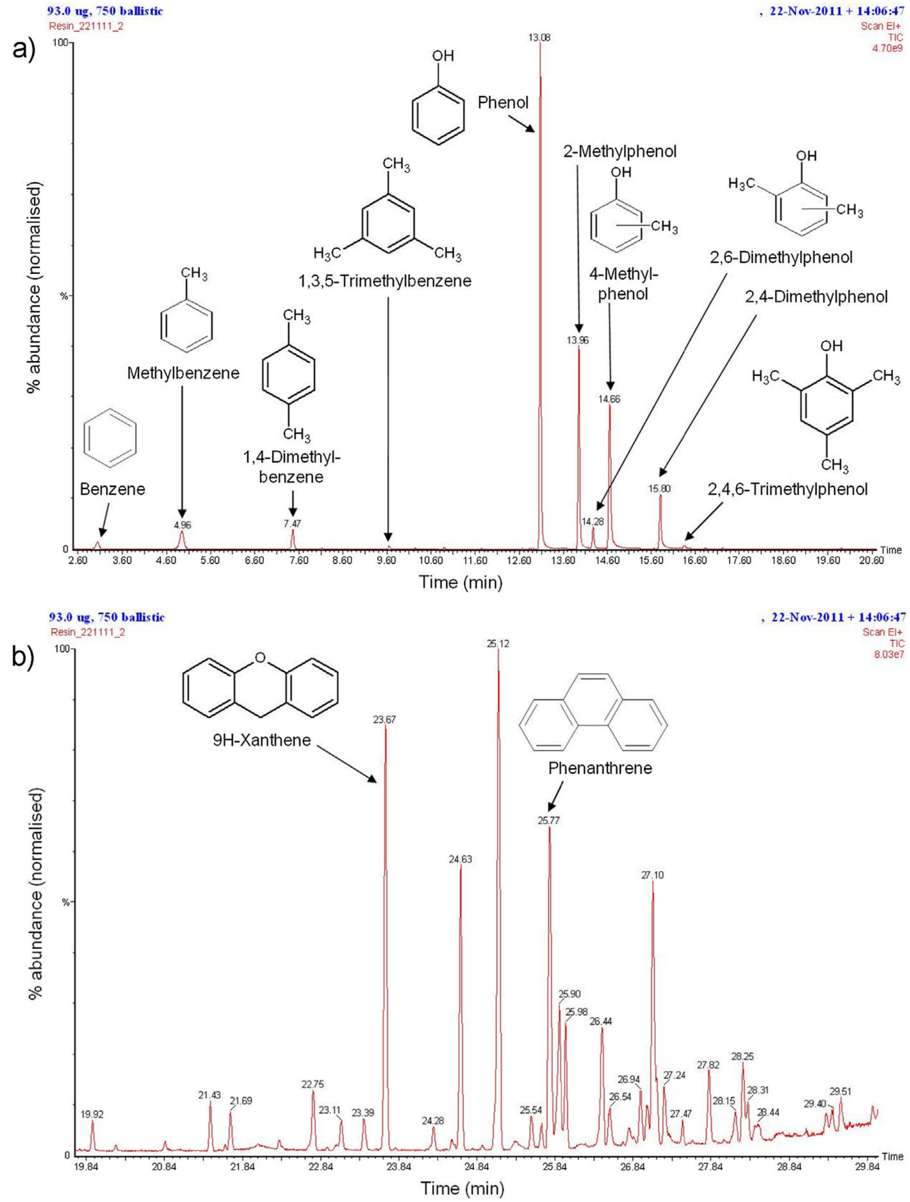

Figure 1.
Chromatograms of the identified VOC products from the pyrolytic decomposition of a phenolic resin, a) 2.6–20.6 min, b) 19.8–29.9 min.

of the detectors in the analytical techniques, mass spectrometry and infrared spectroscopy, necessitates this difference in sample masses.

(ii) Sample preparation. PY-GC/MS uses a single piece of resin shaved from a puck (using a micro-plane) in an open quartz boat (Figure 3a) whereas PY-FTIR uses resin ground in a pestle and mortar packed between quartz wool plugs in a quartz tube (Figure 3b).

(iii) Heating rate. This determines the length of each pyrolysis experiment.

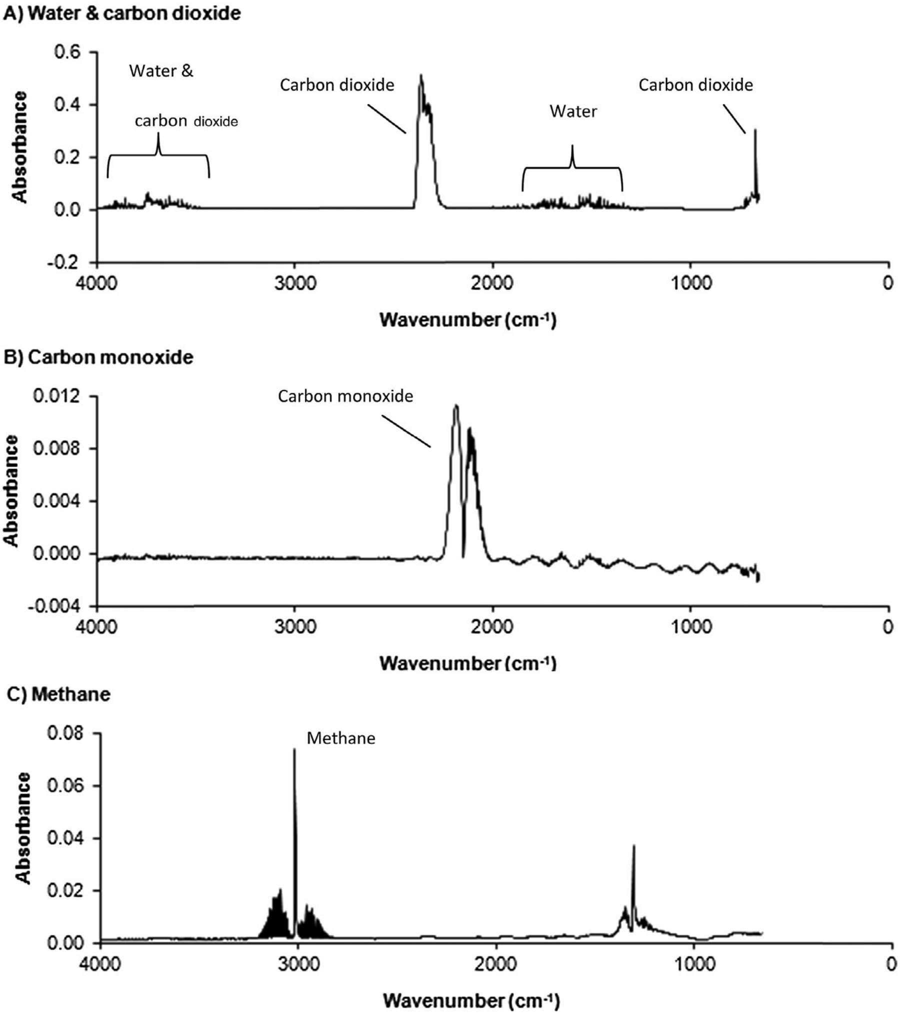

Figure 2.
IR absorbances of carbon dioxide, carbon monoxide, methane and water.

For example, the time taken to reach 200 °C at 20000 °C/s is 10 ms (0.01 s) compared to 10 min (600 s) at 20 °C/min. Therefore the difference in heating time differs by a factor of 60000 (600 s divided by 0.01 s). This means that the experiments heating at 20000 °C/s reach the temperature for each pyrolysis 60000 times faster compared to 20 °C/min prior to the hold time of 15 s once the temperature is reached.

(iv) Absorbance of moisture. There is the possibility that the samples may absorb atmospheric moisture when removed from the pyroprobe for weighing after each pyrolysis step. If absorbance of moisture does occur then it is likely to occur more readily for samples: (a) heated to higher temperatures as the formation of char results in an increased carbon content, and (b) with larger surface area, which in these experiments are the samples analysed by PY-FTIR. Both these factors will affect the recorded mass loss for PY-GC/MS and PY-FTIR.

Table 4.
Mean quantitative VOC data from PY-GC/MS analysis of the pyrolytic decomposition of SC1008 phenolic resin.

Product	Yield (Wt %)			
	Untreated, $20000\,^{\circ}C \cdot s^{-1}$	Untreated, $20\,^{\circ}C \cdot min^{-1}$	Treated, $20000\,^{\circ}C \cdot s^{-1}$	Treated, $20\,^{\circ}C \cdot min^{-1}$
Benzene	0.2	0.2	0.2	0.1
Methyl-benzene	0.4	0.3	0.4	0.2
1,4-Dimethyl-benzene	0.1	0.1	0.1	0.1
Phenol	10.1	6.1	8.4	4.7
2-Methyl-phenol	2.5	0.6	1.9	0.4
2,6-Dimethyl-phenol	0.5	<0.1	0.2	0.1
4-Methyl-phenol	2.5	0.6	1.8	0.4
2,4-Dimethyl-phenol	1.0	0.1	0.6	0.1
2,4,6-Trimethyl-phenol	0.2	<0.1	0.1	<0.1
Xanthene	<0.1	<0.1	0.1	<0.1
Phenanthrene	<0.1	<0.1	<0.1	<0.1
Total VOCs	17.5	8.1	13.8	6.1
Total mass loss	34.4	39.1	40.6	41.1

Table 5.
Mean quantitative data for permanent gases (excluding hydrogen) and water from the pyrolytic decomposition of phenolic resin.

Product	Yield (Wt %)			
	Untreated, $20000\,^{\circ}C \cdot s^{-1}$	Untreated, $20\,^{\circ}C \cdot min^{-1}$	Treated, $20000\,^{\circ}C \cdot s^{-1}$	Treated, $20\,^{\circ}C \cdot min^{-1}$
Water	17.2	25.9	13.9	19.7
Methane	2.1	3.1	2.3	3.2
Carbon dioxide	1.0	8.7	1.1	8.2
Carbon monoxide	2.0	3.2	2.0	2.9
Total gases + water	22.3	40.9	19.3	34.0
Total mass loss	44.5	36.1	41.7	35.3

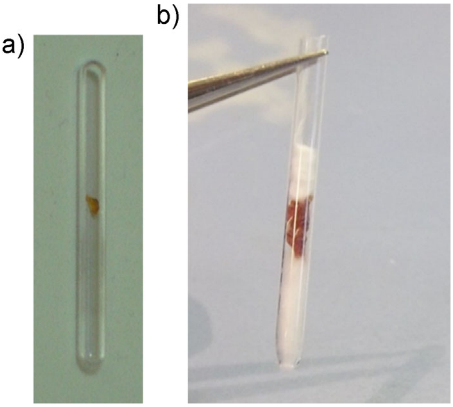

Figure 3.
a) Quartz pyrolysis boat containing a typical sample of SC1008 phenolic resin for analysis by PY-GC/MS; and b) SC1008 phenolic resin packed in a quartz tube using quartz wool plugs for PY-FTIR analysis.

All of these factors may contribute to differences in the heat and mass transfer rate through the respective samples. This in turn can affect the product composition. Ronsse and others,[6] have shown that pyrolysis conditions that affect mass transfer: for example sample size and particle size, can affect the composition of products in cellulose pyrolysis.

Elemental Analysis

Elemental analysis (carbon, hydrogen, nitrogen) was conducted on as received phenolic resin and char residue following pyrolysis of samples of phenolic resin. Oxygen content was calculated by difference and it was assumed that no other elements were present in the resin or the pyrolytic residue. The char residue

Table 6.
Mean elemental analysis data for char residues of each of the four pyrolysis experiments and as received resin.

Material	Experiment	%C	%H	%N	%O
Resin (as received)	No pyrolysis	75.52	5.92	0.33	18.23
Char	Untreated, 20000 °C · s^{-1}	89.06	3.92	0.21	6.81
	Untreated, 20 °C · min^{-1}	90.81	2.99	0.17	6.03
	Treated, 20000 °C · s^{-1}	90.83	2.99	0.19	6.00
	Treated, 20 °C · min^{-1}	89.97	3.40	0.20	6.43

analysed was taken from each of experimental conditions for the pyrolysis of SC1008 phenolic resin. The data presented in Table 6 show that the char formed in these experiments has a relative increase in carbon content of approximately 14% compared with the as received resin. A corresponding decrease in hydrogen and oxygen content is observed. Also of note is the low nitrogen content which is expected given the formulation of the cured resin from a condensation reaction using formaldehyde and phenol. The observed loss of oxygen and hydrogen are consistent with the production of VOCs and gases containing these elements leading to the enrichment of the char with respect to carbon content compared with the resin. The results also show that the elemental composition of the residue is similar across the heating rates used in these experiments.

The consistent composition of the char, irrespective of the experimental conditions for pyrolysis, suggests that the elemental composition of the total products observed for each of the experimental conditions is the same irrespective of the relative proportions of the products.

Conclusion

The VOC and permanent gas products and water formed during pyrolytic decomposition of a phenolic resin under four different pyrolytic conditions have been identified and quantified with the exception of hydrogen. The data demonstrate that the relative proportions of VOCs and permanent gases formed depend on the heating rate during pyrolysis.

The data from elemental analysis of the residue demonstrate a consistent elemental composition in the residues independent of the pyrolysis conditions for the four experiments performed in this research. Together with the differences in evolved product composition observed for the PY-GC/MS and PY-FTIR experiments this provides further evidence for the effect of heating rate on product formation from the same quantity of starting material.

Overall, further investigation is necessary (through more replicate experiments) particularly for PY-FTIR to increase confidence in the trends suggested by the data. Discrepancies between the observed data sets are also likely to be the product of employing two different sample preparative techniques. To overcome this limitation, an alternative approach whereby a single sample is analysed by two analytical techniques simultaneously would need to be employed. It is worth noting that such an approach would necessitate an alternative setup for the gas analysis as the Brill Cell does not allow the VOC products to be captured for analysis. In addition, the difference in sensitivities between analytical systems would require the PY-GC/MS method to use an increased split to enable the same pyroprobe and sample mass to be used for both GC/MS and FTIR. A further improvement would be to use an alternative analytical system, in place of FTIR, for separation and detection of the gases that allows detection of hydrogen, for example gas chromatography with thermal conductivity detection (GC-TCD). Finally, further analysis of the data will demonstrate conservation of elemental composition from the parent material to the gaseous and charred products.

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