Low temperature formation of aromatic hydrocarbon from pyrolysis of cellulosic materials

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Abstract

The major chemical pathways for production of aromatic hydrocarbons in the pyrolysis and subsequent flaming combustion of biomass materials are high temperature secondary reactions of the primary pyrolysis products. The second and less explored route is the evolution of aromatics from the solid substrate in the temperature range of 400–600°C. Primary chars that form around 300–400°C, depending on the starting material, continue to undergo pyrolysis up to temperatures of 600°C and higher. In this work, the formation of aromatic hydrocarbons from the second route was investigated for cellulosic materials. Experimental work was performed primarily using TG/DSC/MS. In order to reduce the formation of hydrocarbons from secondary reactions of the primary pyrolysis products, small sample size, i.e., 2 –10 mg, and a high helium flow rate of 150 ml/min, were used. Heating rates of less than 60°C /Min were used to ensure uniform sample temperature. Py/GC/MS confirmed the identities and relative quantities of masses detected by TG/DSC/MS. Under slow heating conditions, which are typical of thermogravimetric analyzers, simple hydrocarbon products begin to evolve above 350°C, where the primary decomposition of cellulosic materials has completed and the remaining char has begun the carbonization/aromatization process. Most aromatic products such as benzene, toluene, naphthalene, anthracene are detected between 400 to 600°C. Detectable products formed at temperatures above 600°C are methane, benzene, and hydrogen, and carbon monoxide. Some kinetic parameters for the formation of hydrocarbon products are deduced from the experimental findings and discussed in this presentation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Low temperature pyrolysis; Aromatic hydrocarbon; Cellulosic materials

1. Introduction

Formation of aromatic hydrocarbons is one of the major areas of interest in pyrolysis and combustion of fossil and non-fossil materials [1–9]. Decades of research on cellulosic materials have generated a wealth of knowledge and understanding on thermal degradation and chemical kinetics of these materials [10–25]. Nevertheless, work on the formation of aromatic hydrocarbons from these materials is very limited. The high temperature (e.g. >600°C) secondary cracking of primary pyrolysis products in the gas phase is considered to be the major pathway for producing aliphatic and aromatic hydrocarbons [16–21]. A second, but less studied route for aromatics formation that takes place at a moderate temperature (e.g. <600°C) is believed to be the evolution of aromatics from the solid char as it is formed and carbonized during the pyrolysis process. This second route may not be very important in flaming combustion, it may be of significant importance in the smoldering combustion

of solids [9] and in the processes used to flavor meat products using wood smoke [26–31].

It is well known that cellulosic materials in a low to moderate temperature range (e.g. below 400°C) rapidly undergo thermal degradation, forming a variety of permanent gases, a condensable liquid called tar, and a solid residue. The solid residue, primary char that is formed at low temperature, can undergo a chemical transformation at moderate to high temperatures (above 400°C) to produce a more stable and relatively ordered carbon structure [22–25]. This step does not represent a significant weight loss of material compared with the first decomposition step, it is very important in the formation of the primary carbon skeleton for the high temperature graphitization process. Furthermore, this second step may be an important route for the formation of volatile aromatic compounds during chemical transformation from low to high temperature char. While this route may not be important in the formation of aromatics at high temperature, it is believed to be of significant importance during the low temperature reactions in the smoldering combustion of solids.

Some of the ongoing research at Philip Morris USA is

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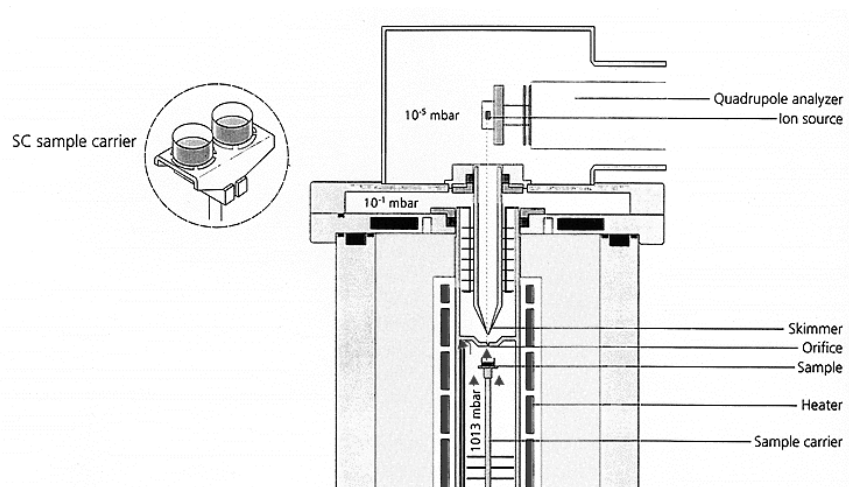*E-mail address:* mohammad.r.hajaligol@pmusa.com (M. Hajaligol).

Fig. 1. Schematic of the TGA/DSC/MS used in this study.

directed towards studying the significance of the low temperature route in the formation of aromatic hydrocarbons. Numerous articles report on the secondary pyrolysis of biomass primary products [16–21], but there has been little emphasis on the formation of aromatic hydrocarbons at low temperatures [26–31]. This is likely due to the lower probability of forming aromatic structures from pyrolysis of heavily oxygenated species at low temperatures. Furthermore, to the authors' best knowledge, there is little literature reporting this second pathway during pyrolysis [29–31].

In this paper we present experimental evidence for the formation of aromatic hydrocarbons during the low temperature pyrolysis of biomass components such as cellulose, hemicellulose, glucose and pectin. In order to eliminate the possibility of including gas-phase secondary cracking of the primary pyrolysis products, pre-charred samples of starting materials are separately prepared and pyrolyzed under identical conditions to the starting materials.

2. Experimental

The main experimental setup for this study is a TG/DSC/MS. A schematic of the reaction zone and sampling system is shown in Fig. 1. The carrier gas flows upward and around the sample pan and leaves the reaction zone quickly to evacuate the volatile products evolved from the reaction zone, thereby reducing the probability of secondary reactions of these volatile products. The sample probe for the mass spectrometer (MS) is located about 5 mm above the sample, in order to minimize the time lag between reaction time and sampling time. About 10 mg of pure material (or previously charred material) is heated in flowing helium (150 ml/min) at constant heating rates of 5–60°C/min. From this experimental data, we obtained temperature-dependent weight loss profiles, rate of weight loss, heat of reaction, and the evolution profiles of volatile products as determined by key masses monitored by the MS.

The second experimental setup used in this study is a Pyroprobe pyrolysis device interfaced to a GC/MS for analysis of volatile products. For these experiments, samples of about 1 mg of pure or previously charred materials are pyrolyzed in helium and the volatile products are swept into the GC/MS for analysis. The Pyroprobe samples are heated to the pyrolysis temperature at about 100°C/s and held there for 20 s. The charring temperature for the pure pectin and glucose are 300°C and for the cellulose is 360°C. The pyrolysis temperature for all the pre-charred samples was 900°C. The PP/GC/MS data was used to aid identification and relative quantification of the TG/MS results.

Starting materials are: (1) reagent grade D-glucose (Acros, less than 0.004% ash). (2) Practical grade citrus pectin (Acros, less than 1% ash and 70% esterification). (3) Hemi-cellulose (xylan) from a hardwood Birch xylan by Fluka comprised of 95% α-D-xylose units, with methyl glucuronic acid side-chain units and about 2.5% ash content. (4) Two forms of cellulose samples: the first cellulose sample is Whatman #41 filter paper (less than 0.007% ash), and the second is a griege (raw) cotton fabric from Wellington–Sears (duck #4, average 5000 ppm K). The latter cellulose sample is used to study the effects of inorganics that are known to affect cellulose decomposition reactions and char yield. Pre-charred samples of the above materials are prepared in a tube furnace in flowing helium (200 ml/min) heating at 20°C/min up to 360°C. To ensure the primary decomposition of the materials is complete, samples are held for 10 min at the final temperatures.

3. Results and discussions

In this section, we first discuss the thermogravimetric data of the pure cellulose, glucose, pectin, xylan and their
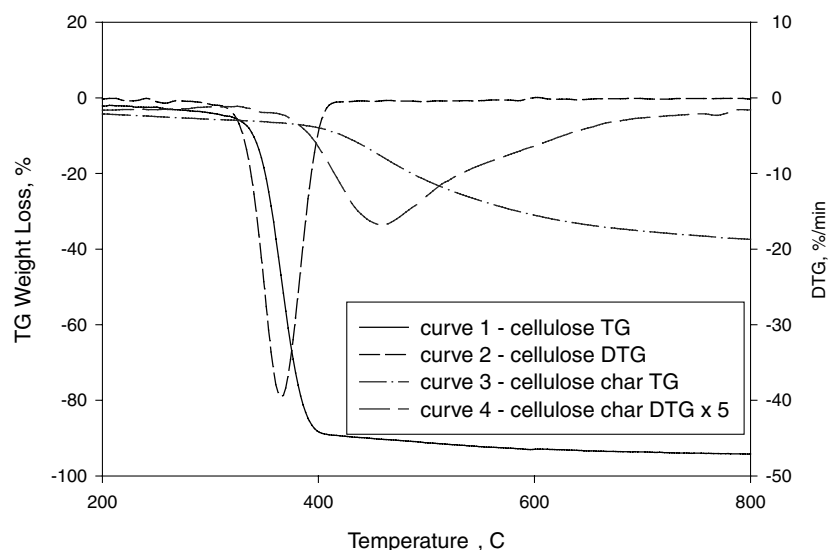
Fig. 2. Pyrolysis of cellulose and pre-charred cellulose samples.

corresponding pre-charred samples. We then discuss the evolution of aromatic hydrocarbons from the pre-charred samples.

3.1. Primary decomposition

Thermogravimetric data of cellulose and pre-charred cellulose are presented in Fig. 2. At a heating rate of about 20°C/min, cellulose rapidly decomposes between 300 and 360°C (Curves 1 and 2). Following this sharp weight loss, there is a gradual weight loss (about 5% of starting cellulose) up to about 700°C. This gradual weight loss can be more readily observed and detected as another step in decomposition if the pre-charred sample of cellulose is heated separately (Curves 3 and 4 in Fig. 2). As can be seen from Fig. 2, most of the weight loss for the pre-charred cellulose takes place between 350 and 700°C. The DTG data

provide two distinct T_{max}, one around 335°C for cellulose decomposition reactions and one around 420°C for the reactions in pre-charred sample. The latter T_{max} depends on the heating rate and the conditions under which pre-charred samples are prepared, and could be as high as 500°C. The decomposition of pre-charred cellulose has been cited in the literature as a small exotherm occurring after the larger endothermic decomposition [15,23]. Likewise, our data suggest that this second step reaction is thermo-neutral.

The presence of impurities is known to affect the decomposition pathways during cellulose pyrolysis [10–15]. As stated above, the pure Whatman filter paper decomposes in one sharp endothermic process starting at about 320°C and peaking at 365°C. This cellulose sample produces about 10% char at 400°C and about 5% char at 700°C. The impure cellulose used in this study is a raw cotton canvas with about 5000 ppm of potassium as well as other naturally occurring
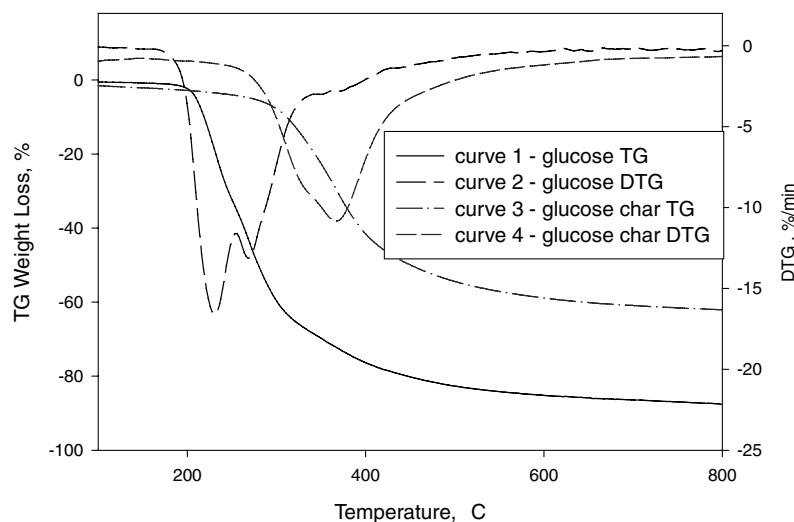

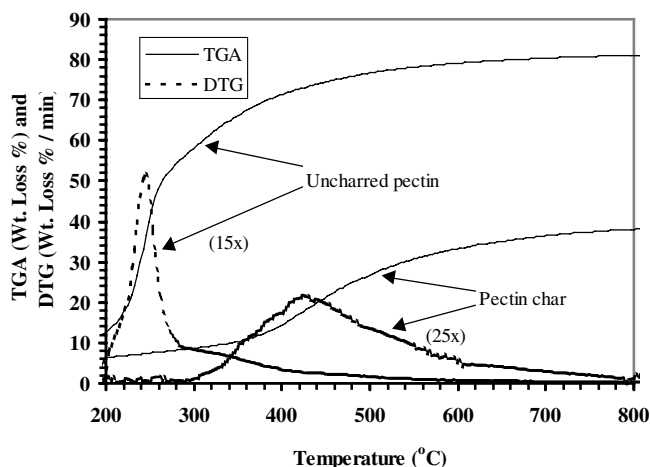Fig. 3. Pyrolysis of glucose and pre-charred glucose samples.

Fig. 4. Pyrolysis of pectin and pre-charred pectin samples.

inorganic species. The cotton peak decomposition was at about 355°C. The most notable differences between the two cellulose samples is that the cotton decomposition is less endothermic, approximately 100 J/g compared with approximately 470 J/g for the pure cellulose. The amount of char produced by the cotton is about 25% at 400°C and about 16% at 700°C, in comparison with 10 and 5%, respectively, at the same temperatures for the pure cellulose. The major products detectable by mass spectrometer for cellulose decomposition are H_2O, CO_2 and CO, as well as some aldehydes, furans, pyrones and other oxygen-containing products such as levoglucosan and other dehydrated sugar units. A notable difference in the MS profiles of the pure cellulose and cotton is a much higher ratio of mass 31 to mass 60 for the cotton, indicating much less levoglucosan (predominately mass 60) relative to mass 31 (probably mostly hydroxyacetaldehyde and methanol). This is consistent with previous literature [10–15,19–24] reports.

Glucose is the basic building block of cellulosic materials.

Under thermogravimetric conditions at a heating rate of 20°C/min, glucose undergoes major decomposition in the temperature range of 200–400°C with major decomposition peaks at around 230 and 270°C. The TGA data of glucose and its char are presented in Fig. 3. Glucose produces about 28% char at 400°C and about 15% char at 700°C (Curve 1). When pre-charred samples of glucose were heated, the major reactions (weight loss) took place above 400°C and continued to take place to above 700°C (Fig. 3, Curve 3). The major decomposition peak for this sample is around 380–400°C (Curve 4). The weight loss for the char sample is about 50% of the starting char, that translates into about 5% of starting glucose. The DSC data shows that glucose melts at about 150°C and undergoes some endothermic processes up to about 300°C. The major products of glucose pyrolysis detectable by the mass spectrometer are H_2O, CO_2, CO as well as furan and furfural and their derivatives.

The thermogravimetric data of pectin and pectin char are presented in Fig. 4. At a heating rate of 20°C/min, pectin rapidly decomposes around 250°C. Analogous with the observations for cellulose and glucose, the weight loss for pectin is not significant above 400°C. When pre-charred samples of pectin are heated, most of the weight loss takes place above 400°C. Comparison of the DTG data provides two distinct T_{max}, one for the starting pectin at around 235°C, and one for pre-charred sample at around 420°C. Approximately 50% of the char made at around 400°C is lost when the material is heated to 700°C. This mass loss corresponds to about 5% of the starting material. In contrast to the cellulose samples, pectin decomposition is not only less endothermic, but the endotherm is also followed by a small exotherm. Pectin undergoes primary decomposition above 200°C, corresponding to an endothermic reaction of about 90 J/g. The primary pyrolysis products of pectin are similar to glucose with the exception of increased amounts of methanol.
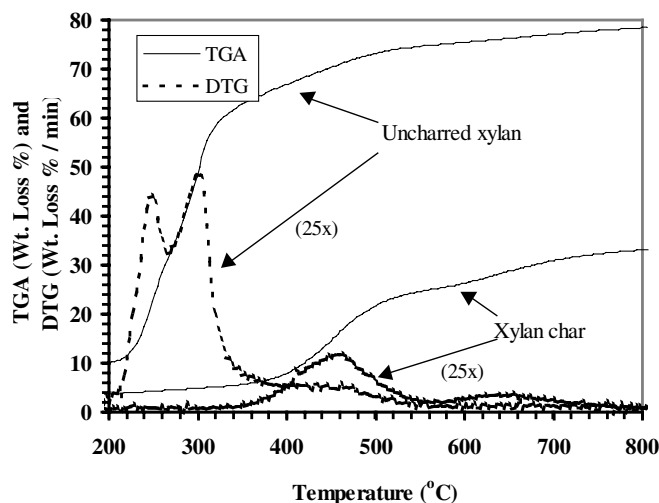

Fig. 5. Pyrolysis of xylan (hemi-cellulose) and pre-charred xylan samples.

Table 1
Elemental analysis of materials used in this study (% by weight)

	C	H	O	N	C/H	C/O	Ash
Cellulose	43.60	6.55	47.90	0.003	6.66	0.91	0.08
Cell-Char	61.33	4.83	29.77	0.003	12.7	2.06	0.12
Glucose	39.99	7.04	52.05	0.03	5.68	0.77	0.007
Glu-Char	50.03	4.84	33.32	0.03	10.34	1.5	0.04
Pectin	42.16	5.85	51.70	0.25	7.23	0.82	0.5
Pect-Char	64.27	3.98	27.89	0.57	16.15	2.30	0.95
Xylan	40.96	6.36	47.30	0.5	6.44	0.87	4.53
Xyln-Char	64.26	4.40	21.73	0.5	14.60	2.30	13.95
Cotton	43.37	6.56	47.43	0.24	6.61	0.91	1.43
Cott-Char	71.62	4.24	19.03	0.89	16.89	3.76	2.51

Weight loss data for xylan and its char at 20°C/min are given in Fig. 5. The xylan sample shows two distinct reactions below 300°C that can be seen from Curves 1 and 2 in Fig. 5. Similar to cellulose, glucose and pectin, the weight loss and corresponding rate of weight loss above 400°C are insignificant. However, when pre-charred samples of xylan are heated in helium at a 20°C/min heating rate, a reaction (or a series of reactions) can be observed to take place between 400 and 600°C, as well as another one above 600°C. The high temperature reaction(s) is believed to arise from the inorganic content of the xylan (2.5% ash content), as seen in Table 1. The endotherms and exotherms associated with the decomposition of the current sample of xylan are spread over a broad temperature range. We can conclude that an exotherm starts at around 150°C and ends near 300°C, which coincides with the completion of primary decomposition reactions. The major decomposition products are typical of carbohydrates such as aldehydes, ketones, methanol, furfurals and anhydrosugars, as well as CO, CO_2 and H_2O.

3.2. Hydrocarbon formation

Formation of aromatic hydrocarbons is more obvious from pre-charred samples of the above materials. Pyrolysis of previously charred samples eliminates the probability of including any secondary reactions of the primary products, as well as focusing on the temperature range where hydrocarbons evolve from these materials under the pyrolysis conditions in this study. Figs. 6–8 show the temperature dependence for masses 2, 15, 27, 78, 92, 116, 128, 166 and 178 from cellulose (Whatman filter paper) char. Mass 2 is from hydrogen, mass 15 is from methane, and mass 27 is from C_2 and bigger aliphatic hydrocarbons. Mass 78 is mostly from benzene, but numerous other oxygenated aromatic compounds are also contributing, especially in the lower temperature range. Mass 92 is mostly from toluene, with some contribution from bigger substituted benzenes. Mass 116 is mostly from indene and similar compounds and mass 128 is mostly naphthalene and substituted naphthalenes. We have also monitored masses 94 and 110, which are primarily phenol and dihydroxybenzenes and are representative of the phenolic compounds. In this work we typically monitored masses such as 78, 92, 116, 128, 166 (major contributor fluorene) and 178 (major contributors anthracene/phenanthrene) as indications of the evolution of aromatic and poly-aromatic hydrocarbon products. Comparison of mass 78 profiles from chars of different materials in Fig. 9 shows that there are two peaks in the benzene evolution profile and that the relative distribution differs depending on the starting char.

From Fig. 6, we can see there is a temperature ordering of the evolved products. The evolution of C_2 and larger aliphatic hydrocarbons decline before CH_4 that in turn declines before H_2 does. As temperature increases above 550°C, the distribution shifts to smaller species. H_2 continues to evolve
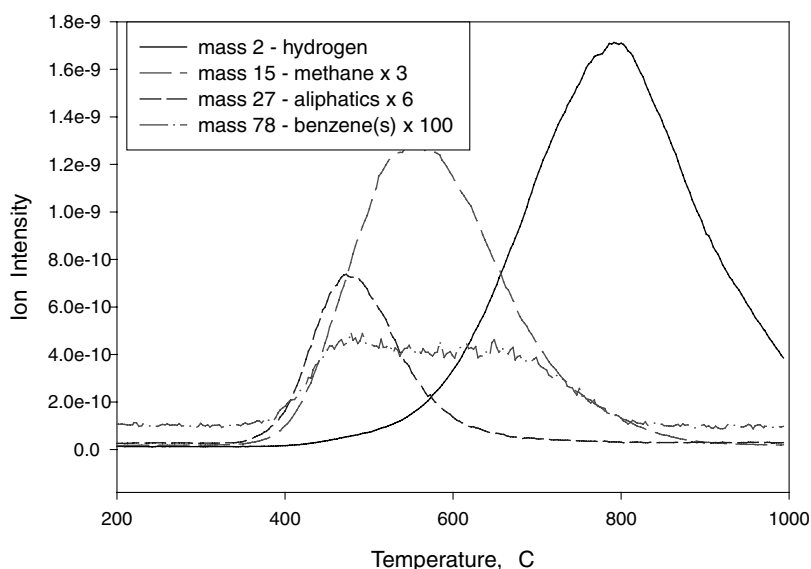

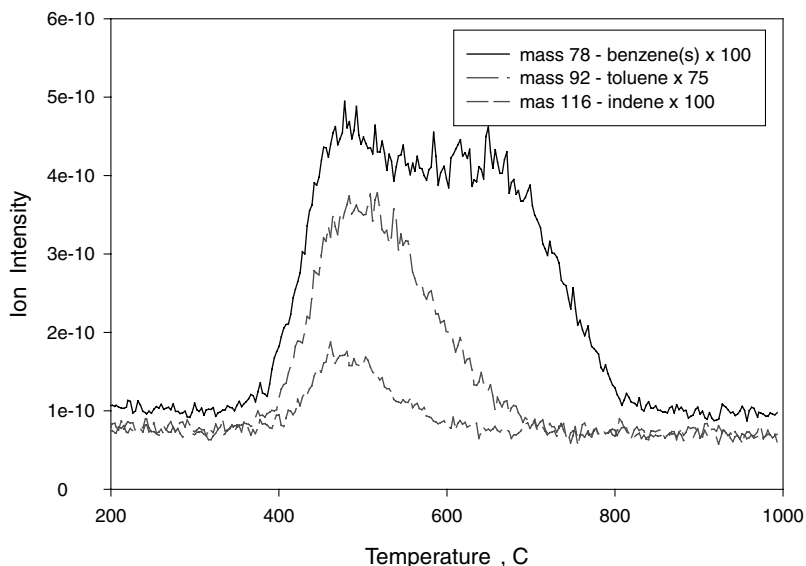Fig. 6. Evolution of masses 2, 15, 27 and 78 from cellulose char.

Fig. 7. Evolution of masses 78, 92 and 116 from cellulose char.

up to 1000°C. The two peaks in mass 78 correspond with the main hydrocarbon peak and with the CH_4 peak in temperature. The first mass 78 peak arises from benzene as well as substituted benzene compounds. The second mass 78 peak is essentially all benzene. With the exception of benzene that continues to evolve above 550°C, all of the aromatic compounds evolve over the same temperature range of 400–600°C. This indicates that they may be simultaneously formed through a similar mechanism within the char matrix. In general, the larger the hydrocarbon, the less abundant its concentration; this is most likely related to the statistical likelihood of forming the larger molecules. As the temperature increases past the peak formation of about 500°C, the

relative abundance of substituted aromatics with respect to non-substituted ones declines. As the char loses the paraffinic bridges/carbons, less of the substituted aromatics are produced. The aromatic char structure continues to condense into larger aromatic clusters — becoming nonvolatile, resulting in the decline in evolution of multi-ring compounds before the eventual decline of benzene and CH_4. Simultaneous with the free radical thermal cracking reactions, elimination of oxygen occurs, resulting in the formation of carbon oxides and water as well as oxygenated aromatics.

The solid char, formed from dehydration, elimination, depolymerization, re-polymerization and cross-linking
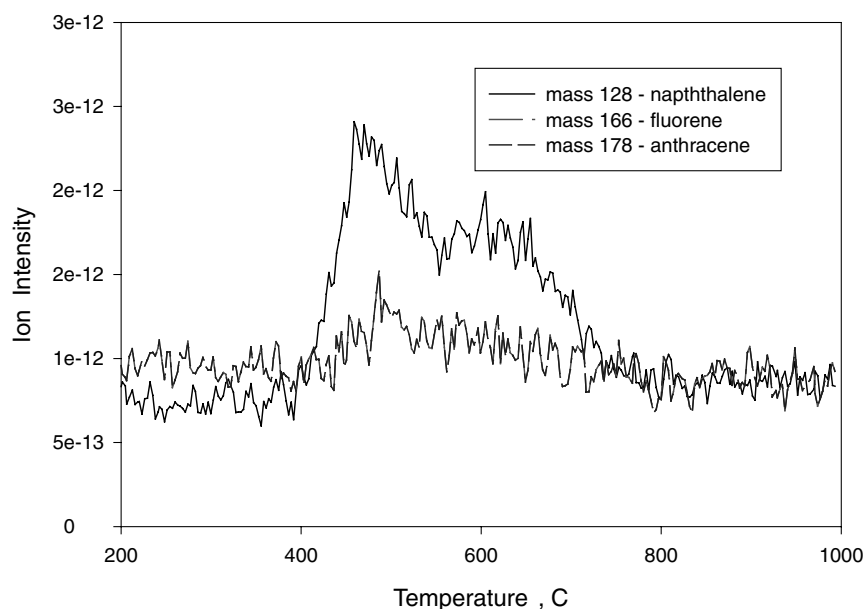

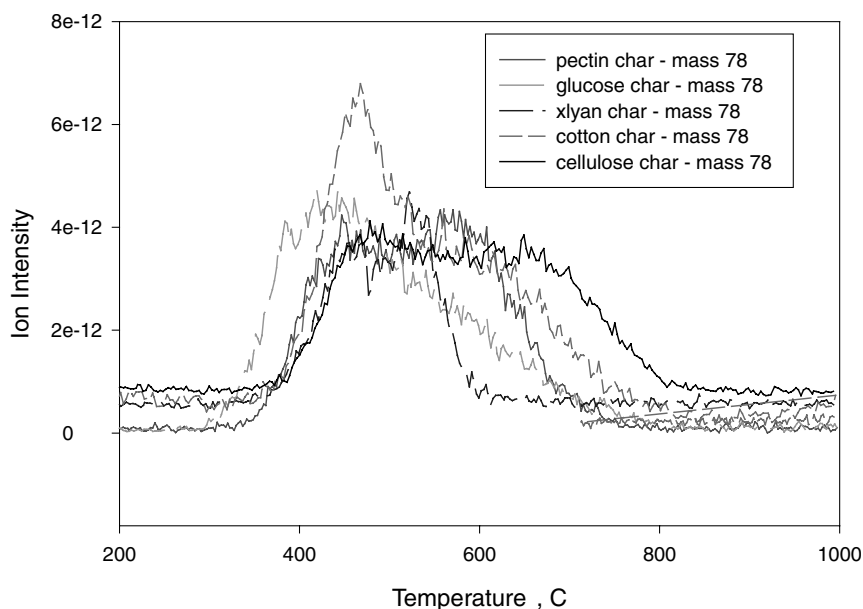Fig. 8. Evolution of masses 128, 166 and 178 from cellulose char.

Fig. 9. Comparison of mass 78 evolution for cellulose, glucose, pectin and xylan samples.

reactions, continues to become more aromatic as temperature increases. Above 350–400°C, free radicals are formed in abundance and thermal cracking proceeds by extraction, addition and fragmentation. This is a gas/solid reaction, where the gas phase products evolving from the solid can react with the solid surface on their way diffusing out of the solid matrix. Elimination of substituents/bridges and dehydrogenation result in a condensation and fusion of the aromatic structure into larger and larger polycyclic aromatic clusters, eventually becoming non-volatile and highly carbonaceous. Elimination of oxygen contained in the char occurs simultaneously with the bulk of the hydrocarbon

evolution. Elimination of CO, CO_2, H_2O and oxygenated aromatics and aliphatics may be part of the process of making aromatic hydrocarbons, but also competes for the carbon source. PAHs are formed in and evolved from the solid char during this process from 400 to 600°C, even beginning as low as 350°C. This data is in good agreement with the depletion of aliphatic carbon, formation of aromatic carbon and polycyclic carbon and with formation of free radicals in the solid char from the studies reported by others [22–25].

The presence of aromatic hydrocarbons from the charred materials is confirmed by the Pyroprobe/GC/MS data
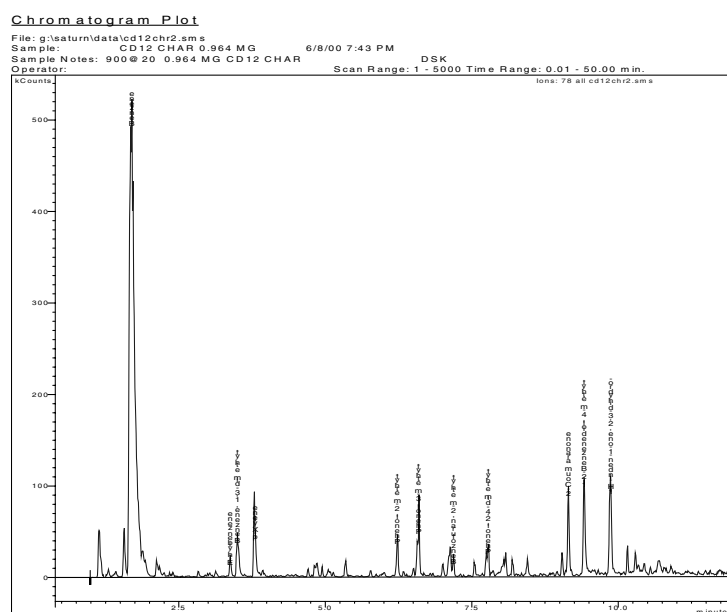

Fig. 10. Chromatogram of selected mass 78 to show the species that have mass 78 as part of their cracking pattern.
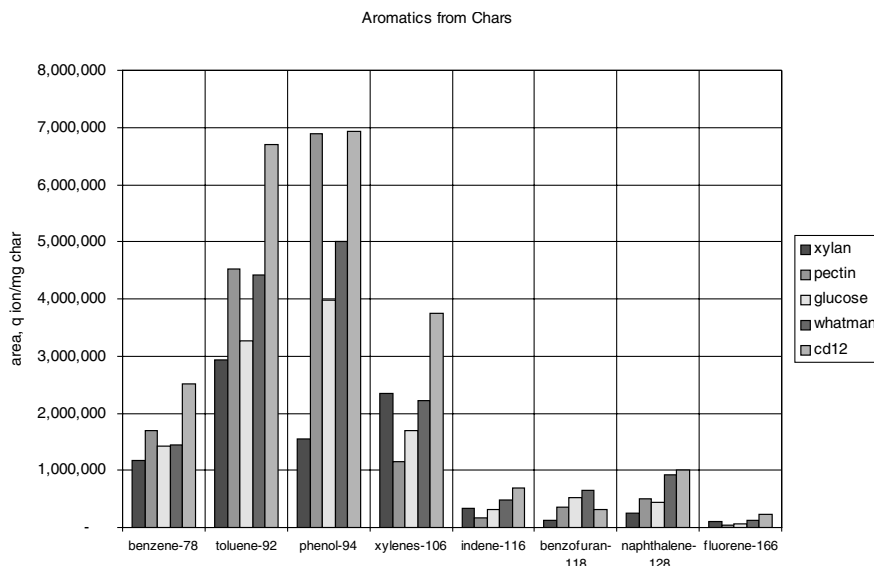
Aromatics from Chars

Fig. 11. Comparison of evolved aromatic products from pyrolysis of cellulose, glucose, pectin and xylan.

showing that these compounds generally account for most of, or are the major compound contributing to, the above ascribed masses. However there are other compounds that contribute to different extents to the specific masses monitored during pyrolysis. For instance, other benzoid compounds (such as benzenediols and coumaranone) contribute to mass 78. There were significant oxygenated compounds (pyrones) contributing to mass 128 for cellulose. Figs. 10 and 11 present the relative amounts of some aromatics (using pyroprobe/GC/MS experiments) from the pre-charred samples. Fig. 10 is a chromatogram of mass 78 which shows that a number of species have mass 78 fragments as part of their mass spectrum cracking patterns. The

largest peaks in the *m/z* 78 ion chromatogram correspond to benzene; the rest are substituted benzenes and oxygenated benzoid compounds. Fig. 11 shows the areas under the *q* (quantifier — the fragment with the highest intensity) ion for several aromatic compounds. The effect of inorganic additives can be observed by comparison of the Whatman filter paper with cotton duck. In all cases, more aromatics are produced from cotton than from the Whatman paper.

By performing TG experiments at three different heating rates; 5, 20, and 60°C/min we can deduce some comparative activation energies for the formation of hydrocarbons by plotting the heating rate vs. inverse of formation peak temperatures. Typical results are shown in Fig. 12 for
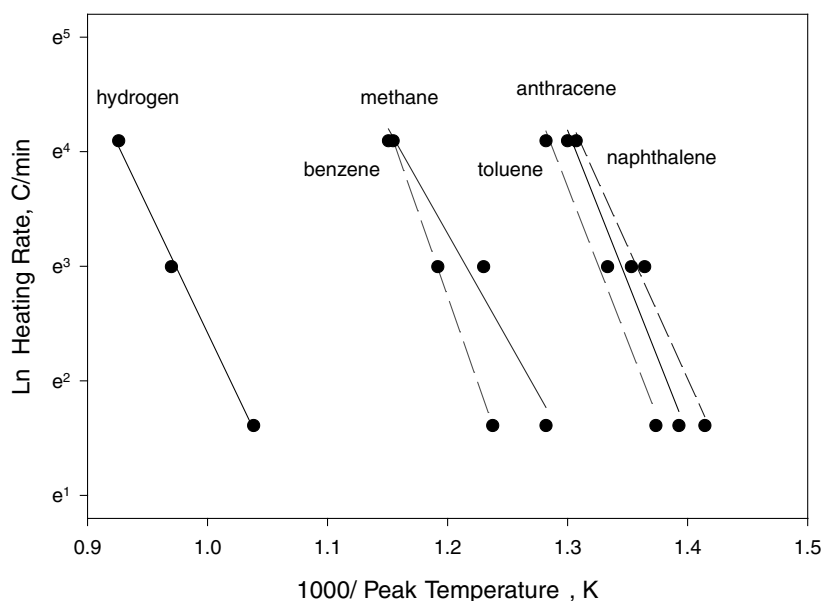

Fig. 12. Presentation of heating rate vs. reciprocal of T_{max} for the evolved masses.

cellulose, the other chars (pectin, xylan and cotton) gave very similar results. This graphical representation shows the temperature separation or coincidence of the classes of species, and a comparison of activation energies from their slopes. The activation energies fall into three groups — hydrogen and methane (about 150–180 kJ/mol), benzene (about 240 kJ/mol for higher temperature), and all other species (about 200–220 kJ/mol).

4. Conclusions

This study clearly indicates that there is a direct pathway for production of aliphatic and aromatic hydrocarbons from the solid substrate during pyrolysis of cellulosic materials. The temperature range (400–600°C) where this pathway becomes significant correlates with the temperature range where the char structure develops first an aliphatic and then a more aromatic structure. This study also shows that inorganic species could significantly change the yields of aromatic hydrocarbons.

Acknowledgements

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