

# FORMATION OF AROMATIC HYDROCARBONS FROM PYROLYSIS OF CARBOHYDRATES

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## INTRODUCTION

Formation of aromatic hydrocarbons is one of the major areas of interest in pyrolysis and combustion processes (1-5). The secondary cracking of initial pyrolysis products in the gas phase is considered to be the major pathway producing aliphatic and aromatic hydrocarbons under conditions approaching flaming combustion. A second, but less studied route for aromatics formation is evolution of aromatics from the solid char as it is formed and degassed during the pyrolysis process. While this second route may not be important in flaming combustion, it may be of significant importance in the smoldering combustion of solids. Under these conditions, the char generated during the primary pyrolysis is the fuel for sustained combustion (6-7). Furthermore, the products generated during primary pyrolysis have little probability of experiencing a higher temperature than the temperature at which they were formed.

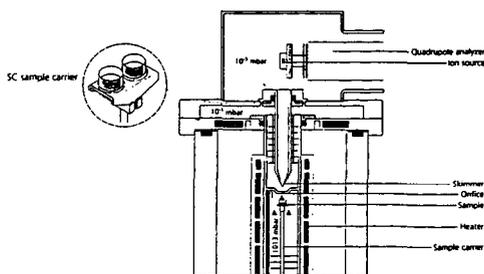
The ongoing research at Philip Morris USA is directed toward studying the significance of the latter route in the production of aromatic hydrocarbons. Numerous literature reports on the secondary pyrolysis of biomass primary products (8-14) exist, but there has been little emphasis on the formation of aromatic hydrocarbons (2, 5, 11). This is likely due to the lower probability of forming aromatic structures from pyrolysis of heavily oxygenated species. Furthermore, to the Authors best knowledge, there is little literature reporting this second pathway during pyrolysis. The most notable exception is the work of Shafizadeh and his co-workers (15, 16) which focused on the aromatic structure formed in the char during pyrolysis, but not on the evolution of gaseous chemical species from the char during the charring process.

In this study, the second route for formation of aliphatic and aromatic hydrocarbons is examined using small sample sizes (1-20 mg) of starting material; and 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. The major plant carbohydrates cellulose, glucose, and pectin, are used as the starting materials. The starting materials were pyrolyzed at constant heating rates from 5 - 60 °C/min up to a temperature of 1000 C in a TG/DSC/MS. Complementary data was also collected on the same materials by pyrolyzing them in a CDS Pyroprobe followed by analysis of products in a GC/MS. Under our experimental conditions, aliphatic and aromatic hydrocarbons evolve over the temperature range of 350 °C- 600 °C, with hydrogen continuing to evolve above 600 °C. We observed one evolution temperature for small aliphatic compounds; and a second evolution temperature for the larger aliphatic and aromatic compounds. Some kinetic parameters for hydrocarbon formation are deduced and discussed.

## EXPERIMENTAL PROCEDURES

The main experimental setup for this study is a Netzsch TG/DSC/MS. A schematic of the reaction zone and sampling system is shown in Figure 1.

Figure 1.  
Schematic of TG/DSC/MS



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 reaction of these volatile products. The sample probe for the 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 about 20 mg of previously charred material) is heated in flowing helium (150 cc/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 CDS Pyroprobe pyrolysis device interfaced to a Varian Saturn 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 set temperature at about 100 °C/sec and held there for 20 sec. The set temperature for the pure pectin and glucose are 300 °C and for the cellulose is 360 °C. The pyrolysis temperature for all the chars 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 reagent grade d-glucose (Acros, less than 0.004% ash); practical grade citrus pectin (Acros, less than 1% ash, and 70 % esterification); and two forms of cellulose. The first cellulose sample is Whatman #41 filter paper (less than 0.007% ash), and the second is a griegre (raw) cotton duck fabric from Wellington-Sears (duck #4, average 5000 ppm K). The latter cellulose sample is used to study the effects of inorganic species which 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 300 °C for glucose and pectin, and 360 °C for cellulose. To ensure the primary decomposition of the materials is complete, samples are held for 10 minutes at the final temperatures.

## RESULTS AND DISCUSSION

### Primary Decomposition

First, we characterize the primary decomposition of the pure materials and then discuss the evolution of hydrocarbons from the chars. Glucose is the basic building block of cellulose, and it undergoes major decomposition in the temperature range of 200-400 °C with peaks at 230 and 270 °C. The DSC data shows that glucose melts at about 150 °C and undergoes some endothermic processes up to 300 °C, and then it goes through a mildly exothermic process. The major products of glucose pyrolysis detectable by MS are H<sub>2</sub>O, CO<sub>2</sub>, CO as well as furans and furfural derivatives. Glucose produces about 35% char at 300 °C and about 15% char at 1000 °C. Aliphatic and aromatic hydrocarbons are evolved from glucose starting about 350 °C where the primary decomposition of the material is largely complete and continues until about 600 °C. Hydrogen continues to evolve at higher temperatures.

Pectin undergoes a major decomposition in the temperature range of about 200 - 300 °C which continues through about 400 °C. Pectin undergoes melting at about 150 °C with a second major endothermic process around 250 °C followed by an exothermic process during the major weight loss around 300 °C. Pectin produces about 40% and 25% char at about 300 °C and 1000 °C respectively. The primary pyrolysis products of pectin are similar to glucose with the exception of increased amounts of methanol and large esters. Pectin, like glucose, begins to produce hydrocarbons above 350 °C and continues to produce H<sub>2</sub> after the hydrocarbons production ceases around 600 °C.

The presence of impurities is known to affect the decomposition pathways during cellulose pyrolysis. We used both "pure" and "impure" cellulose samples. The pure Whatman 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 1000 °C. The cotton duck material was a raw cotton cellulose with about 5000 ppm K as well as other naturally occurring inorganic species. The cotton duck 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 to approximately -470 J/g for the pure cellulose. The amount of char produced by the cotton duck is about 25 % at 400 °C and about 16 % at 1000°C, comparing to 10% and 4% at the same temperature for the pure cellulose. The major products detectable by MS for cellulose decomposition are H<sub>2</sub>O, CO<sub>2</sub>, and CO, as well as some aldehydes, furans, pyrones and other oxygen-containing products (levoglucosan). Another notable difference in the MS profiles of the pure cellulose and cotton fabric 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). This is consistent with previous literature (ref.) reports.

### Hydrocarbon Formation

Now, we focus our attention on the formation of hydrocarbons from pyrolysis of the above carbohydrates. Pyrolysis of previously charred samples eliminates the probability of including any secondary reactions of the primary products, as well as focusing on the temperature ranges where hydrocarbons evolve from these materials under the pyrolysis conditions in this study. Figure 2 shows the temperature dependence for masses 2, 15, 27 and 78, representing primarily  $H_2$ ,  $CH_4$ ,  $C_2$  hydrocarbons, and benzene from pectin char. Our data indicate similar temperature dependence for masses 78 and 92, primarily benzene and toluene, for untreated glucose and pectin, and their respective chars. We have used masses 78, 92, 106, 116, 118, 128, 166, and 178 to follow evolution profiles of aromatics from the carbohydrates. Figure 3 is an example showing masses 78, 92, 128 and 178 representing primarily benzene, toluene, naphthalene and anthracene/phenanthrene from cotton duck char. These data show that all the hydrocarbons from these chars evolve over a similar temperature range with a few exceptions, such as the evolution of  $CH_4$  and benzene (second peak) at above 500 °C and  $H_2$  at temperatures above 600°C. The presence of these chemical species from the char materials is confirmed by the Pyroprobe/GC/MS data 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. Other benzoid compounds (such as benzenediols and coumaranone) contribute to mass 78. There were significant oxygenated compounds (pyrones) contributing to mass 128 for cellulose. We are continuing to investigate all the products contributing to masses used to monitor aromatic hydrocarbons.

These experimental results indicate that substituted benzene, larger aromatic and aliphatic hydrocarbons evolve first, and as they are depleted, continued evolution of  $CH_4$  and benzene occurs, and as these are depleted evolution of  $H_2$  continues. At this point, a highly carbonaceous char has been produced. This is consistent with Shafizadeh's work (15) where he studied the aliphatic and aromatic concentration of char as a function of temperature. Shafizadeh did not measure the evolved gases in his study, but his data on the solid concentration and our data on the evolved gases over the temperature range studied matches well. From comparing mass 78 profiles from the different carbohydrate chars, the relative distribution of benzene in the two peaks differs among the carbohydrates. Glucose and pure cellulose char are very similar, the pectin and cotton chars produce more benzene above 500°C. The pectin, glucose and pure cellulose all produced comparable amounts of benzene, the cotton produced more benzene which may be an effect of the high inorganic content. A table of relative amounts of some aromatics (using pyroprobe/GC/MS experiments) from the chars are presented in Table 1.

**Table 1. Relative abundance of different masses from pyrolysis of carbohydrates**

	78	92	106	116	118	128	166	178
<b>Pectin</b>	91,372	143,892	123,503	19,587	50,444	63,436	7,915	12,878
<b>Cotton</b>	1,343,907	209,604	221,938	48,996	34,142	141,962	40,346	44,653
<b>Cellulose</b>	56,868	107,414	138,885	46,716	59,409	113,237	21,751	33,598
<b>Glucose</b>	42,551	91,351	129,130	24,116	55,828	56,181	14,393	17,795

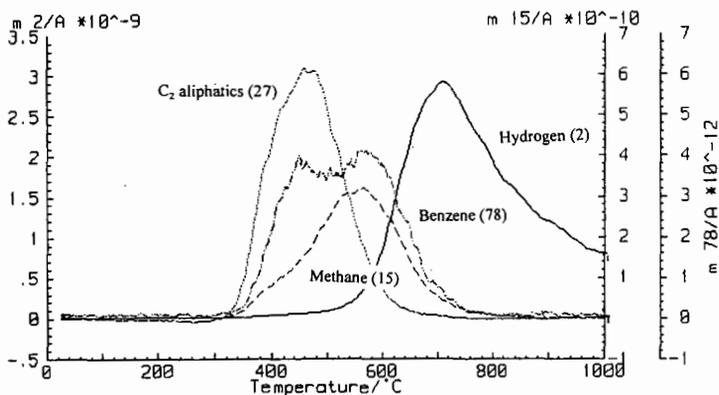
By performing TG experiments at three different heating rates; 5, 20, and 60°C/min we can deduce some comparative activation energies for the formation of hydrocarbons by plotting the heating rate vs. inverse of formation peak temperatures. These results are shown in Figure 4 for cotton duck char. This graphical representation demonstrates 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 kJ/mol), benzene (about 240 kJ/mol), and all other species (about 200kJ/mol).

### CONCLUSIONS

This study clearly indicates that there is a second pathway for production of aliphatic and aromatic hydrocarbons during pyrolysis of carbohydrates. The temperature range 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 shows that inorganic species could significantly change the yields of hydrocarbons.

Figure 2

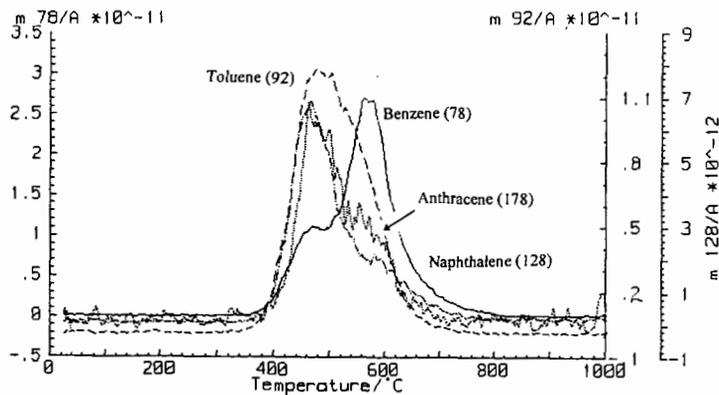
Product Yield of 320°C Char Pectin Pyrolysis



IDENTITY No.	320apech4dscn20	SAMPLE	ac320tfchrpectn 20.77
DATE	18 Nov 1998	ATMOSPHERE	Helium /150.25 ccm
LABORATORY	badlab	REMARK	MID16s5.0e-6orf
OPERATOR	bewdsk		
NETZSCH	409/429-403		

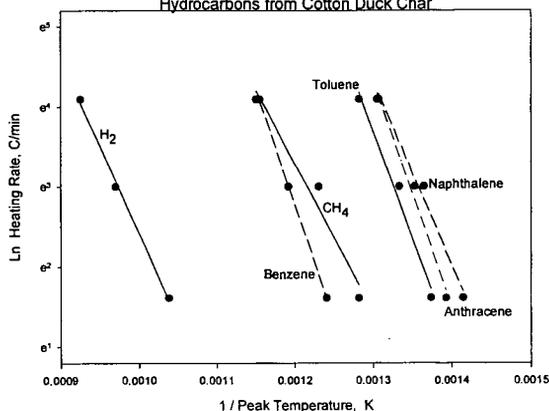
Figure 3

Product Yield of 360°C Char Cotton Duck Pyrolysis



IDENTITY No.	360dckch5dscn20	SAMPLE	duck4 370-60020 17.01
DATE	19 Nov 1998	ATMOSPHERE	Helium /150.25 ccm
LABORATORY	badlab	REMARK	MID16s5.0e-6orf
OPERATOR	bewdsk		
NETZSCH	409/429-403		

Figure 4  
Activation Energies for the Formation of  
Hydrocarbons from Cotton Duck Char



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