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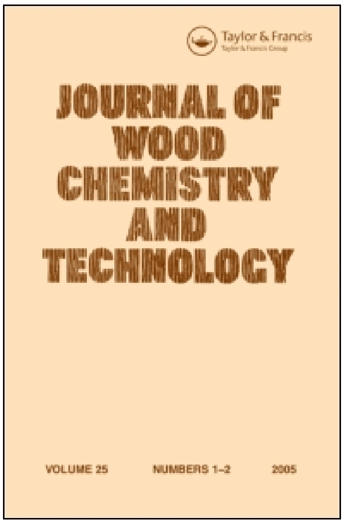

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HYDROTREATING OF HYDROCHLORIC ACID LIGNIN IN A HYDROGEN-DONOR SOLVENT

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ABSTRACT

The depolymerization of hydrochloric acid sweetgum lignin by hydrotreating in hydrogen-donor solvents in the temperature range of 375-425°C (707-797°F) has been studied. Analysis of the phenolic products showed that the principal depolymerization reactions were the cleavage of ether and C_α-C_β bonds. A maximum yield of approximately 11% monomeric phenols was obtained, with the intermediate compounds for the most part being further degraded into gases and neutral products. The reaction kinetics were found to be first order, with an activation energy of 24 Kcal (100 kJ). The addition of a heterogeneous catalyst did not increase the yield of monomeric phenols.

INTRODUCTION

Many countries have experienced petroleum supply problems in the last few years because of declining reserves, increased demand, and political events in oil-exporting countries. This has created difficulties for oil-importing nations which depend upon petroleum to supply much of their energy and chemical needs.

Lignin, one of the major constituents of woody biomass, is the most abundant aromatic polymer on earth. Varying degrees of success have been reported by investigators who have attempted to degrade lignin into useful chemicals[1]. One technique involves the exposure of lignin to high temperatures, thus thermally cleaving covalent bonds. The radicals which are formed by the bonds undergoing homolytic cleavage could then be reduced using either catalysts or hydrogen-donating solvents.

Hydrogen-donor solvents have been employed in many coal liquefaction studies. The methods employed usually involve heating coal in the presence of hydrogen, a heterogeneous catalyst, and a solvent[2]. The coal is reductively decomposed by heat and the reduced solvent, which in turn is rehydrogenated by the catalyst. Mechanistic studies have shown that the rate determining step is the thermal cracking of covalent bonds, with the rate being first order[3-6]. The energy of activation for the various reactions were found to be between 25 and 40 Kcal per mole (105 to 167 kJ/mole). Recondensation of the coal degradation products does not occur at a significant rate except in the absence of a suitable hydrogen-donor solvent. Without a suitable solvent, the products recondense after a slight initial depolymerization. Interestingly, the addition of different heterogeneous catalysts had no measurable effect on the rate of coal liquefaction.

In comparison to coal, the use of hydrogen-donor solvents in lignin hydrotreating experiments has received little attention. In one recent study, kraft lignin was pyrolyzed at 400°C in the presence of tetralin[7]. A maximum yield of 7% monomeric phenols was reported. While the hydrogen-donor solvent did prevent recondensation of the lignin, further breakdown of most of the lignin products into gases and neutral products occurred.

Recently, this laboratory has investigated several different methods for depolymerizing a hardwood lignin prepared by hydrolysis of the polysaccharides using superconcentrated hydrochloric acid. This hydrochloric acid lignin has been shown to have a relatively low fraction of carbon-carbon bonding between phenylpropane units, and thus is relatively reactive[8].

The object of this research was to determine the yield of monomeric phenols obtainable by hydrotreating hydrochloric acid lignin in a hydrogen-donor solvent at varying temperatures and reaction times.

EXPERIMENTAL PROCEDURE

Hydrochloric acid lignin was prepared by the following procedure. Extracted sweetgum wood meal (*Liquidambar styraciflua* L.) was added to superconcentrated hydrochloric acid (44-45%) in a reaction vessel cooled to -5°C. Acid to wood ratio was about 13:1 (v/w). The wood-acid mixture was left at -5°C for one hour before slowly raising the temperature. The mixture was then stirred for eight additional hours at ambient temperature. It was filtered at the completion of the hydrolysis and the insoluble lignin repeatedly washed with distilled water, sodium carbonate solution, and finally water again. A light-brown powder was isolated in 24% yield. Klason lignin determinations on the same wood showed a total lignin content of 25.8% (22.3% insoluble plus 3.5% soluble).

The reactor used for hydrotreating was a 1 liter Parr rocking hydrogenation autoclave. When hydrotreating lignin in prereduced anthracene the procedure was as follows: One hundred grams of anthracene was added together with 30 grams of iron oxide catalyst (Fe_2O_3/Al_2O_3, 20% Fe_2O_3) to the autoclave, which was then pressurized with 1,000 psig (70 kg/cm^2) hydrogen. The anthracene was reduced at 450°C for 30 minutes, with the reactor then cooled overnight. Ten grams of hydrochloric acid lignin was then added to the prereduced anthracene-catalyst mixture. The reactor was refilled with hydrogen, and the lignin hydrotreated at the reported operating conditions given in Table 1. At the completion of the experiment, the reaction mixture was cooled, removed from the autoclave and vacuum distilled. The distillates with boiling points up to 140°C at 3 torrs were collected and then extracted with ether and aqueous alkali to separate the neutral and acidic fractions.

When hydrotreating hydrochloric acid lignin in tetrahydronaphthalene (tetralin), 15 grams of lignin and 100 ml of tetralin were added to the reactor. After hydrotreating the lignin, the bomb was cooled before removing the reaction mixture using ether and aqueous alkali. The alkaline solution was continuously extracted with ether for 36 hours to obtain the ether-soluble neutral products. The aqueous layer was acidified with hydrochloric acid to a pH of 4, and then extracted with ether for 24 hours to obtain the either-soluble phenolics. After removing the ether, the phenolic fraction was vacuum distilled, collecting all material boiling up to 175°C at 3 torrs.

Ether-insoluble residuals were measured by filtering the aqueous layer after the extractions had been performed. The fraction which was water soluble was determined by UV absorbance and was generally less than 1.5% of the original lignin. The yield of soluble phenolics is the combined total of ether and water-soluble phenolics. The material balance is the sum total of the residue and soluble phenolic fraction, but does not include any gaseous or neutral products. A portion of the phenolic distillates was acetylated and analyzed by GC using a 180 cm x 2.2 mm i.d. OV-17 column[9]. The reaction products were identified using the relative retention times of known reference compounds. For comparison, one reaction was run in a nonhydrogen-donating solvent, i.e. naphthalene.

RESULTS AND DISCUSSION

The data obtained by hydrotreating hydrochloric acid lignin with hydrogen and prereduced anthracene under the catalytic influence of Fe_2O_3 are given in Table 1. It can be seen that the catalyst had little if any effect on depolymerizing lignin to monomeric products. However, pyrolysis of lignin in the presence of a hydrogen-donor solvent (prereduced anthracene) gives about 10% by weight of distillable phenols. While a heterogeneous catalyst should also be capable of reducing radicals,

TABLE 1

Hydrotreating of Hydrochloric Acid Lignin in Anthracene Using Fe_2O_3 and an Initial Hydrogen Pressure of 1,000 psig at Room Temperature.

Reaction	Prereduced Anthracene	Temperature, °C	Time, hr.	Distillable Phenolics, Weight %
1	-	400	2	4
2	-	400	2	1.4
3	+	400	2	10.6
4	-	425	1	3.4
5	+	425	2	9
6	+	425	2	10
7	+	425	2	9.5

transport of the compound to active sites in the catalyst pores may be diffusion limited because of size, viscosity or solubility. Thus, the radicals which are formed by the homolytic cleavage of covalent bonds may not be reduced at a rate sufficient to prevent excessive recondensation.

Table 2 shows the results obtained when hydrochloric acid lignin was hydrotreated with tetralin. Analysis of the data shows that the reaction apparently follows first order irreversible kinetics. Figure 1 shows the log of the residue versus reaction time at temperature. As mentioned in the introduction, previous investigators who studied coal liquefaction in hydrogen-donor solvents also reported first order reaction rates.

The yield of soluble phenolics versus reaction time (Figure 2) shows that a maximum yield of approximately 35% is obtainable by hydrotreating hydrochloric acid lignin with tetralin. This is similar to results reported by Connors *et al.*[7] who hydrotreated kraft lignin in tetralin, i.e. 37.4%.

TABLE 2

Products Obtained by the Pyrolysis of Hydrochloric Acid Lignin in Tetralin

Reaction	Solvent	Time at Temperature, hr.	Temperature, °C	Maximum Pressure, psig	Yield, Weight%				
					Neutrals[1]	Residue	Soluble Phenolics	Distillable Phenolics	Material Balance[2]
10-A	Tetralin	0	375	439	95	44.2	26.5	4.8	70.7
10-B	Tetralin	0	400	550	99	29.9	34.1	8.7	64.0
10-C	Tetralin	0	425	640	97	21.2	25.9	8.9	47.1
11-A	Tetralin	0.25	375	400	100	37.0	32.7	9.0	69.7
11-B	Tetralin	0.25	400	570	98	33.7	29.8	9.0	63.5
11-C	Tetralin	0.25	425	660	100	21.6	24.8	9.8	46.4
12-A	Tetralin	1.0	375	500	97	32.4	35.7	9.9	68.1
12-B	Tetralin	1.0	400	590	100	27.4	28.9	9.6	56.3
12-C	Tetralin	1.0	425	690	102	14.7	18.6	8.5	33.3
13-A	Tetralin	2.0	375	490	102	24.8	32.9	10.1	57.7
13-B	Tetralin	2.0	400	620	98	21.6	20.1	7.6	42.7
14	Naphthalene	0.25	400	-	ND[3]	ND[3]	6.4	0.6	ND[3]

[1] Weight percent of original tetralin.

[2] Residue plus soluble phenolics. (Does not include any neutral or gaseous products).

[3] Not determined.

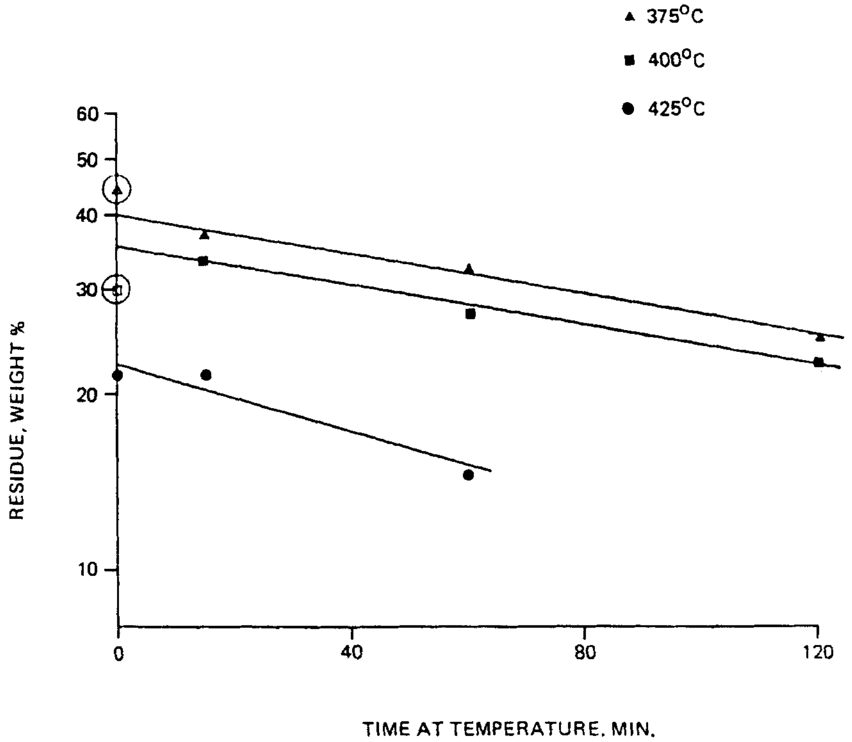

FIGURE 1

Residue versus reaction time for hydrochloric acid lignin hydrotreated in tetralin.

TABLE 3

Reaction Rates and Coefficient of Determination (r^2) Obtained from the Pyrolysis of Hydrochloric Acid Lignin in Tetralin.

	Residue, Weight %		Material Balance, Weight %	
Temperature, °C	Rate of Reaction	r^2	Rate of Reaction	r^2
375	-3.58×10^{-3} min^{-1}	0.99	-1.65×10^{-3} min^{-1}	0.89
400	-3.77×10^{-3} min^{-1}	0.99	-3.34×10^{-3} min^{-1}	0.96
425	-6.67×10^{-3} min^{-1}	0.92	-6.15×10^{-3} min^{-1}	0.96

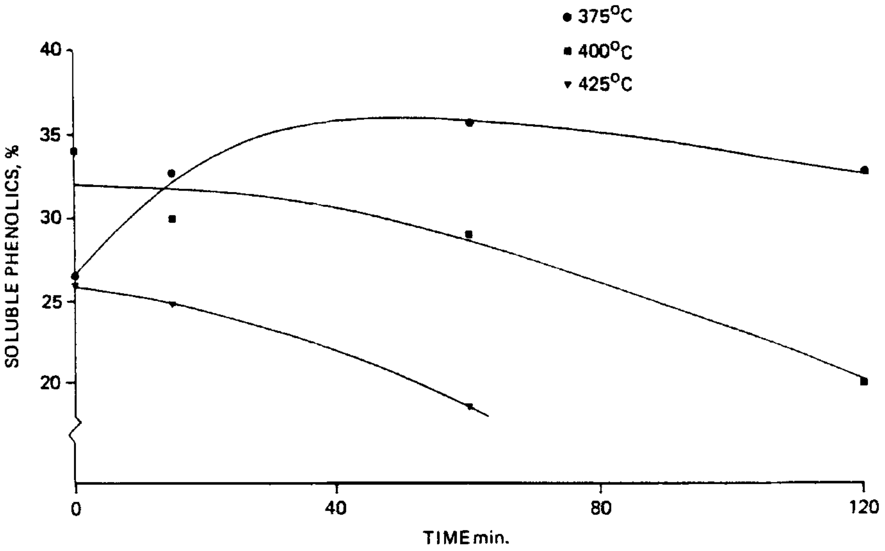

FIGURE 2

Yield of soluble phenolics obtained by hydrotreating hydrochloric acid lignin in tetralin for various reaction times.

The formation of gases and neutrals is also first order, as can be seen by plotting the log of the material balance versus reaction time (Figure 3). The reaction rates and coefficient of determination (r^2) calculated from the residue and material balance data are given in Table 3.

An activation energy of 24 Kcal (100 kJ) ($r^2 = 0.99$) can be calculated from the material balance rate constants. Stamm[10] and Van Krevelen et al.[11], when examining the thermal degradation of lignin, determined that the weight loss followed first order kinetics, with an activation energy of 23 and 28 Kcal (96 and 117 kJ), respectively.

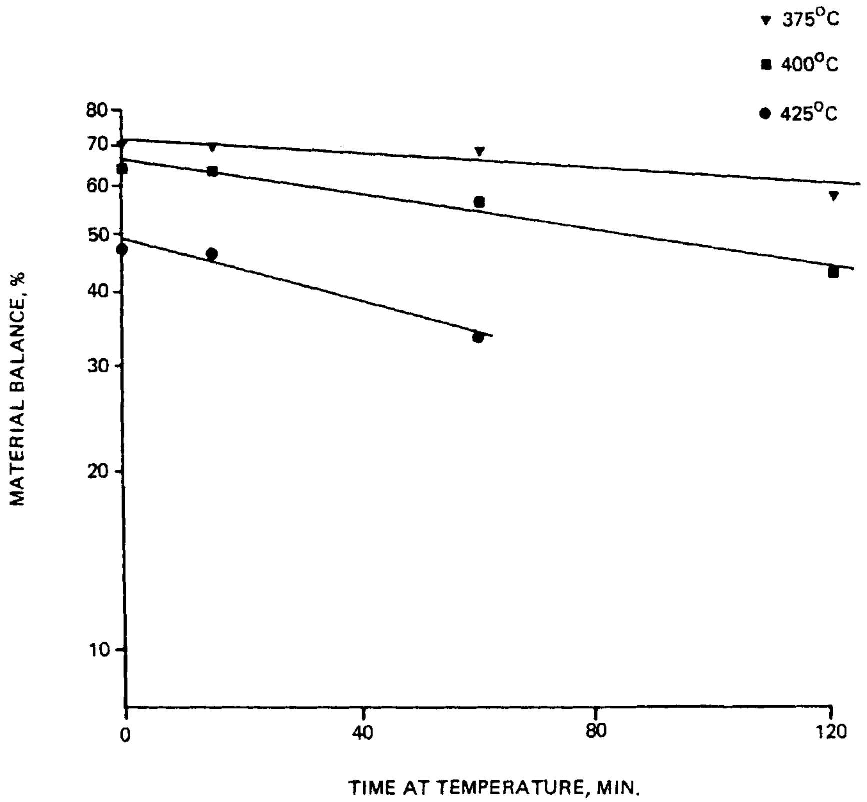

FIGURE 3

Material balance versus reaction time for hydrochloric acid lignin hydrotreated in tetralin.

A possible technique which might increase the yield of monomeric phenols would be to add a catalyst to the tetralin-lignin mixture. However, similar yields of distillable phenols were obtained when hydrotreating hydrochloric acid lignin in either tetralin or a prereduced anthracene-catalyst mixture. Curran _et al._[6], when studying the kinetics of coal pyrolysis in tetralin, also found that the addition of various catalysts

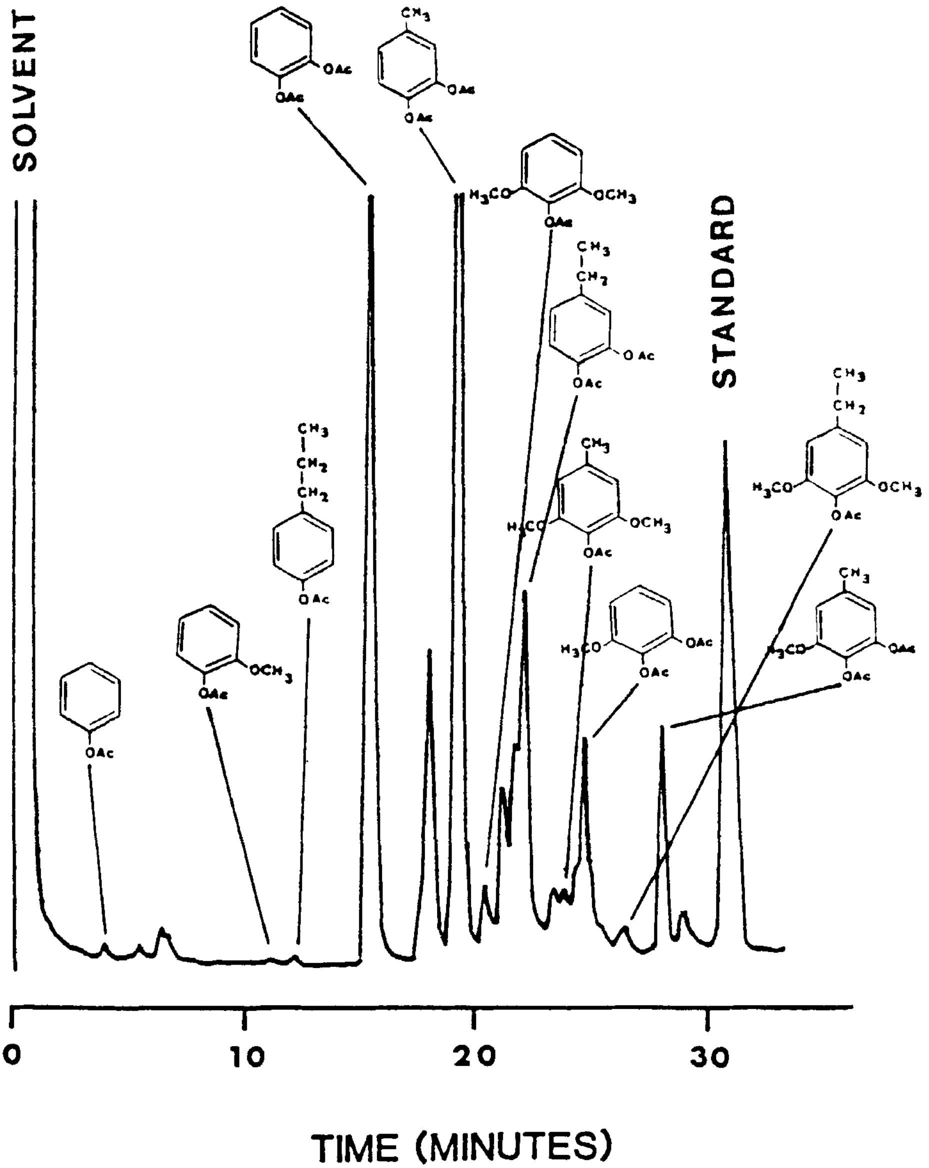

FIGURE 4

GC chromatogram of the acetylated phenolic distillates from reaction 11-C. The gas chromatograph used was a Perkin-Elmer 990 equipped with a flame ionization detector. A 180 cm x 2.2 mm i.d. OV-17 column was used, with an initial temperature of 85°C and a temperature rise of 3°C per minute

TABLE 4

CC Analysis of the Phenolic Distillates

	375°C Reaction Temperature				400°C Reaction Temperature				425°C Reaction Temperature		
Reaction	10-A	11-A	12-A	13-A	10-B	11-B	12-B	13-B	10-C	11-C	12-C
Time at Temperature, hr.	0	0.25	1.0	2.0	0	0.25	1.0	2.0	0	0	1.0
Distillates Yield, Weight %	4.8	9.0	9.0	13.0[1]	8.7	9.9	9.6	11.4[1]	8.9	9.8	8.5
Compound[2]											
Phenol	Trace	Trace	0.1	0.1	Trace	0.1	0.3	0.7	0.1	0.1	0.7
Methylphenol											1.1
Ethylphenol	Trace	Trace	Trace	Trace		Trace	Trace	Trace	Trace	0.1	Trace
Propylphenol	0.1	Trace	0.1	0.2	Trace	0.1	0.2	0.3	0.1	0.1	0.3
Guaiacol	2.5	1.9	1.4	0.9	1.1	0.9	0.4	0.3	0.3	0.1	0.1
Methylguaiacol	2.5	2.2	1.8	0.6	0.8	0.6	0.2	0.1	0.1	0.1	
Ethylguaiacol	0.9	0.2	0.3								
Propylguaiacol								1.2			
Syringol	11.2	8.1	5.2	2.5	4.5	3.4	1.6	5.7	1.7	1.6	1.8
Methylsyringol	14.8	10.9	6.4	2.2	4.1	2.8	0.8	1.3	0.8	1.1	1.6
Ethylsyringol	1.7	2.1	1.4	0.9	0.5	0.5	0.7	1.2	0.6	0.8	1.0
Catechol	2.6	2.4	3.1	5.9	4.7	4.2	9.8	8.8	10.3	11.0	14.3
Methylcatechol	2.2	2.9	4.3	9.3	7.2	6.8	16.1	9.1	15.4	17.7	18.0
Ethylcatechol	0.6	0.9	1.4	3.3	2.1	2.4	5.6	2.5	4.4	5.9	5.7
Pyrogallol ether[3]	8.0	7.0	7.3	8.1	9.2	8.1	7.9	1.5	6.7	4.8	2.8
Methylpyrogallol ether	7.6	8.0	8.8	8.8	10.9	9.7	5.8	0.3	6.0	3.8	0.8
% of Distillates Identified	54.7	47.0	41.6	42.8	44.9	39.6	49.4	33.0	46.5	47.1	48.2

[1] Uncorrected for tetralin contaminates.

[2] Alkyl substituent para to the phenolic hydroxy group.

[3] 1,2-Dihydroxy-3-methoxybenzene.

did not affect the reaction rate. These results were explained by suggesting that the rate determining step is the thermal homolytic cleavage of covalent bonds.

GC analysis of the phenolic distillates is shown in Table 4, with a representative chromatogram given in Figure 4. Approximately 50 weight percent of the distillates were identified. Examination of the chromatograms showed that traces of tetralin and naphthalene were present, with these compounds eluting at five and six minutes, respectively. Since naphthalene and p-methylphenol eluted together, the concentration of p-methylphenol was not determined. However, examination of Figure 4 shows that the combined peak area of p-methylphenol and naphthalene was very small, suggesting that only traces of p-methylphenol were present. The triacetyl derivative of 1,2,3-trihydroxybenzene and its p-methyl and p-ethyl derivatives were not eluted from the column, and may account for a large portion of the unidentified fraction.

Inspection of the results from the GC analysis suggest that the primary depolymerization reactions taking place were cleavages of ether and C_α-C_β bonds. This latter reaction is consistent with data presented by Szwarc[12], who reported that the C_α-C_β bond of propylbenzene had a lower bond energy than either the C_1-C_α or C_β-C_γ bonds. Thus, the C_α-C_β bond would be preferentially broken under thermal conditions. The p-methyl derivatives which are formed when the C_α-C_β bond is cleaved may possibly be further degraded by the cleaving of the C_1-C_α bond, which would form dealkylated phenols.

In general, the total yield of monomeric phenols identified is similar to the results reported by Connors *et al.*[7] However, the exception is that Connors *et al.*[7] reported a high yield of *p*-methylphenol, which would be formed by demethoxylation of *p*-creosol. The results from this study show that catechol and *p*-methylcatechol were present in far greater amounts than phenol and *p*-methylphenol. This suggests that demethylation of the methoxy groups is the dominant reaction occurring under thermal conditions. Previous investigators who have examined the pyrolytic reactions of methoxybenzene reported that only demethylation occurred[13,14]. Examination of the GC chromatogram published by Connors *et al.*[7] shows that tetralin eluted near phenol, but that no naphthalene peak was reported. In the present study, it was determined that naphthalene overlapped *p*-methylphenol, with tetralin eluting just after phenol. It is possible that naphthalene and *p*-methylphenol were eluting together in the previous study[7], and thus the reported high yield of *p*-methylphenol may be in error.

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