

Primary and Secondary Lignin Pyrolysis Reaction Pathways

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The reaction pathways involved in the pyrolysis of kraft lignin, kraft lignin plus tetralin, a milled wood lignin, and pine wood were examined. The temporal variations of the quantitative yields of 33 different products, including 12 gases, water, methanol, and 19 phenolics allowed resolution of primary and secondary pathways, description of the influence of reactor design and lignin type on product yields, and formulation of a simple kinetic lumping scheme. Products within separate guaiacol and catechol lumps attained maximal proportions at 7.5 and 15 min, respectively, during kraft lignin pyrolysis at 400 °C. Within a lump, the secondary reactions of individual species were nearly synchronous. Further, the similarity of the observed rate of the secondary decomposition of guaiacols during kraft lignin pyrolysis with that previously reported for pyrolysis of pure guaiacol suggests that the reactions of lignin's thermally liberated single-ring products are insensitive to the presence of other molecular species or polymer residuum. All of the foregoing indicates that a simple reaction network based on phenol, guaiacol, and catechol lumps could be a useful model of phenolics product evolution.

Introduction

The conversion of macromolecular resources like coal and woody biomass (cellulose, hemicellulose, and lignin) into lower molecular weight products by pyrolysis, gasification, liquefaction or combustion processes involves pyrolysis as either the single or an important cause of fragmentation. Because of this, and also because lignin appears especially significant among coal's biomass precursors (Given and Raj, 1978; Raj, 1979; Hayatsu et al., 1979), lignin pyrolysis has received considerable attention (Iatridis and Gavalas, 1979; Graef et al., 1979; Chan and Krieger, 1981; Connors et al., 1980; Domburg et al., 1971; Kirshbaum et al., 1976).

The information obtained from lignin pyrolysis experiments is dependent on the apparatus of choice. Primary reactions have been emphasized in reactors with either or both of rapid heating and primary product removal by an inert carrier gas stream. The reactors may well be effective in maximizing volatile product yields, but they also allow little resolution of the fundamental pathways and kinetics of the yield-reducing condensation, coking, or other secondary reactions of volatile products that their designs disfavored. Along these lines, Iatridis and Gavalas (1979) studied kraft lignin pyrolysis in a "heated grid" apparatus where volatiles were removed with a flow of helium. Volatile products were also removed during a helium plasma pyrolysis of kraft lignin (Graef et al., 1979), and Chan and Krieger (1981) used 1.5 kW microwave power to decompose a kraft lignin in a flow of inert carrier gas. A rapid pyrolysis of an aspen lignin in a micro-unit allowed identification of 32 phenolic products (Kirshbaum et al., 1976).

Other pyrolysis reactor designs have permitted the observation of lignin thermal reactions during the heat-up to, and subsequent hold at, the nominal pyrolysis temperature. Thus, Domburg et al. (1971) identified 21 phenolics from pyrolysis of a spruce lignin in a covered crucible, and Connors et al. (1980) studied lignin pyrolysis by heating a 1:4 kraft lignin-tetralin mixture to 400 °C in a 300-cm³ autoclave for holding times ranging from 15 to 615 min. Although these reactors do allow observation of secondary reaction pathways, extraction of kinetic parameters is complicated by the nonisothermality.

The present pyrolyses of kraft lignin, kraft lignin plus tetralin, a milled wood lignin, and a pine wood were aimed at quantifying both primary and secondary lignin pyrolysis

reactions because the latter would be unavoidably important during pyrolysis, liquefaction, or gasification in commercial processes. This was accomplished under experimental conditions that (1) did not permit the escape of primary volatile products from the reaction hot zone and (2) closely approached isothermal pyrolysis. Complementary to most lignin pyrolyses that preceded it, this work was directed toward the resolution and quantitative kinetic description of pyrolysis reaction pathways and not the achievement of optimally desirable product spectra. It is quite reasonable, however, to expect these results to aid in the optimization of lignin thermochemical conversion processes.

In outline of what follows, the experimental details of materials, reactors, procedures, and product analysis are reported first. Pyrolysis results are presented next, and the Discussion section comprises a comparison of the present results with previous results in the light of the pyrolysis reactor environment, a comparison of the present results obtained with each substrate, and a simple kinetic analysis that suggests a tentative lumping scheme for lignin pyrolysis phenolic products. Finally, important results and conclusions are listed.

Experimental Section

Kraft lignin, kraft lignin plus tetralin, a milled wood lignin, and the pine wood from which the milled wood lignin was obtained were pyrolyzed at 400 °C; the kraft lignin was also pyrolyzed at 300 and 500 °C. Here are provided the details of the materials, reactors, procedures, and analytical chemistry methods used.

Materials. Kraft pine lignin (Indulin AT) was supplied by the Westvaco Corp. and was used as received. Pine wood was obtained as a standard board from a local hardware store and used in the whole wood pyrolyses after filing. A milled wood lignin was obtained from the same filings following a method due to Harkin (1966) and executed as follows.

Thirty grams of coarse filings were placed in a 1000-cm³ ball mill along with 750 cm³ of toluene and 1/2 in. diameter steel balls. This mixture was milled for 48 h after which the suspension was filtered and the toluene discarded. Low molecular weight products were extracted with ethyl acetate, and the lignin was then extracted with a 9:1 dioxane-water mixture. A small amount of alumina, along with 8-cm³ increments of benzene/100 cm³ of solution, was

added to the extract to precipitate any carbohydrates present. After filtering, for solids removal, evaporation of the solution left the lignin as residue. All other chemicals, i.e., reagents, tetralin, and chromatography standards, were available commercially and used as received.

Reactors. Stainless steel (316) microtubing bomb reactors, each comprising a Swagelok port connector and two Swagelok caps, were used in all pyrolyses. Reactors fashioned from nominal $1/2$ -in. components (~ 3.5 cm³ internal volume) were used for the vast majority of kraft lignin and wood pyrolysis experiments, while $1/8$ -in. reactors (~ 0.1 cm³ internal volume) permitted conservation of the more valuable and less plentiful milled wood lignin. A limited number of kraft lignin pyrolyses in each of $1/2$ -, $1/8$ -, and also $1/4$ -in. reactors showed no discernible dependence on surface to volume ratio, and, by inference, reactor wall effects were not further examined in subsequent experiments.

Procedure. A typical experimental procedure comprised the following steps. An appropriate reactor was purged with nitrogen, which served as an internal standard for later gas chromatographic analyses, and tared. Substrate and biphenyl, a thermally stable internal standard (Klein, 1981) used in subsequent quantitative analyses, were added to the reactor and weighed. For the $1/2$ -in. reactors 300 mg of either kraft lignin or wood and 1.5 mg of biphenyl were added, whereas 20 mg of the milled wood lignin and 1.0 mg of biphenyl were added to the $1/8$ -in. reactors. Preliminary screening experiments showed no quantitative influence of biphenyl on the pyrolyses and this point was not further considered in the quantitative analyses reported below. If used, tetralin was added at this point, and the reactor was then again purged with nitrogen and sealed.

Loaded reactors were then immersed in a Tecam fluidized sand bath held constant at the desired reaction temperature. The heat-up time of the $1/2$ -in. reactors to about 90% of the desired reaction temperature was empirically, analytically, and experimentally (with added thermocouple) ascertained to be less than 2.5 min, which was much less than typical reaction times. The $1/8$ -in. reactors were of about 20% of the mass of the $1/2$ -in. reactors and were presumed to heat (and cool) more quickly. Upon completion of the prescribed reaction time the reactors were removed and placed in either a room temperature fluidized sand bath or an ice-water bath; the former quench mode was preferred when analysis for pyrolysis product water was attempted since quench water could linger on reactor threads and often obscure later GC analyses. Reactors were allowed to cool and dry before weighing to check for overall material balance. In the few instances where this check was indicative of a significant leak (material balance <90%), the reactor and its contents were discarded and not subjected to the further analysis that follows.

Opening the reactors in a glovebag maintained with a helium environment prevented contamination of gas samples, which were withdrawn by syringe from within the reactor's internal volume, by atmospheric nitrogen. Since the reactors had been purged previously with the internal standard nitrogen, only relative proportions of nitrogen and product gas were needed for quantitative determination of product gas yields. This procedure was thus useful to the extent that gas diffusion or convection from the reactor was well mixed.

Quantification of water and methanol product yields was accomplished through the addition of the external standard ethylacetate in 8- μ L increments to the $1/2$ -in. reactors and 1- μ L increments to the $1/8$ -in. reactors. A 50:50 ace-

tone-methylene chloride (water-free) mixture was then added to each reactor for extraction of the light liquids and phenolic products from the pyrolysate. The accuracy of this protocol was verified experimentally through the GC analyses of blanks and standard mixtures.

After analysis for light liquids (see below), the entire reactor contents were sacrificed for acetylation which facilitated GC analysis of phenolics. Acetylation followed the procedure of Schultz et al. (1981) and involved adding about 0.33 cm³ of acetic anhydride along with 7 μ L of pyridine to the $1/2$ -in.-reactor contents (0.17 cm³ and 3.5 μ L, respectively, for the $1/8$ -in. reactors). Samples of this mixture were used for later GC analyses for phenolics.

Product Analysis. The procedure detailed above divided pyrolysis products into three categories, namely, gases, light liquids, and phenolics. All three fractions were analyzed routinely by gas chromatography using an HP 5880 gas chromatograph equipped with dual TCD and dual FID detectors and an electronic integrator.

For gas analyses, 1.5-cm³ samples were withdrawn by syringe from the $1/2$ -in. reactors and separated over a 6 ft \times $1/8$ -in. stainless steel column packed with 80/100 mesh silica gel. Prepacked gas mixtures obtained from Scotty were used for both product identification and the calculation of quantitative product response factors. Gas products were additionally identified by GC-MS.

Injection of a 2- μ L sample of the acetone-methylene chloride mixture onto a 2 ft \times $1/8$ -in. disposable column packed with 80/100 mesh Porapak P enabled separation of water, methanol, and ethyl acetate and thus quantification of the former two. Identification of these products and calculation of quantitative response factors were accomplished by analysis of standard mixtures.

Phenolic products were analyzed by a procedure quite like that suggested by Schultz et al. (1981). A 2- μ L sample of the acetylated pyrolysate was injected onto a 6 ft \times $1/8$ -in. stainless steel column packed with 3% OV-17 and heated from 85 to 220 °C at 3 °C/min and then to 270 °C at 10 °C/min. Products were identified in three ways. First, GC with standard coinjection enabled identification of phenol, *o*-, *m*- + *p*-cresol, 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 4-propylphenol, guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol, catechol, 4-methylcatechol, 6-methylcatechol, and 3-methoxycatechol. Second, direct agreement with the retention times observed by Schultz et al. (1981) enabled identification of xylenol and 4-ethylcatechol. Third, interpolation between phenol homologues enabled identification of 6-ethylguaiacol and 6-ethylcatechol. In all, 19 different phenolic product yields were quantified.

The maximum sum of the yields of gases, light liquids, and identified single-ring phenolics was approximately 30% by weight of the original lignin; an additional group of 11 unidentified species that eluted near the single-ring phenolics on the GC traces (see below) was found in approximately 10% maximum yield. The remaining 60% of lignin pyrolysis products, including char, multiring phenolics, and other complex phenolics, were not examined quantitatively, and this precluded calculation of detailed carbon, hydrogen, and oxygen elemental balances. Details are available (Jegers, 1982).

Results

Table I summarizes the experimental conditions of pyrolysis temperature, time, reactor size, and the ratio of added tetralin to substrate for each material pyrolyzed. A total of 33 different products were quantified, including 12 gases, 2 light liquids, and 19 phenolics. Typical yields from each substrate for pyrolysis at 400 °C are listed in

Table I. Summary of Experimental Pyrolysis Conditions

substrate	T, °C	substrate charged to reactor, mg	tetralin to substrate, g/g	nominal reactor size, ^a in.	max reaction time, min
kraft lignin	300, 400, 500	300	0	1/2	130, 110, 60
kraft lignin plus tetralin	400	300	4	1/2	100
milled wood lignin	400	20	0	1/8	60
pine wood	400	300	0	1/2	60

^a Standard Swagelok component sizes.

Table II. Representative Product Yields (wt %) from Pyrolysis of Kraft Lignin, Kraft Lignin Plus Tetralin, Milled Wood Lignin, and Pine Wood at 400 °C

product	kraft lignin		kraft lignin + tetralin		milled wood lignin		pine wood ^a	
	7.5 min	60 min	10 min	55 min	8 min	20 min	10 min	50 min
methane	0.34	0.99	0.72	2.5	0.0065	0.0090	0.39	0.52
ethane	0.023	0.95	0.041	0.25	0.014	0.010	0.12	0.19
propane	0.014	0.0062	0.020	0.16	0.019	0.019	0.082	0.14
n-butane	0.0046	0.0189	0.0030	0.031	0.060	0.061	0.038	0.095
isobutane	0.0025	0.0015	0.0024	0.018	0.038	0.019	0.0081	0.024
ethylene	0.0087	0.0095	0.017	0.010	0.0027	0.0037	0.058	0.048
propylene	0.0086	0.0097	0.012	0.026	0.017	0.016	0.064	0.059
carbon monoxide	0.54	0.54	0.78	1.1	0.0066	0.0087	1.5	2.5
carbon dioxide	1.56	2.61	2.2	3.6	0.21	0.43	7.0	9.6
hydrogen sulfide	0.69	0.084	0.11	0.17	c	c	c	c
methylmercaptan	0.0022	0.0011	0.059	0.057	c	c	c	c
hydrogen	tr	tr	tr	tr	tr	tr	tr	tr
water	4.7	11.0	0.79	3.9	10.0 ^d	10.0 ^d	0.62	3.0
methanol	1.4	1.2	0.66	0.68	2.3 ^d	2.3 ^d	0.37	0.77
phenol	0.13	0.35	0.14	0.21	0.85	0.94	0.050	0.060
o-cresol	0.057	0.29	b	b	0.27	0.69	0.016	0.025
m + p-cresol	0.14	0.52	b	b	0.31	0.90	0.013	0.062
2-ethylphenol	0.0049	0.015	b	b	c	c	c	c
3-ethylphenol	c	0.051	0.13	0.25	c	c	c	c
4-ethylphenol	0.052	0.26	0.82	0.48	0.22	0.58	0.024	0.053
xlenol	0.065	0.22	0.58	0.27	0.19	0.51	0.029	0.047
4-propylphenol	c	0.65	0.16	0.22	0.14	0.44	c	c
guaiacol	2.6	0.12	1.1	0.34	0.22	0.43	0.44	0.015
4-methylguaiacol	2.6	0.046	1.9	0.13	0.34	0.80	0.58	c
6-ethylguaiacol	0.26	c	0.29	0.18	c	c	c	c
4-ethylguaiacol	1.2	c	1.3	0.17	0.22	0.50	0.28	c
4-propylguaiacol	0.82	0.19	1.1	c	0.29	0.67	0.80	c
catechol	1.1	0.37	1.1	1.3	0.50	0.94	0.35	0.10
6-methylcatechol	0.35	0.39	0.33	0.47	0.39	0.73	0.17	0.13
4-methylcatechol	1.1	0.40	0.86	1.6	0.45	0.32	0.70	0.16
6-ethylcatechol	0.19	0.17	0.14	0.31	0.11	0.14	0.083	0.069
4-ethylcatechol	0.42	0.15	0.72	0.85	0.31	0.40	0.26	0.15
3-methoxycatechol	0.34	0.051	0.62	0.60	0.30	0.19	0.29	0.18

^a Pine wood pyrolysis product yields in wt % wood. ^b Indicates overlap of product peak by tetralin. ^c Indicates that yield was either zero or below analytical threshold. ^d Average.

Table II. The temporal variations of product yields are illustrated in Figures 1 through 5, wherein solid curves are presented to facilitate examination of individual data and are not intended to be of theoretical or correlative significance. In the more detailed delineation of results that follows, substrates are considered in the order (1) kraft lignin, (2) kraft lignin plus tetralin, (3) milled wood lignin, and (4) pine wood. Within each of these headings, products are considered in the order of gases, light liquids, phenolics, and total volatiles. Quantitative yields, in weight percent of the original substrate charged, are quoted at relative maximal for those products observed to undergo secondary decomposition reactions and at asymptotic or upper limits for stable end products. Replicate experiments suggest these yields to be approximately within $\pm 40\%$, 50% , and 20% for gas, light liquid, and phenolic products, respectively.

Kraft Lignin. Kraft lignin pyrolysis products are listed in Table II.

Gases. Gaseous products could be divided into three categories, namely: (1) hydrocarbons, (2) carbon oxides, and (3) sulfur-containing compounds. Hydrocarbons were methane, ethane, ethylene, propane, propylene, *n*-butane,

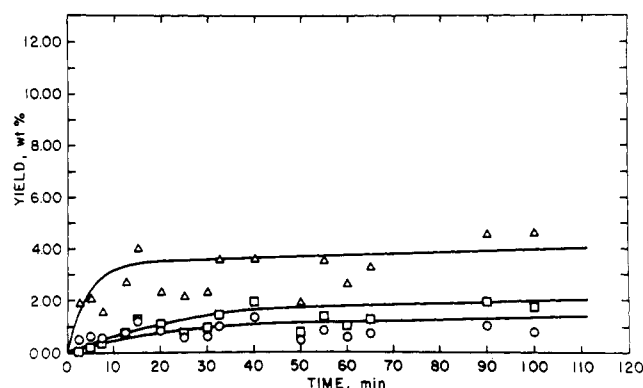


Figure 1. Temporal variations of methane (\square), carbon dioxide (Δ), and carbon monoxide (\circ) yields from kraft lignin pyrolysis at 400 °C.

and isobutane. Both carbon monoxide and carbon dioxide were observed and hydrogen sulfide and methyl mercaptan were the sulfur-containing compounds detected.

The temporal variations of the three major gaseous products—methane, carbon dioxide, and carbon mon-

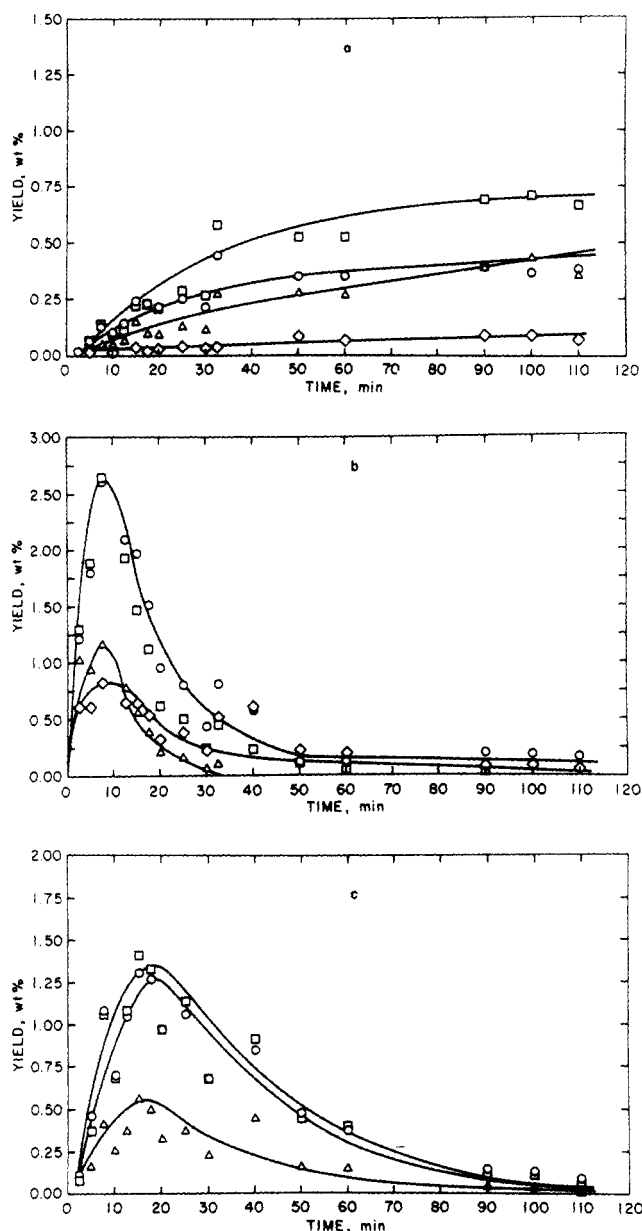


Figure 2. Temporal variation of phenolics yields from kraft lignin pyrolysis at 400 °C: (a) phenol (O), *m* + *p*-cresol (□), 4-ethylphenol (Δ), and 4-propylphenol (◇); (b) guaiacol (O), 4-methylguaiacol (□), 4-ethylguaiacol (Δ), and 4-propylguaiacol (◇); (c) catechol (O), 4-methylcatechol (□), and 4-ethylcatechol (Δ).

oxide—are shown in Figure 1 for kraft lignin pyrolysis at 400 °C. The maximum yield of methane ranged from 0.066 at 300 °C (130 min) to 3.7 at 500 °C (60 min). The next most abundant hydrocarbon gas, ethane, showed maximal yields of 0.0076 at 300 °C (130 min) and 0.4 at 500 °C (60 min). Propane yields ranged from 0.0064 (300 °C, 130 min) to 0.22 (500 °C, 60 min). The butanes were found in minor proportions as was evidenced through yields of only 0.055 for *n*-butane and 0.054 for isobutane at 500 °C and 60 min. The maximum yields of ethylene and propylene were about 0.040 at 500 °C and 4 min.

Carbon dioxide was the predominant gas product. Maximum yields of 2.2 at 300 °C and 12 at 500 °C were realized quickly. Carbon monoxide, the third most appreciable gas product behind carbon dioxide and methane, also evolved readily and attained maximal yields of 0.28, 1.3, and 2.8 at 300, 400, and 500 °C, respectively.

The yields of the two identified sulfur-containing compounds generally showed substantial uncertainty. A maximum hydrogen sulfide yield of 0.26 was obtained at

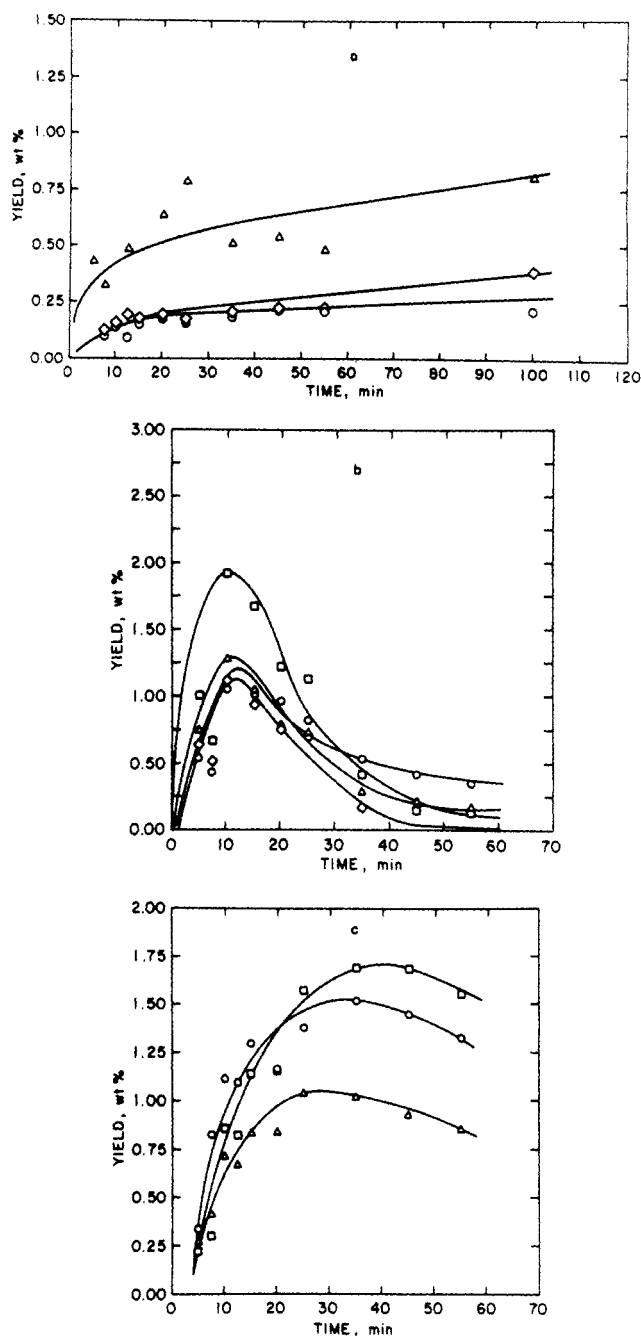


Figure 3. Temporal variation of phenolic yields from kraft lignin pyrolysis in tetralin at 400 °C: (a) phenol (O), 4-ethylphenol (Δ), and 4-propylphenol (◇); (b) guaiacol (O), 4-methylguaiacol (□), 4-ethylguaiacol (Δ), and 4-propylguaiacol (◇); (c) catechol (O), 4-methylcatechol (□), and 4-ethylcatechol (Δ).

500 °C and 60 min, while methylmercaptan reached its maximum yield of 0.072 at 300 °C and 55 min. Methylmercaptan secondary decomposition appeared to be appreciable even at 300 °C. Hydrogen was detected only at 500 °C in a yield of about 0.0084 at 60 min.

Light Liquids. Only water and methanol were significant among the GC peaks that appeared in the vicinity of typical light liquid products (Allan and Matilla, 1971) on the Porapak P column chromatogram.

Water formation was rapid at each pyrolysis temperature. Its yield was constant at about 2.0 for pyrolysis at 300 °C, whereas at 400 °C its yield increased with pyrolysis time until it reached 10.0 at 20 min, thereafter remaining fairly constant. A yield of about 8.0 was reached after 15 min at 500 °C.

Methanol yields increased monotonically with pyrolysis

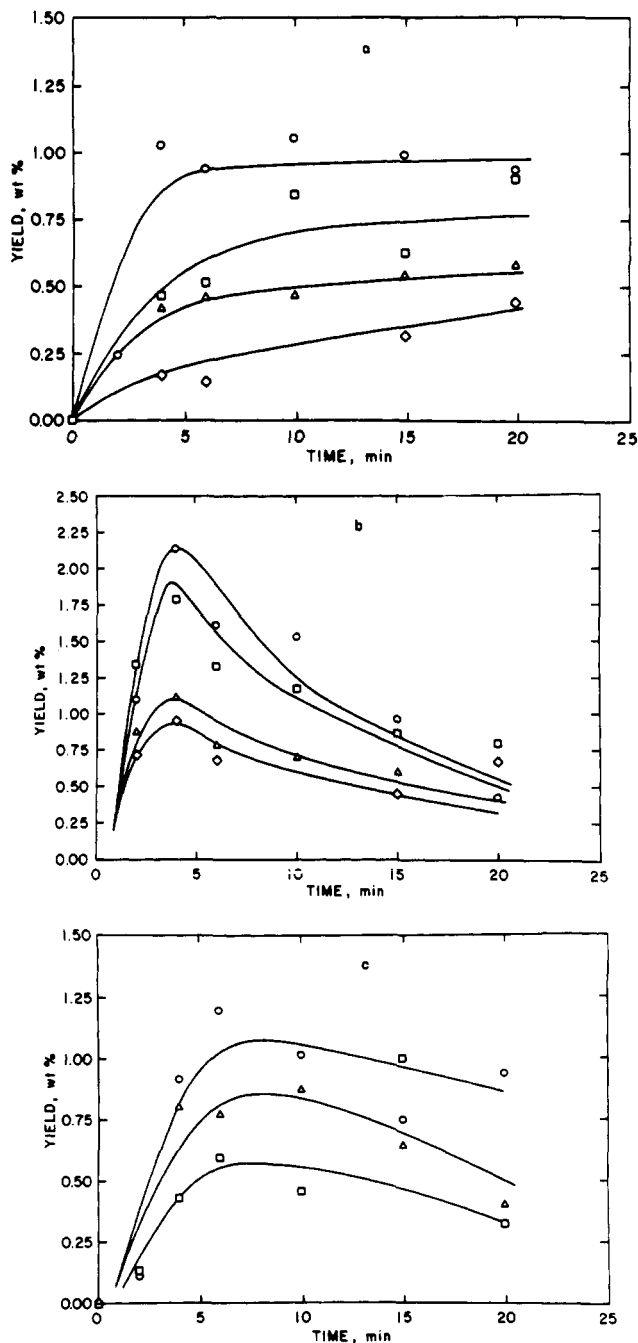


Figure 4. Temporal variations of phenolic yields from milled wood lignin pyrolysis at 400 °C: (a) phenol (O), *m* + *p*-cresol (□), 4-ethylphenol (Δ), and 4-propylphenol (◇); (b) guaiacol (O), 4-methylguaiacol (□), 4-ethylguaiacol (Δ), and 4-propylguaiacol (◇); (c) catechol (O), 4-methylcatechol (□), and 4-ethylcatechol (Δ).

time at 300 °C, reaching a value of 0.65 after 50 min, whereas its yields attained maxima of 2.7 and 0.22 at 400 °C (15 min) and 500 °C (10 min), respectively, before decreasing at longer pyrolysis times.

Phenolics. Quantified phenolics were all single-ring aromatics that could be categorized as follows: (1) monohydroxyl phenols, (2) guaiacols (2-methoxyphenols), and (3) catechols (1,2-dihydroxybenzenes). Phenols included phenol, *o*-cresol, *m* + *p*-cresol, 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 4-propylphenol, and xylenols. Guaiacols consisted of guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 6-ethylguaiacol, and 4-propylguaiacol. Finally, catechols comprised catechol, 4-methylcatechol, 6-methylcatechol, 4-ethylcatechol, 6-ethylcatechol, and 3-methoxycatechol.

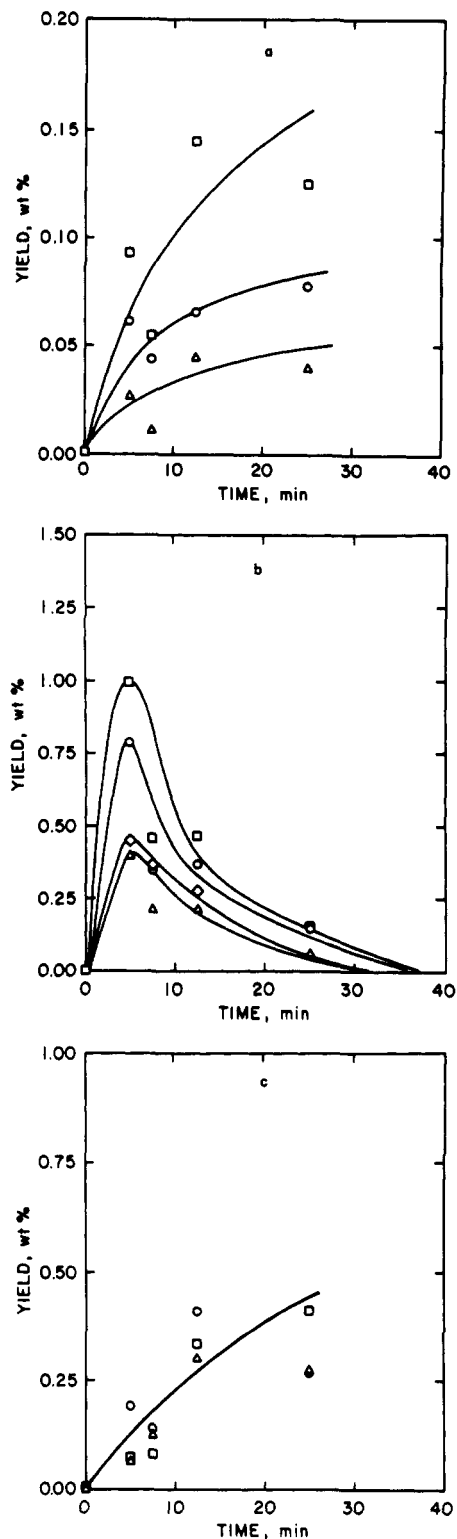


Figure 5. Temporal variations of phenolic yields from pine wood pyrolysis at 400 °C: (a) phenol (O), *m* + *p*-cresol (□), and 4-ethylphenol (Δ); (b) guaiacol (O), 4-methylguaiacol (□), 4-ethylguaiacol (Δ), and 4-propylguaiacol (◇); (c) catechol (O), 4-methylcatechol (□), and 4-ethylcatechol (Δ).

The temporal variations of the phenols' yields are illustrated in Figure 2a, a plot of the yield of phenol, *m* + *p*-cresol, 4-ethylphenol, and 4-propylphenol vs. time for pyrolysis at 400 °C. Almost nonexistent at 300 °C, monohydroxyl phenolics were more favored at long pyrolysis times and higher temperatures. Only phenol was appreciable at 300 °C, where a yield of 1.2 was reached after 130 min; at 400 and 500 °C its yield was typically 0.3 and 1.5, respectively. Cresol, 4-ethylphenol, and xylenol yields were

Table III. Yields of Guaiacols, Catechols, and Phenols from Kraft Lignin Pyrolysis at 400 °C and 7.5 and 60 min Holding Time

product no.	product	% yield ^a	
		7.5 min	60 min
1	guaiacol	2.61	0.12
2	4-methylguaiacol	2.64	0.05
3	4-ethylguaiacol	1.17	0.00
4	catechol	1.01	0.15
5	4-methylcatechol	1.06	0.11
6	4-ethylcatechol	0.42	0.15
	sum of 1-6	8.91	0.58
7	phenol	0.13	0.35
8	cresol	0.15	0.52
9	4-ethylphenol	0.05	0.26
10	<i>o</i> -cresol	0.05	0.29
	sum of 7-10	0.38	1.42
	sum of 1-10	9.29	2.0

^a Weight percent original lignin.

also about 0.3 at 400 °C, and the remaining phenols were found in yields of about 0.035.

Important guaiacols' yield patterns for pyrolysis at 400 °C are illustrated in Figure 2b, which shows these to be primary products that underwent an appreciable secondary decomposition that was also observed at 500 °C. The maximum yield of each guaiacol occurred at essentially 7.5 min for pyrolysis at 400 °C, where, individually, 4-methylguaiacol, guaiacol, 4-ethylguaiacol, 4-propylguaiacol, and 6-ethylguaiacol were found in yields of 2.6, 2.6, 1.2, 0.82, and 0.26, respectively. Yield patterns were qualitatively similar at 500 °C.

The temporal variations of catechols' yields, shown in Figure 2c for pyrolysis at 400 °C, were qualitatively similar to those of the guaiacols but displaced in time. Thus, as shown in Figure 2c, the maximum value of essentially all the catechol yields occurred at about 15–20 min, where, individually, methylcatechol and catechol were found in yields of 1.4 and 1.3, respectively. Remaining detected catechols were, in order of descending prevalence, 6-methylcatechol, 4-ethylcatechol, 3-methylcatechol, and 6-ethylcatechol, and they had yields of about one-fourth to one-half that of catechol. It is noteworthy that secondary catechol decomposition was not observed at 300 °C.

Catechols' proportions were higher at 500 °C, where 4-methylcatechol and catechol both attained yields of 3.1, and the remaining catechols were again found in yields from one-fourth to one-half the yield of catechol.

The yields of 11 unidentified products with GC peaks that eluted in the vicinity of the phenolic products were estimated by using a response factor equal to that for guaiacol. The fraction of the total GC area for all products that was attributed to these 11 unidentified "phenolics" varied from about 10% at 300 °C to about 4% at 500 °C.

The maximum total identified volatile yields, namely, the sum of the individual yields of identified gas, light liquid, and phenolic products, ranged from about 12% of the original lignin at 300 °C and 130 min to 30% at 400 °C and 15 min. The maximum at 500 °C, about 23%, is lower than that observed at 400 °C, presumably due to the secondary char-forming reactions of guaiacols and catechols.

The foregoing results suggest that monohydroxyl phenols were stable end products while guaiacol and catechol products were reactive. These two types of products are compared in Table III, where individual product yields, the total phenols' yields, and the sum of total guaiacols' plus total catechols' yields are listed for pyrolysis at 400

°C for both 7.5 and 60 min; the former reference time corresponds to a point of near maximal yields of guaiacols and catechols, whereas the latter time is a convenient point where these primary products had undergone extensive secondary reaction. Pyrolysis for 7.5 min gave guaiacols and catechols in 8.9% yield and phenols and cresols in 0.38% yield, for a total yield of these phenolics of 9.3%. Pyrolysis for 60 min gave 0.58% yield of guaiacols and catechols and 1.4% of phenols and cresols, which total 2.0%. These data show that of the 8.3% lower yield of guaiacols and catechols observed from 60 min pyrolysis relative to 7.5 min pyrolysis, only about 1% of this, at most, resulted in the production of phenols and cresols. The remaining 7.3% was evidently lost to coking, polymerization, and other degradation reactions. The secondary reactions of guaiacol and catechol evidently show high selectivity toward formation of coke over phenols.

Kraft Lignin in Tetralin. Kraft lignin pyrolysis with tetralin present in the weight ratio tetralin:lignin = 4:1 was accomplished at 400 °C. Products are delineated in the order gases, light liquids, and phenolics.

Gases. Gaseous products were hydrocarbons, carbon oxides, and sulfur-containing compounds. Methane, the predominant hydrocarbon gas, was found in a yield of 6.1 after 100 min, where the less prevalent hydrocarbons ethane, propane, *n*-butane, and isobutane had yields of 1.0, 0.62, 0.11, and 0.62, respectively. These yields are significantly higher than those obtained from neat kraft lignin pyrolysis and point to decomposition of tetralin (Bredael and Vinh, 1979) as a collaborative source of hydrocarbon gases. Ethylene and propylene were found in maximal proportions of 0.032 and 0.019 after 15 min, after which time their yields decreased.

Carbon dioxide and carbon monoxide both evolved readily and rose to maximum yields of 12.1 and 1.2, respectively, after 100 min. These yields closely match those noted previously for neat kraft lignin pyrolysis at 400 °C.

The yield of hydrogen sulfide increased with time and reached a value of 0.21 after 100 min. The yield of methylmercaptan steadily rose to a maximum value of 0.092 after 15 min. Hydrogen was detected in trace quantities of about 0.023 after 35 min.

Light Liquids. Both of the water and methanol light liquid products quickly approached their asymptotic yields of 6.01 and 1.06, respectively. It is interesting that the methanol yields were slightly higher and the water yields slightly lower than observed from neat pyrolysis at 400 °C.

Phenolics. The coincidence of GC retention times of tetralin and *o*-cresol, *m* + *p*-cresol, and 2-ethylphenol precluded quantification of these phenolics' yields. Phenols, guaiacols, and catechols were otherwise analyzed as before.

Figure 3a is a plot of the temporal variations of the yields of phenol, 4-ethylphenol, and 4-propylphenol. Inspection of Figure 3a reveals that phenol's yield increased with time, reaching a value of 0.21 after 100 min. Xylenol and 3-ethylphenol, not shown in Figure 3a, followed a pattern similar to that for 4-ethylphenol, and these products attained yields of 0.47, 0.32, and 0.81, respectively, after 100 min. The yield of 4-propylphenol rose to a value of 0.39 at 100 min.

The data in Figure 3b, a plot of the yields of guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol vs. pyrolysis time at 400 °C, accord with the general observation that all guaiacols' yields attained relative maxima; this was also observed in neat kraft lignin thermolysis. These maxima were reached after about 10 min, where yields for guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and

4-propylguaiacol were 1.1, 1.9, 1.3, and 1.1, respectively.

Important catechols' yields are shown in Figure 3c. The secondary decomposition of these products was not as conspicuous as that observed during neat kraft lignin pyrolysis. The most prevalent of these products, 4-methylcatechol, had a yield of 1.75 after 45 min, at which time catechol and 4-ethylcatechol were observed in yields of 1.5 and 1.0, respectively.

The uncertainty regarding hydrocarbon gas origins as well as the overlap of tetralin and the cresolic phenolic products prevented decisive quantification of total volatile product yields.

Milled Wood Lignin. Products evolved from the pyrolysis of the milled wood lignin at 400 °C are presented in the order gases, light liquids, phenolics, and total volatile yields.

Gases. Hydrocarbon gases evolved from milled wood lignin pyrolysis included, in order of descending prevalence, propane, methane, ethane, *n*- and isobutane, propylene, and ethylene. Yields of propane, methane, and ethane after 60 min were 0.036, 0.032, and 0.026, respectively. The yields of *n*- and isobutane were of the order 0.0011, and propylene and ethylene had maximum yields of 0.02 and 0.0043, respectively, after 10 min of pyrolysis.

Carbon dioxide evolution was facile in the approach to an ultimate yield of 0.76 after 60 min. This is considerably less than the yield of 4.0 observed from kraft lignin pyrolysis at 400 °C for 60 min. Carbon monoxide, also evolved quickly, reached a yield of only 0.015 after 60 min, once again considerably less than the carbon monoxide yield observed from kraft lignin pyrolysis at identical conditions. Sulfur-containing compounds were not identified.

Light Liquids. The average water yield, time invariant from about 25 to 60 min, was 8.9. Methanol followed a similar pattern and was observed in a yield of about 2.2.

Phenolics. Phenolic products were alkyl-substituted phenols, guaiacols, and catechols.

The temporal variations of the yields of phenol, *m* + *p*-cresol, 4-ethylphenol, and 4-propylphenol are illustrated in Figure 4a. The appearance of phenol was rapid and this product reached an asymptotic yield of 1.1 after 10 min; *o*-cresol and *m* + *p*-cresol reached yields of 0.69 and 0.90, respectively, after 20 min. Of the three ethylphenol isomers, only 4-ethylphenol was detected and this product was found in a yield of 0.58 after 20 min.

Important guaiacols' yields are plotted vs. pyrolysis time in Figure 4b. Each guaiacol attained a maximum yield after about 4 min, where individual yields of 2.1, 1.8, 1.1 and 0.95 were observed for guaiacol, 4-methylguaiacol, 4-ethylguaiacol and 4-propylguaiacol, respectively.

Figure 4c is a plot of the yields of catechol, 4-methylcatechol, and 4-ethylcatechol vs. pyrolysis time. Catechols' formation and decomposition patterns were similar to those for the guaiacols, and although a precise time of the maximal yield was difficult to discern due to experimental uncertainty, it appeared to occur at about 8 min holding time for each catechol. The yield of catechol, about 1.3, was highest, and this product was followed by 6-methylcatechol, 3-methoxycatechol, 4-ethylcatechol, 4-methylcatechol, and 6-ethylcatechol in yields of 1.0, 0.92, 0.87, 0.46, and 0.30, respectively.

The total yield of volatiles rose to a maximum value of about 22.0 at 10 min, after which time it decreased due to the disappearance of guaiacols and catechols.

Pine Wood Pyrolysis. Pyrolysis of the whole wood from which the milled wood lignin was extracted was accomplished at 400 °C. In the discussion that follows,

product yields are reported on a weight percent of wood basis.

Gases. The yield of methane, which was the major hydrocarbon gas, rose steadily until it reached 0.526 after 50 min. Other stable products, listed in order of descending proportions, were ethane, propane, and *n*- and isobutane in yields of 0.19, 0.14, 0.95, and 0.024, respectively, after 50 min. Ethylene and propylene yields attained maxima of 0.059 (12.5 min) and 0.064 (10 min), respectively, after which times the yields decreased. Carbon dioxide and carbon monoxide evolved readily at early pyrolysis times and thereafter slowly approached values of 9.6 and 2.5, respectively, realized after 50 min of pyrolysis. No hydrogen or sulfur-containing compounds were detected.

Light Liquids. Although water yields showed substantial variations, a maximum value of 3.0 could be discerned. Methanol yields were more certain and approached 0.94 after 15 min of pyrolysis.

Phenolics. The temporal variations of the yields of phenol, *m* + *p*-cresol, and 4-ethylphenol are illustrated in Figure 5a. Phenol reached a maximum yield of 0.077 after 25 min, and the other phenols detected, namely, *m* + *p*-cresol, *o*-cresol, xylenol, and 4-ethylphenol, had yields of 0.13, 0.050, 0.041, and 0.040, respectively, after 25 min; 2- and 3-ethylphenol and 4-propylphenol were not observed.

As illustrated in Figure 5b, a plot of important guaiacols' yields vs. pyrolysis time, guaiacols' yields peaked after about 5 min reaction time. The 4-methylguaiacol yield of 1.0 was the highest of all guaiacols, followed by guaiacol, 4-propylguaiacol, and 4-ethylguaiacol with respective yields of 0.79, 0.45, and 0.40 at 5 min; 6-ethylguaiacol was not observed.

Figure 5c, a plot of important catechols' yields vs. pyrolysis time, reveals that the yield of catechol rose to a value of 0.41 after about 12.5 min pyrolysis time. Other product yields were 0.33, 0.32, 0.30, 0.25, and 0.14 for 4-methylcatechol, 3-methoxycatechol, 4-ethylcatechol, 6-methylcatechol, and 6-ethylcatechol, respectively.

Discussion

The discussion to follow comprises three major sections. In the first, the present and previous lignin pyrolysis results are considered in light of the experimental reactors employed. In the second section the present results obtained from the pyrolysis of kraft lignin, kraft lignin plus tetralin, and milled wood lignin are compared. The final section concerns a simple kinetic analysis of kraft lignin pyrolysis and a tentative lumping scheme suggested therein.

Pyrolysis Reactor Design. Comparison with previous pyrolyses is complicated by variations in lignin substrates, temperature-time histories, reactor types, and even fragmentation method (e.g., plasma vs. pyrolysis). Nevertheless, some relevant comparison is possible, and this nonuniformity can emphasize the role of various process design variables. In the discussion to follow, the maximum product yields obtained at closely matching pyrolysis temperatures are used for the comparison of the influence of reactor environment on previous and the present results. It should be emphasized that the dramatic variations in substrates and reactors noted above would be expected to cause significant variations in the product yields compared below.

Iatridis and Gavalas (1979) pyrolyzed a kraft lignin in a heated grid apparatus with a flow of inert gas designed to emphasize primary reactions. A direct comparison with the present neat kraft lignin pyrolysis results at 400 °C

is possible. Their maximum methane yield of 0.52 was less than the 1.73 maximum yield found in the present work. These workers did not report catechols as products, which couples with the relatively low methane yields to confirm that their reactor suppressed the secondary reactions of guaiacols to catechols and methane (Klein and Virk, 1981). Iatridis and Gavalas found slightly greater maximum carbon dioxide yields ($5.97 > 4.6$, respectively) and slightly lower methanol yields ($2.37 < 2.73$) than in the present work; these workers did not report water. Water and carbon dioxide evolve quickly and from, predominantly, origins within the lignin macromolecule (Klein and Virk, 1981), and their yields should thus be somewhat insensitive to the reactor design and the fate of primary volatile products. Methanol origins have been proposed to be both of the characteristic lignin aromatic methoxyl group (Allan and Matilla, 1971) and cinnamyl alcohol-type propanoid side chains (Klein and Virk, 1981). Both of these appear in potential primary products that could be removed before secondary reaction to methanol in the Iatridis and Gavalas reactor.

Kirshbaum et al. (1976) pyrolyzed an alkali aspen lignin at 400 °C under conditions of rapid heating. These workers did not report gases or light liquid products and analysis of their extensive list of phenolic products obtained from this hardwood lignin, which contains appreciable proportions of not only coniferyl but the dimethoxylated sinapyl alcohol lignin monomer, can be attempted by comparing the sum of their syringols and guaiacols yields against the present yields of guaiacols. It should be noted, however, that the formation of guaiacol from 2,6-dimethoxyphenol is formally akin to the formation of phenol from guaiacol, and thus some of the guaiacol in the syringol plus guaiacol lump will have arisen from secondary pyrolyses of primary syringols.

Yields of guaiacols plus syringols reported by Kirshbaum et al. (1976) were similar to the present yields of guaiacols. Thus, guaiacol + syringol, 4-methyl-(guaiacol + syringol), 4-ethyl-(guaiacol + syringol), and 4-propyl-(guaiacol + syringol) were reported in yields of 2.4, 3.0, 1.3, and 0.16, respectively, and the present maximum yields of guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol obtained from neat kraft lignin pyrolysis at 400 °C and 7.5 min were 2.6, 2.6, 1.2, and 0.82, respectively. Kirshbaum et al. reported less phenol ($0.05 < 0.39$), *m* + *p*-cresol ($0.03 < 1.2$), *o*-cresol ($0.01 < 0.62$), and catechol ($0.07 < 1.30$) than the maximum yields found in the present work at 400 °C which, in view of the similar maximum yields of guaiacols plus syringols, noted above, suggests that their reactor favored the recovery of the most primary volatile products (i.e., guaiacols plus syringols).

Domburg et al. (1971) pyrolyzed an alkali spruce lignin in a covered crucible held in an oven at 475 °C. Gases, water and methanol were not reported, and comparison of the present results with their list of single-ring phenolic products is best accomplished by using the neat kraft lignin pyrolysis results at 500 °C.

Monohydroxyl phenols were found in smaller yields by Domburg et al. than the maxima observed in the present work. Thus phenol, *m* + *p* + *o*-cresol, and 4-ethylphenol compared as ($0.10 < 1.46$), ($0.50 < 2.60$), and ($0.10 < 0.63$), respectively. Likewise, catechol yields found by these workers were always lower than the maxima at 500 °C in the present work, as catechol, 4-methylcatechol, 4-ethylcatechol, and 3-methoxycatechol yields were ($0.80 < 3.1$), ($1.10 < 3.1$), ($0.50 < 1.2$), and ($0.05 < 0.5$), respectively. Guaiacol yields, on the other hand, were generally observed in higher yields by Domburg et al., as guaiacol, 4-

methylguaiacol, and 4-ethylguaiacol yields compared as ($1.4 \sim 1.3$), ($3.9 > 1.4$), and ($1.2 > 0.66$), respectively; propylguaiacol yields compared as ($0.10 < 0.63$). Evidently, the lignin distillate analyzed by Domburg et al. had undergone little secondary decomposition.

Comparison of the present kraft lignin pyrolyses with the thermolyses of Chan and Krieger (1981), who pyrolyzed a kraft lignin at 1.5 kW microwave power for 5 min, and with Graef et al. (1979), who decomposed a kraft lignin in a helium plasma, is less straightforward. Chan and Krieger reported methane and water yields that are comparable to those observed here. Ethane, carbon dioxide, phenol, *o*-cresol, *m*-cresol, *p*-cresol, and guaiacol were all found in smaller yields from the microwave pyrolysis, and ethylene, acetylene, carbon monoxide, and hydrogen were found in higher yields. Chan and Krieger also reported the formation of nonphenolic fused-ring products such as naphthalene, methylnaphthalene, methyldiphenyl, fluorene, and anthracene, which were not observed in the present work. The plasma yielded acetylene (14.0) and carbon monoxide (47.5) as the predominant products, along with appreciable amounts of hydrogen (3.32). Nonphenolic aromatics such as styrene, phenylacetylene, naphthalene, acenaphthene, and anthracene were also observed.

A final relevant comparison can be made between the present kraft lignin plus tetralin pyrolysis results and the work of Connors et al. (1980), who pyrolyzed a kraft lignin at 400 °C in a 300-cm³ autoclave with tetralin in a ratio of tetralin:lignin = 4:1. The autoclave was brought to 400 °C in 90 to 100 min, and only single-ring phenolics were quantified.

Maximal yields of phenols reported by Connors et al. and obtained here were similar, as phenol and 4-ethylphenol compared ($0.13 \sim 0.15$) and ($0.50 < 0.92$), respectively. Maximal guaiacol, 4-methylguaiacol, 4-ethylguaiacol, and 4-propylguaiacol yields reported by these workers were generally less than in the present work, as these product yields were ($0.70 < 1.0$), ($0.89 < 1.7$), ($0.98 \sim 1.1$), and ($0.35 < 0.94$), respectively. Yields of catechol, 4-methylcatechol, and 4-ethylcatechol compared as ($0.99 < 1.30$), ($1.11 \sim 1.14$), and ($0.80 \sim 0.84$), respectively, and were in substantial accord. In all, the agreement between these product spectra suggests that the influence of heat-up time is less significant than the reactor environment.

Influence of Lignin Structure and Additives. It is also informative to compare some of the products obtained from the pyrolyses of kraft lignin, kraft lignin plus tetralin, and the "milled wood" lignin.

Tetralin was evidently an active donor solvent that could influence kraft lignin pyrolysis pathways. Along these lines, more ethyl- and propylguaiacols were observed, and less methylguaiacol and guaiacol, from pyrolysis with tetralin present than without. Thus, tetralin was able to cap the highly reactive allyl- (to propyl-) and vinyl- (to ethyl-) substituted guaiacol intermediates (Petrocelli and Klein, 1984) that decompose to methyl- and propyl-substituted guaiacols during pyrolysis without tetralin. Note also that yields of ethyl- and propylphenol were higher, and the yield of phenol was lower, from pyrolysis with tetralin added than from neat pyrolysis. Analysis of catechols is complicated by the apparent suppression of catechol decomposition reactions by tetralin.

Methanol yields were higher from pyrolysis of the milled wood lignin than from pyrolysis of kraft lignin, either neat or in tetralin. Since kraft and native lignins contain approximately equal numbers of aromatic methoxyl groups, this information suggests that the aliphatic methylol

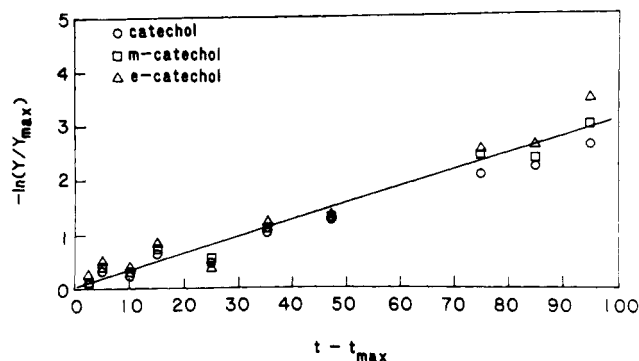


Figure 6. Decomposition of catechol (○), 4-methylcatechol (□), and 4-ethylguaiacol (Δ) during kraft lignin pyrolysis.

groups in the propanoid side chains were important methanol precursors. It is relevant that roughly 15 of 18 units in the Freudenberg (1968) structure contain methylol groups compared to 5 of 14 units in the Marton (1971) structure.

Pyrolysis of the milled wood lignin evolved more propyl-substituted phenolics than were found from pyrolysis of the kraft lignin; negligible quantities of 2- and 3-ethylphenol formed also. These difference can be traced to the condensation reactions that alter lignin structure during kraft pulping (Jegers, 1982). For example, the side chains in a kraft lignin often contain two, three, or four carbon atoms, while propanoid chains predominate in native lignins. Also, pulping-related condensation reactions can result in the formation of interunit linkages at potential products' "3" or "5" position, and these linkages are rare in native lignins.

Secondary Reactions of Catechols and Guaiacols. The present results demonstrated that not only guaiacols but also catechols undergo secondary decomposition during lignin pyrolysis. Pseudo-first-order rate constants for the decomposition of these products during kraft lignin pyrolysis at 400 °C were estimated as follows. Catechol and guaiacol temporal variations, shown in Figures 2b and 2c, respectively, were modeled by the global lumping scheme of eq 1, where A represents all precursors of the discrete



product B, of interest, and C represents the decomposition products of B. Since A is a collection of polymeric and, possibly, discrete molecular species, it is difficult to assign a fundamentally interpretable rate constant to step 1 in eq 1. On the other hand, the decomposition of the discrete molecular species B (once liberated from a macromolecule, in the present case) can be easily described with a rate constant that is consistent with fundamental kinetic principles. This rate constant k_2 was estimated by following the temporal variations of B at high conversion of A since, from eq 1

$$\frac{dB}{dt} = k_1A - k_2B \quad (2)$$

and if A is small, say at long times, then

$$\frac{dB}{dt} \approx -k_2B \quad (3)$$

and

$$\ln \frac{B}{B^*} \approx -k_2(t - t^*)$$

B^* and t^* are some convenient reference yield and time, respectively, here taken at the point of maximal proportions of B.

Table IV. Estimated Rate Constants and Associated Uncertainties for Catechol and Guaiacol Decomposition During Kraft Lignin Pyrolysis at 400 °C

compd	$k \times 10^4$, s^{-1}	std dev, $s \times$ 10^4 , s^{-1}	t	(95% conf limit = $st) \times 10^4$
catechol	4.5	0.27	2.31	0.61
4-methylcatechol	5.0	0.35	2.31	0.81
4-ethylcatechol	5.3	0.45	2.31	1.04
all catechols	4.9	0.25	1.96	0.49
guaiacol	10.5	1.1	2.31	2.54
4-methylguaiacol	12.7	0.83	2.31	1.92
4-ethylguaiacol	17.5	2.7	2.57	6.94
4-propylguaiacol	4.0	0.82	2.31	1.88
all guaiacols	7.1	1.6	1.96	3.12
pure guaiacol ^a	6.3			

^a Klein and Virk (1981).

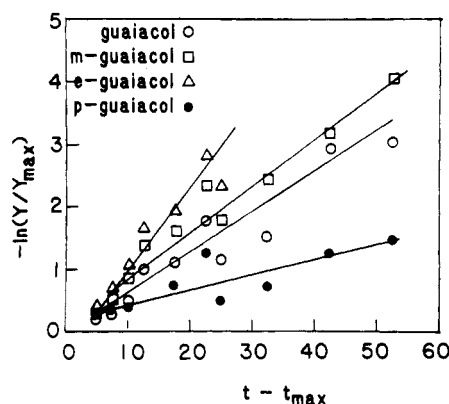


Figure 7. Decomposition of guaiacol (○), 4-methylguaiacol (□), 4-ethylguaiacol (Δ), and 4-propylguaiacol (●) during kraft lignin pyrolysis at 400 °C.

Figure 6 is a plot of $\ln B/B^*$ vs. $t - t^*$ for catechol, methylcatechol, and ethylcatechol. Note that although the absolute yields of these catechols were different, normalized values ($\ln B/B^*$) fall closely about the least-squares line with a slope of $4.9 \times 10^{-4} s^{-1}$ in Figure 6. Values of k_2 obtained by least-squares linear regression for each individual catechol as well as that just noted for the collective lump of all catechols are reported in Table IV along with their associated standard deviations and 95% confidence intervals. The qualitative coincidence of the rate constants and the quantitative overlap of confidence limits suggest that the secondary decomposition reactions of catecholic moieties during kraft lignin pyrolysis are evidently not appreciably dependent upon the nature of para-substituents.

Similar analyses of the decomposition reactions of the various guaiacols were less compelling. The plots of $\ln B/B^*$ vs. $t - t^*$ in Figure 7 illustrate the greater experimental uncertainty associated with the guaiacols relative to that with the catechols.

The statistical information summarized in Table IV shows that the 95% confidence limits on k_2 for guaiacol, methylguaiacol, and ethylguaiacol overlap; the confidence limit for propylguaiacol does not overlap that for any other individual guaiacol. The confidence limits on k_2 for the collective lump, "all guaiacols," however, very nearly overlap the confidence limits for each individual guaiacol. It is interesting, however, that the values of the individual rate constants show no obvious dependence on the chemical nature of the guaiacols' substituents. It is also informative to note that the previously reported (Klein and Virk, 1981) rate constant of $6.3 \times 10^{-4} s^{-1}$ for pyrolysis of

pure guaiacol is of the same order of magnitude as the k_2 values calculated herein and within the confidence limits on the value of k_2 for the collective lump of all guaiacols.

In summary of the above, it is reasonable to assert that during kraft lignin pyrolysis one rate constant can usefully characterize the secondary decomposition of all catechols and also that another single rate constant can characterize the decomposition of guaiacol, methylguaiacol, and ethylguaiacol; compelling quantitative evidence to include propylguaiacol in the latter lump is lacking. However, since the chemical logic to suggest that substituents should profoundly affect the secondary reactions of guaiacols but not catechols is also lacking, it seems qualitatively reasonable to consider the secondary reactions of the variously substituted guaiacols as synchronous during kraft lignin pyrolysis at 400 °C.

These results are significant in two manners. First, a simple model of lignin pyrolysis might depict phenolic products through a lumping scheme involving guaiacol, catechol, and, by extension, phenol groups. The observation that all guaiacols' maximal proportions came at about 7.5 min pyrolysis time and that all catechols' maximal proportions came at about 15 min pyrolysis time is consistent with the lumping scheme. Second, the rate constants measured here for the guaiacols' degradation during kraft lignin pyrolysis and that for pure guaiacol pyrolysis are of the same order of magnitude, which suggests that during lignin pyrolysis the secondary decomposition reactions of discrete molecular species are relatively independent of the presence of both other molecular species and also the residual polymeric material. One consequence of this, for example, is that model compound reaction pathways and kinetics should be relevant to the pyrolysis of macromolecules.

Model compound information does provide some insight into the plausibility of this lumping scheme, which would focus on the reaction of lignin guaiacyl moieties and devote less attention to the reactions of propanoid side chains. The underlying implication of this scheme is that relative to guaiacyl reactions, secondary side chain reactions would be either very fast, and hence occur quickly upon cleavage of interaromatic unit bonds, or be very slow, in which case the cleavage of interaromatic unit bonds would render a thermally stable side chain substituent. Examples in the former category might be degradation of vinyl substituents to methyl, ethyl, and propyl substituents (Klein, 1981), and examples in the latter category would evidently be protium, methyl, ethyl, and propyl substituents generated through interaromatic unit cleavage. Here it is noteworthy that diphenylethane, diphenylmethane, and stilbene (diphenylethylene), which mimic the important interaromatic unit linkages found in kraft lignins, fragment to, predominantly, stable toluene, benzene, and polymeric products (Petrocelli and Klein, 1984; Panvelker et al., 1982; Kistiakowsky and Smith, 1934; Sweeting and Wilshire, 1962). The former two products correspond to the formation of methyl- and propyl-substituted phenols, guaiacols, and catechols, respectively, from the interunit bond fragmentation that occurs during lignin pyrolysis.

Application of the lumping scheme noted above to native lignins would require greater care, since different types of interunit bonds and thus primary side chain pyrolysis products would be involved.

Summary and Conclusions

1. A total of 33 products, including 12 gases, water, methanol, and 19 phenolics, were identified and quantified from the pyrolyses of kraft lignin, kraft lignin plus tetralin, a milled wood lignin, and actual pine wood at 400 °C and

also 300 and 500 °C for the kraft lignin.

2. For pyrolysis at 400 °C, all important guaiacols attained maximal proportions at 7.5 min pyrolysis time before undergoing secondary decomposition reactions; the decomposition rate constants for guaiacol, methylguaiacol, and ethylguaiacol were quite similar. Guaiacols also attained their maximal proportions nearly synchronously during pyrolysis at 300 and 500 °C for the kraft lignin and also for the kraft lignin plus tetralin, milled wood, and whole wood pyrolyses.

3. All important catechols attained maximal proportions at about 15 min pyrolysis time before undergoing secondary decomposition reactions with virtually identical decomposition rate constants during kraft lignin pyrolysis at 400 °C. Catechols also attained their maximal proportions nearly synchronously during pyrolysis at 300 and 500 °C and for milled wood and whole wood pyrolyses, but catechol decomposition was less severe during pyrolysis in tetralin.

4. Comparison of various sets of lignin experimental pyrolysis results in the light of the reactor's emphasis of primary only or both primary and secondary reactions allows a reasonable qualitative interpretation of the variations in reported product yields.

5. Pyrolysis with tetralin present resulted in the formation of higher yields of ethyl- and propyl-substituted single-ring phenolics than obtained from neat kraft lignin pyrolysis at a given pyrolysis temperature and time.

6. Methanol yields were higher from milled wood lignin pyrolysis than from kraft lignin pyrolysis. This was attributed to the greater proportion of aliphatic methylol groups present in milled wood lignins than found in kraft lignins.

7. The similarity of guaiacol, methylguaiacol, and ethylguaiacol decomposition rate constants during kraft lignin pyrolysis at 400 °C, and also the coincidence of catechol, methylcatechol, and ethylcatechol decomposition rate constants at 400 °C, suggested that a lumping scheme involving phenols, guaiacols, and catechols would be useful in analysis and modeling of lignin pyrolysis.

8. The overlap of confidence limits for the rate constants for the secondary decomposition of guaiacol products during kraft lignin pyrolysis with a previously reported rate constant for pyrolysis of pure guaiacol suggests that the reactions of thermally liberated discrete molecular species during lignin pyrolysis are relatively insensitive to the presence of other molecular species or polymeric residuum.

Acknowledgment

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Registry No. Kraft lignin, 8068-05-1; milled wood lignin, 8068-00-6; tetralin, 119-64-2; catechol, 120-80-9; 4-methylcatechol, 452-86-8; 4-ethylcatechol, 1124-39-6; guaiacol, 90-05-1; 4-methylguaiacol, 93-51-6; 4-ethylguaiacol, 2785-89-9; 4-propylguaiacol, 2785-87-7.

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Interaction Second Virial Coefficients of Polar Mixtures from Parameters of the Components

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Procedures are presented for the calculation of interaction second virial coefficients B_{12} of polar mixtures from the parameters of the components. Relationships for the second virial coefficients of polar fluids for the Kihara spherical core potential with temperature-dependent molecular constants are utilized in conjunction with combining rules for the mixture parameters. The input data required are the critical temperatures, critical pressures, acentric factors, and polarity factors of the components. For 111 experimental points this approach resulted in an average deviation of 25 cm³/mol in comparison with available experimental values of B_{12} . Comparable results are obtained with a simplified procedure based on the use of the Pitzer-Curl equations for the second virial coefficient with temperature-dependent critical constants. A procedure for the separation of induction contributions for nonpolar-polar mixtures is also described which results in improved values of B_{12} for most of the systems considered.

Interaction second virial coefficients of polar gas mixtures are required for many applications, including the calculation of vapor-liquid equilibrium values at moderate pressures. Most of the previous methods for the determination of this property require experimental data to obtain reliable values. It is desirable to have an improved procedure for polar mixtures to enable the calculation of values for systems for which data are not available and to permit suitable combining rules for the mixture parameters to be established. In this study a method has been developed for the determination of interaction second virial coefficients of polar mixtures from parameters of the components by the use of a four-parameter intermolecular potential function for polar fluids.

Previous Studies for Polar Mixtures

O'Connell and Prausnitz (1967) presented a relationship for the second virial coefficients of polar fluids of the following form

$$\frac{BP_c}{RT_c} = B^{*(0)}(T_R) + \omega_h B^{*(1)}(T_R) + B_{\mu}^*(\mu_R, T_R) - \eta B_a^*(T_R) \quad (1)$$

where $B^{*(0)}$ and $B^{*(1)}$ are the reduced functions of Pitzer and Curl (1957) for nonpolar fluids, ω_h is the acentric factor of a nonpolar substance having a similar size, $\mu_R = 10^5 \mu^2 P_c / T_c^2$ is a reduced dipole group, and η is a parameter representing the effects of association. Analytical expressions were obtained for B_a^* and B_{μ}^* . For polar mixtures, O'Connell and Prausnitz presented relationships for the calculation of T_{c12} , P_{c12} , ω_{h12} , μ_{R12} , and η_{12} from the parameters of the components. Average errors of up to 150 cm³/mol were obtained for various types of polar

mixtures. For several polar-polar mixtures an interaction constant η_{12} obtained from the experimental data was required to obtain reasonable results.

Halm and Stiel (1971) utilized experimental second virial coefficient data for 13 polar fluids to determine the coefficients $B^{*(2)}$, ..., $B^{*(5)}$ of the following relationship as functions of reduced temperature

$$B^* = B^{*(0)} + \omega B^{*(1)} + \chi B^{*(2)} + \chi^2 B^{*(3)} + \omega^6 B^{*(4)} + \omega \chi B^{*(5)} \quad (2)$$

where $B^{*(0)}$ and $B^{*(1)}$ are the values for the Pitzer-Curl equation and χ is the polarity factor of the fluid. For polar substances, Halm and Stiel developed relationships between available molecular parameters for a four-parameter intermolecular potential function and critical constants, acentric factors, and polarity factors. These relationships were utilized with combining rules for the molecular parameters to obtain equations for the mixture parameters T_{c12} , P_{c12} , ω_{12} , and χ_{12} from the parameters of the components. These mixture parameters resulted in an average error of 7.0% in mixture second virial coefficients for nine polar systems.

Tsonopolous (1974) proposed a relationship for the second virial coefficient of polar fluids of the form

$$\frac{BP_c}{RT_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + \frac{a}{T_R^6} - \frac{b}{T_R^8} \quad (3)$$

where $f^{(0)}$ and $f^{(1)}$ are modified functions similar to $B^{*(0)}$ and $B^{*(1)}$, and a and b are constants determined from data for each substance. For non-hydrogen bonding substances $b = 0$, and separate relationships between a and the dipole group μ_R were developed for several groups of substances