

Investigations of Simultaneous Coal and Lignin Liquefaction: Kinetic Studies

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Liquefaction of mixtures of an Illinois bituminous coal and a caustic lignin was studied. Reactions were conducted at an initial hydrogen pressure of 1.1 MPa and at a temperature of 375 °C, in tetralin. The liquid product from the coal-lignin mixture contains a lower fraction of the undesirable benzene insolubles than the product for coal alone. Size-exclusion chromatography studies indicate that, with the coal-lignin mixture, the weight-averaged molecular weight for the overall liquid product is lower than the molecular weight obtained by reacting coal or lignin alone. The experimental data also show that a 22% enhancement in coal conversion results due to the addition of lignin. A mathematical model that describes the reaction chemistry has been developed and analyzed. The influence of recycling of the liquid product was also studied. Preliminary experiments indicate that the overall coal depolymerization yields decrease, albeit gradually.

1. Introduction

For the past few decades, the main source for liquid fuels has been petroleum. On one hand, petroleum reserves are declining, and on the other hand, coal reserves are still abundant. Coal, a solid, can be converted into liquid fuel by hydrogenation.¹ One method used to hydrogenate coal is to subject it to reaction with a hydrogen donor solvent, such as tetralin.² For an efficient coal depolymerization process, cleavage of selective coal fragments is necessary. While thermal cracking is nonselective and requires high temperature, catalytic cracking can accomplish selective cleavage under less severe conditions. Triflic acid and iodine, for example, are good coal conversion catalysts;³ *p*-toluenesulfonic acid is another catalyst that has been used.⁴ Recently, a review of coal liquefaction by phenolation was presented.⁵ Coal can be depolymerized in phenol at high temperatures (around 425 °C)⁶ or at lower temperatures (e.g., 100 °C) using a catalyst such as BF₃.⁷

Lignin, an abundant byproduct of the paper and pulp industry, is a renewable raw material. It can be viewed as an inexpensive source of aromatic compounds.⁸ It is hypothesized that phenoxy radicals, as well as other types of radicals produced by lignin at relatively moderate temperatures, can attack the coal molecule, causing scission of the aliphatic C-C bonds in the coal.⁹

Recent reports⁹⁻¹² have shown that the addition of lignin to coal during liquefaction significantly enhances the

depolymerization of coal and the quality of the liquid products obtained at temperatures as low as 300 °C, but under high pressure, 6.9-13.9 MPa. Recent work in our laboratories^{13,14} has shown an enhancement in coal liquefaction yields and rates due to lignin addition at lower pressures (1.1-4.6 MPa) and temperatures in the range 325-375 °C. It was found that the liquid products obtained from coal-lignin mixtures contain appreciably lower amounts of benzene-insoluble compounds and higher quantities of the desirable lower molecular weight asphaltene and pentane-soluble fractions over the corresponding fraction of liquids that are obtained by processing either coal or lignin alone. Similar enhancement in coal conversion and improvement in product quality were observed when coal was processed in the presence of lignin-derived liquids under the same reaction conditions. This paper further describes the role of lignin in enhancing the conversion yields and rates of coal depolymerization. Also presented is a mathematical model for the proposed reaction chemistry that permits evaluation of various rate constants.

2. Experimental Section

2.1 Materials. **2.1.1 Coal.** A bituminous coal was used. It was Illinois Basin Coal Sample Bank No. 105 of particle size less than 75 μm, obtained from the Argonne Premium Coal Bank.

2.1.2 Lignin. A caustic lignin, obtained from steam-exploded aspen, was used that was donated by Stake Technology Ltd., Ontario, Canada. Moisture was removed by drying the sample to a constant weight in a vacuum oven at 105 °C. Elemental and proximate analyses of coal and lignin are listed in Table I.

2.1.3 Tetralin. Tetralin purchased from Aldrich Chemical Co. was used as received.

2.2 Depolymerization Procedure. Coal and lignin were charged into a glass-lined, 300-mL autoclave reactor. The procedure is described elsewhere.^{13,14} Briefly, the reactor was

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Table I. Analyses of Coal and Lignin

element	elemental analysis	
	coal	lignin
C	76.24	56.47
H	5.36	6.06
S	5.39	3.35
N	1.57	<0.50
O (by difference)	11.44	34.12

component	proximate analysis	
	coal	lignin
volatiles	37.51	68.05
ash	18.31	11.57
fixed carbon	44.18	20.38

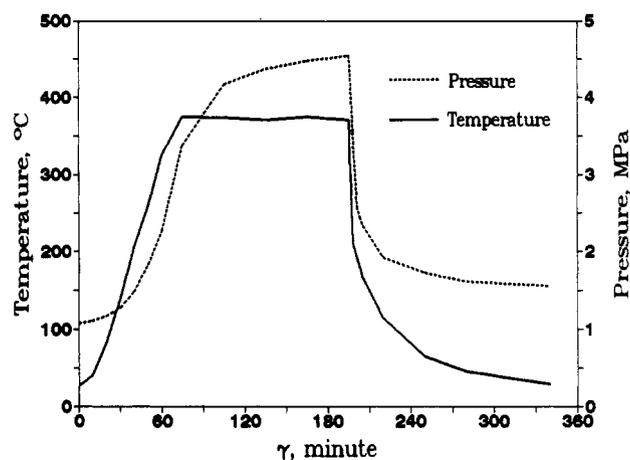


Figure 1. Temperature of pressure profiles. A total of 4 g of coal and 6 g of lignin were reacted in 120 mL of tetralin at 375 °C for a reaction time of 2 h. The reaction time is defined as the number of hours for which the reactor is maintained at the desired temperature (375 °C).

heated at a constant heat rate of 5 °C/min until the desired reaction temperature of 375 °C was attained. The temperature was maintained at 375 ± 5 °C for the duration of the reaction. At the end of the reaction period, the mixture was cooled rapidly by water flowing through an immersed cooling coil. Figure 1 shows a typical temperature–pressure vs time profile of a 2-h reaction time experiment. The reaction time is defined as the number of hours the reactor was maintained at the desired reaction temperature. Gases were collected and analyzed by a gas chromatograph, which was equipped with a 15 ft × 2.1 mm i.d., 60/80 Carboxen-1000 packed column. The contents of the reactor were filtered to separate solids from liquids. The solids were dried to a constant weight in a vacuum oven at 115 °C. The depolymerization yield is defined as the amount of solid material (daf basis) reacted per unit mass of the solids (daf basis) charged to the reactor.

2.3 Determination of Boiling Range Distribution. Tetralin was removed from the liquid residue using a rotary evaporator. The liquid residue (i.e., the concentrated liquid product) was analyzed in a gas chromatograph equipped with a 3% OV-101, 80/100 Supelcoport, 6 ft × 1/8 in. o.d. packed column. The ASTM D-2887 procedure was used to determine the boiling range distribution by gas chromatography.

2.4 ¹H NMR and Molecular Weight Studies. The concentrated products were subsequently separated into benzene-soluble and benzene-insoluble fractions; the benzene-soluble fraction was then extracted with pentane to generate a pentane-soluble fraction.¹⁵ To prepare soluble forms of the benzene-insoluble fractions, these samples were first silylated by refluxing with hexamethyldisilazane and trimethylchlorosilane using standard procedures.¹⁶ NMR spectra were integrated over spectral regions representing gamma hydrogen (H_γ), beta hydrogen (H_β),

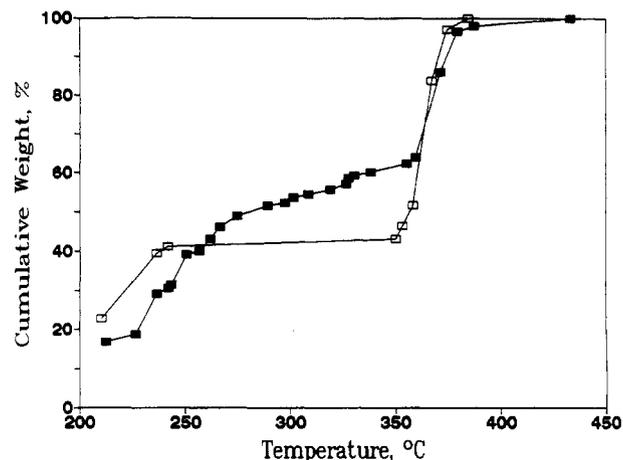


Figure 2. Comparison between boiling range of the coal liquid product (□) and the lignin liquid product (■).

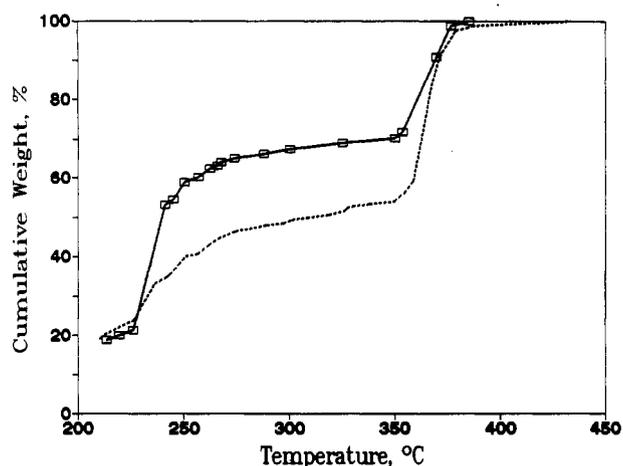


Figure 3. Comparison between the boiling range of liquid product obtained by coal–lignin mixture (□) and the predicted values calculated by arithmetic averaging of the boiling point data of liquid products from coal and lignin (---).

alpha hydrogen (H_α), ring-joining methylene hydrogen (H_F), and aromatic plus phenolic hydrogen (H_A + H_{OH}) using the spectral definitions of Bartle and co-workers.¹⁷ All NMR spectra were corrected for the contributions of residual tetralin (generally present at concentrations of only a few percent) within the samples. Size-exclusion chromatography was performed using the procedure described by Yau et al.¹⁸ The procedure is also given in another publication involving coal and lignin-derived liquids.¹³

3. Results and Discussion

A boiling range distribution was obtained for liquid products from coal, lignin, and coal–lignin mixtures. Figure 2 shows a comparison between boiling range distributions of coal liquid products and lignin liquid products. About 40% of the starting material of coal liquids, as well as lignin liquids, is distillable at 250 °C. However, as seen in Figure 3, about 55% distillable products are obtained from the coal–lignin mixture at the same temperature (250 °C). A predicted boiling range curve was also constructed by arithmetic addition (using data in Figure 2) of the liquids that would be obtained by reacting coal and lignin together, assuming no synergism. When the predicted boiling range data are compared with

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Table II. Gas Produced from Various Reactions^a
(mg gas/g solid (daf))

sample	carbon monoxide (%)	methane (%)	carbon dioxide (%)	total (%)
coal (A)	2.5 (24.3)	2.0 (19.4)	5.8 (56.3)	10.3 (100)
lignin (B)	25.5 (36.4)	17.6 (25.1)	27.0 (38.5)	70.1 (100)
coal-lignin (C)	17.0 (36.2)	12.7 (27.1)	17.2 (36.7)	46.9 (100)
coal-lignin ^b (D)	17.2 (35.4)	12.0 (24.7)	19.4 (39.9)	48.6 (100)
% change ^c	1.2	-5.8	11.3	3.5

^a Sample descriptions. Coal: 4.0 g of coal was reacted in 120 mL of tetralin at 375 °C for 1 h. Lignin: 4.0 g of lignin was reacted in 120 mL of tetralin at 375 °C for 1 h. Coal-lignin: 1.6 g of coal + 2.4 g of lignin were reacted in 120 mL of tetralin at 375 °C for 1 h. ^b Expected value computed using data from A and B. ^c [(D - C)/D] × 100.

Table III. Fractionation of Liquefied Products

sample ^a	pentane solubles (%)	asphaltenes (%)	benzene insolubles (%)
coal	56.09	34.45	9.46
coal-lignin	50.81	46.52	2.66
lignin	52.99	44.89	2.11

^a See Table II for experimental conditions.

the actual data as shown in Figure 3, one can conclude that the addition of lignin to coal is synergistic in that more low boiling point fractions are produced.

The amounts of gases produced for coal, lignin, and coal-lignin reacted in tetralin are shown in Table II. The gases produced are mainly CO, CH₄, and CO₂. As compared to coal, a larger amount of gas is produced when lignin alone is reacted under identical reaction conditions. The amount of gases produced for the coal-lignin mixture was also computed assuming that the addition of lignin to coal does not change the reactivity of either of the two solids. The experimental data show that the total amount of gases produced is slightly less (by 3%) than the corresponding amount of gases computed. Note that a significantly lower amount (11.3%) of CO₂ is produced than what one would calculate assuming no synergism (Table II).

The product distributions in terms of pentane solubles (oils), asphaltenes, and benzene insolubles (pre-asphaltenes) for the runs performed at constant mass of starting material are given in Table III. The liquid product from the coal-lignin mixture contained a lower fraction of the undesirable benzene insolubles than did the product from coal alone. Also listed are the proton NMR distributions obtained for these samples; the results are comparable to those obtained for samples that have been previously reported.^{13,14}

Table IV also lists estimated aromatic-to-aliphatic hydrogen ratios for the liquid samples. Once again, the trends observed were comparable to those reported previously.^{13,14} To provide confirmation of the aromatic-to-aliphatic estimates obtained using only NMR data, the procedure of Brown and Ladner¹⁹ was used to determine aromaticity (*f_a*) of the various fractions by combining elemental data with NMR data, as shown in Table V. The same trends were observed, as the pentane-soluble fraction for the coal-lignin mixture provided the highest aromaticity value. Table VI also provides size-exclusion chro-

Table IV. Proton Distribution via NMR Spectroscopy

	coal ^a	coal-lignin ^a	lignin ^a
Pentane Solubles			
H _γ	13.03	8.88	9.39
H _β	34.41	17.89	39.54
H _α	25.26	26.27	26.06
H _F	1.06	7.84	5.30
H _A + H _{OH}	26.24	28.11	19.69
Asphaltenes			
H _γ	7.08	5.14	5.44
H _β	23.66	19.56	18.08
H _α	30.39	32.23	29.46
H _F	5.53	13.59	16.82
H _A + H _{OH}	35.40	29.46	30.21
Silylated Benzene Insolubles			
H _γ	4.13	6.09	3.65
H _β	25.85	24.26	18.73
H _α	26.27	23.26	25.55
H _F	0.00	5.11	12.10
H _A + H _{OH}	43.75	24.31	39.97
Ratios of Aromatic-to-Aliphatic H (Estimated)			
pentane solubles	0.31	0.32	0.20
asphaltenes	0.46	0.35	0.34
silylated benzene insol	0.75	0.36	0.58

^a See Table II for experimental conditions.

Table V. Determination of Aromaticity (*f_a*) Using the Hydrogen Distribution Data and Elemental Data

sample ^a	elemental analysis			¹ H NMR data		
	% C	% H	C/H	H* _a	H* _o	<i>f_a</i>
Pentane Solubles						
coal	85.77	8.45	0.85	0.25	0.48	0.56
coal-lignin	82.59	8.58	0.80	0.26	0.35	0.62
lignin	82.32	9.10	0.75	0.26	0.54	0.47
Asphaltenes						
coal	81.74	7.39	0.92	0.30	0.36	0.64
coal-lignin	77.33	6.93	0.93	0.32	0.38	0.62
lignin	75.11	6.70	0.93	0.29	0.40	0.63

^a See Table II for experimental conditions.

Table VI. SEC, Computation of Molecular Weights (with corrections for SBB and sk), and Dispersivity (*D*)^a

sample ^b	ret. volume	<i>M_n</i>	<i>M_w</i>	<i>D</i>
Pentane Solubles				
coal	10.63	451.5	1280.4	2.8
coal-lignin	10.88	300.4	611.9	2.0
lignin	11.21	157.2	999.5	6.4
Asphaltenes				
coal	9.65	330.2	849.6	2.6
coal-lignin	9.30	287.5	758.4	2.6
lignin	9.66	222.0	928.7	4.2
Silylated Benzene Insolubles				
coal	7.85	679.4	2565.5	3.8
coal-lignin	7.95	849.5	2695.5	3.2
lignin	7.50	1721.8	3619.3	2.1
Overall				
coal		431.3	1253.5	2.9
coal-lignin		309.0	735.4	2.4
lignin		219.3	1022.9	4.7

^a SBB: Symmetrical band broadening; sk: skew asymmetrical band broadening. *D* is defined as *M_w*/*M_n*, where *M_w* and *M_n* are the weight-averaged and number-averaged molecular weights, respectively. ^b See Table II for experimental conditions.

matography data indicating that the weight-averaged molecular weight for the coal-lignin product is lower than that for either the coal or lignin alone.

In addition, some studies focused on more specific characterization of the fixed-mass products. Table VII lists the phenolic contents based on an alkaline extraction

Table VII. Phenolic Content of Coal Liquids^a

sample ^b	% phenolics	sample ^b	% phenolics
coal	75.9	lignin	89.4
coal-lignin	91.3		

^a A 0.500-g sample was used in each case. The procedure used for phenolic content estimation is given by Pauls et al. in ref. 20. ^b See Table II for experimental conditions.

Table VIII. Weight % of Neutral Alumina Fractions of Asphaltenes^a

sample ^b	compound type			
	HC	PAH	NPAH	HPAH
coal	0.23 (0.3)	6.36 (7.8)	12.65 (15.6)	61.81 (76.3)
coal-lignin	0.45 (0.7)	4.47 (7.0)	8.86 (13.8)	50.45 (78.5)
lignin	2.74 (5.0)	3.68 (6.8)	7.86 (14.5)	40.00 (73.7)

^a Values are percentages of the recovered material on the basis of the asphaltene sample mass fractionated; values in parentheses are percentages based on the total mass isolated. The procedure used is given by Later et al. in ref. 21. ^b See Table II for experimental conditions.

Table IX. Molecular Weight Data for Hydroxy Polyaromatic Hydrocarbon Fractions

sample ^a	M_n	M_w	D
coal	120	831	6.9
coal-lignin	253	798	3.2
lignin	368	797	2.2

^a See Table II for experimental conditions.

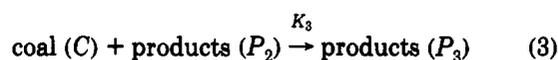
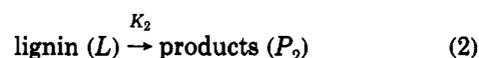
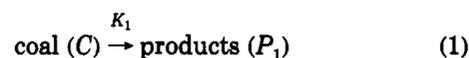
procedure.²⁰ These data indicate that most of the material in all of the products has some acidic character, but the products for lignin and coal-lignin mixtures are especially acidic. Comparison with the data in Table V (i.e., estimating oxygen content as the remainder of the mass) indicates that the products derived from starting materials contain lignin are particularly rich in oxygen. These data suggest that the quality of the products should be improved by further hydrogenation. Asphaltenes for the products were further fractionated into aliphatic hydrocarbons (HC), neutral polyaromatic hydrocarbons (PAH), N-containing polyaromatics (NPAH), and hydroxy polyaromatics (HPAH),²¹ as shown in Table VIII. In all three cases, the bulk of the recovered material was HPAH, which is consistent with the alkaline extraction data; the poor mass balance for this fractionation was likely due to irreversible adsorption of some species to the fractionation column. Size-exclusion chromatography was also performed for the HPAH fraction, as indicated in Table IX. The similarity of these data to the molecular weight data for the whole asphaltenes (Table VI) indicates that HPAHs are very representative of the asphaltenes in these coal liquids.

The influence of recycling of the liquid produced was studied. The extent of conversion slightly decreases with recycling. Initially, 1.6 g of coal and 2.4 g of lignin were liquefied in tetralin for 1 h at 375 °C and under a hydrogen atmosphere using 120 mL of tetralin. The solid conversion was found to be 79.3%. To the filtrate recovered after liquefaction (110 mL) was added 10 mL of tetralin, and the coal-lignin mixture was liquefied under identical reaction conditions. The solid conversion was found to

be 78.2%. To the filtrate obtained from this experiment (100 mL) was added 20 mL of tetralin, and the coal-lignin mixture was liquefied once again. The solid conversion was found to be 77.6%. These preliminary experiments indicate that the overall yields decrease, albeit gradually, as the liquids produced are recycled for the subsequent liquefaction of the coal-lignin mixture. The material recovery data for a number of experiments are presented in Table X. The data show that the overall material recovery is fairly good, between 94 and 98% of the original mass charged to the reactor. A complete description of atomic mass balances and the liquid product stability will be presented in another paper.

4. Mathematical Model Development

The following reaction mechanism is proposed to explain the enhancement in coal conversion with time due to lignin (solid) addition:



Reactions 1 and 2 are hypothesized to occur when coal and lignin alone are reacted. When lignin is added to coal, the intermediates from reaction 2 further depolymerize coal via reaction 3. The enhancement in the coal conversion rate obtained is due to reaction 3. Further improvement in the extent of coal conversion is possible by the attack of reaction 2 products on the coal sites that are not otherwise reactive when coal alone is reacted in tetralin under identical reaction conditions. P_2 should be dependent on time; it is zero at the beginning of the experiment and should increase with time as lignin is reacted further (see eq 2). At a certain time, t_m , P_2 should reach a maximum value, after which it would decline as it is consumed in reaction 3. Thus, the enhancement in coal conversion should also increase with an increase in P_2 and hence with the time of reaction.

In our experiments corresponding to zero reaction time (the reactor was heated to the desired temperature, and upon the achievement of that temperature, it was immediately cooled), appreciable yields for solid conversion were observed. Thus, we believe that during the reactor heat-up period, depolymerization reactions (eqs 1-3) take place. In the analysis presented here, τ refers to the time axis whose origin corresponds to the beginning of the reactor heat-up. It is assumed that during the reactor heat-up, at time τ_0 , depolymerization reactions begin to take place. A new time axis, t , is defined, having its origin corresponding to time τ_0 . Thus, one can state that $\tau = t + \tau_0$. In order to better understand the relationship between τ and t , refer to Figures 4-6.

4.1 Coal Depolymerization in Tetralin.¹⁴ The fractional coal conversion in tetralin is given by the following expression:

$$X_C = A[1 - e^{-k_1 t}] \quad (4)$$

4.2 Lignin Depolymerization in Tetralin. Lignin conversion chemistry, as shown in eq 2, can be modeled

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Table X. Material Recovery for Lignin-Assisted Coal Depolymerization^a

experiment legend	mass in (g)				mass out (g)			material lost (g)	material recovery (B/A) (%)
	tetralin	coal	lignin	total (A)	liquid + solid	gases ^b	total (B)		
I. tetralin									
BTO	115.17			115.17	113.13		113.13	2.04	98.2
BDT1	115.89			115.89	113.59		113.59	2.30	98.0
BDT2	115.53			115.53	113.18		113.18	2.35	98.0
II. coal									
CDT-375-2	115.86	4.00		119.86	113.31	0.03	113.34	6.52	94.6
CDT-375-3	112.71	4.01		116.72	109.60		109.63	7.12	93.9
III. lignin									
LDT-375-10	115.82		4.00	119.82	112.4	0.27	112.67	7.14	94.0
IV. coal-lignin									
CLDT-375-10	113.76	1.60	2.40	117.76	110.97	0.18	111.15	6.61	94.4

^a Experiments were conducted at 375 °C for 1 h under an initial hydrogen gas pressure of 140 psig. ^b Estimated average.

by the following *n*th-order rate expression:

$$\frac{dL}{dt} = -K_2[L - (1 - B)L_0]^n \quad (5)$$

By integrating eq 5 and using the stoichiometry of eq 2, the extent of lignin conversion and formation of P_2 is found to be

$$X_L = X_{P_2} = \frac{P_2}{L_0} = B - \frac{1}{L_0}[(BL_0)^{1-n} - K_2(1-n)t]^{1/(1-n)} \quad (5a)$$

From eq 5a, we see that the extent of conversion of P_2 increases rapidly with time (almost exponentially) and reaches a maximum value of B .

4.3 Coal Depolymerization in the Presence of Lignin in Tetralin. The rate expressions for the three reactions (eqs 1-3) are given:

$$\frac{dC_m}{dt} = -K_1[C_m - (1 - A')C_0] - K_3[C_m - (1 - A')C_0]P_2 \quad (6)$$

$$\frac{dL_m}{dt} = -K_2[L_m - (1 - B)L_0]^n \quad (7)$$

$$\frac{dP_2}{dt} = K_2[L_m - (1 - B)L_0]^n - K_3[C_m - (1 - A')C_0]P_2 \quad (8)$$

In the above analysis, we have assumed that, due to the addition of lignin, the fractional number of the total reactive sites available in coal has increased from an initial value of A to A' .

Although an analytical solution for P_2 and hence for C_m is not possible, an acceptable approximate solution is deduced. P_2 increases rapidly due to lignin depolymerization (see eqs 2 and 5a); however, it decreases due to its reaction with coal (see eq 3). The following expression is an approximate equation that describes exponential growth and decay of P_2 as a function of time:

$$P_2 \approx ae^{bt} - de^{-ft} \quad (9)$$

where the various constants (a , b , d , and f) remain to be determined. The first term on the right-hand side of eq 9 corresponds to the generation of P_2 , while the second term corresponds to the disappearance due to the formation of products P_3 . Substituting eq 9 into eq 6 and using the appropriate initial conditions ($t = 0$, $C = C_0$) yields the following expression for the fractional conversion of coal in the mixture, X_{Cm} :

$$X_{Cm} = \frac{C_0 - C_m}{C_0} = A' \left(1 - \exp \left[-K_1 t - \frac{K_3 a}{b} (e^{bt} - 1) + \frac{K_3 d}{f} (e^{-ft} - 1) \right] \right) \quad (10)$$

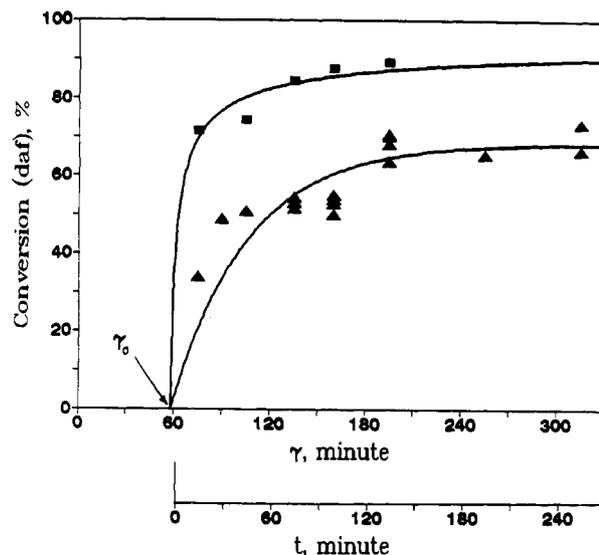


Figure 4. Coal conversion (\blacktriangle) and lignin conversion (\blacksquare) in tetralin at 375 °C. The upper abscissa corresponds to time since the beginning of the experiment. The lower abscissa corresponds to time since the beginning of the chemical reaction. Note that $\tau = t + 58$ min. The following equations are valid for $\tau \geq 58$ min: $X_C = 68.6[1 - 3.32 \exp(-0.021\tau)]$; $X_L = 97[1 - 1.22(\tau - 56.5)^{-0.506}]$; $n = 2.98$; $K_2 = 0.000198$; and $L_0 = 44.215$ g/L.

It must also be noted that at time $t = 0$, $P_2 = 0$; hence, from eq 9:

$$a = d \quad (11)$$

Experimental data for coal and lignin are shown in Figure 4 and for coal in the coal-lignin mixture are shown in Figure 5. The amount of coal converted in the mixture is calculated assuming that lignin conversion is unaffected by the presence of coal. The numerical values of the rate constants were chosen such that they permit the generation of those conversion vs time curves from eqs 4, 5a, and 10 that closely approximate the experimentally obtained conversion data. Note in Figures 4-6 that the time at which chemical reactions begin is about 58 min (τ_0) after the commencement of the experiment. Thus, the calculated conversion is zero at time corresponding to 58 min ($t = 0$). The reactions begin after a delay because heating the reactor takes a finite time (75 min). Experiments were conducted to determine the amount of coal conversion for a total time of τ_0 (58 min, i.e., $t = 0$). The conversion of coal in the coal-lignin mixture was estimated to be negligible (<3%). Thus, we believe our mathematical treatment of the kinetic data is vindicated. The results also show that the fractional number of the total reactive sites present in the coal matrix increases from an initial value of A (68.6%) when it is reacted in tetralin alone to

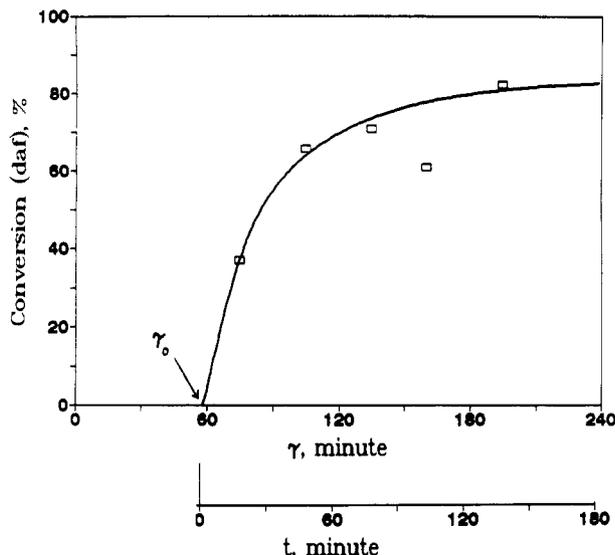


Figure 5. Coal conversion in coal-lignin mixture at 375 °C. Coal conversion in the mixture was calculated assuming that lignin conversion is not influenced by the addition of coal. The following equation is valid for $\tau \geq 58$ min: $X_{Cm} = 83.8[1 - 2.062 \exp(-0.021\tau - 3578e^{-0.0953\tau} + 3075e^{-0.0921\tau})]$; $b = -0.0921$; $f = 0.0953$; and $K_3a = K_3d = 1.356$.

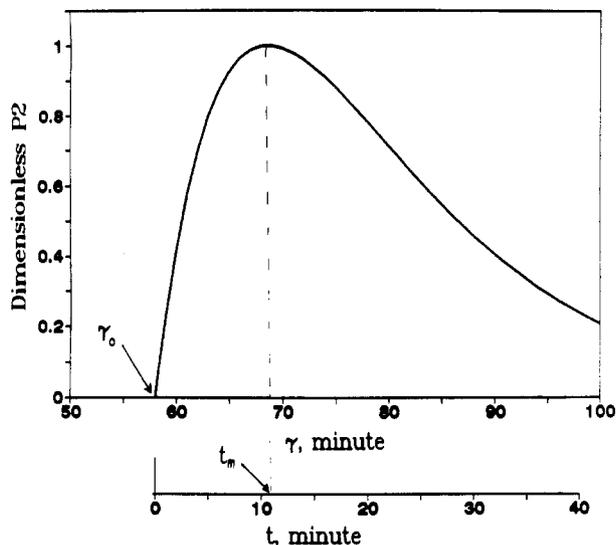


Figure 6. Calculated dimensionless concentration of P_2 vs. time.

a value of A' (83.8%) when coal is coprocessed with lignin. This represents an enhancement of 22% in the number of sites that become reactive in coal due to lignin addition. Thus, the analysis shows that, in addition to an enhancement in the reaction rate, the extent of coal depolymerization can also be increased due to lignin addition. The computed rate equations are shown in Figures 4 and 5. A plot of eq 9 is shown in Figure 6. As predicted, the dimensionless normalized concentration of P_2 (concentration divided by maximum concentration) increases with time initially and reaches a maximum before it declines. The reaction time (t_m) at which it reaches the maximum is given by the following expression:

$$t_m = -\left(\frac{1}{(b+f)}\right) \ln(-b/f) \quad (12)$$

The analysis indicates that P_2 should reach a maximum at about 10 min after the chemical reactions ensue.

5. Conclusions

1. Addition of lignin is effective in enhancing the depolymerization of coal with mild reaction conditions. There is a 22% enhancement in coal conversion upon lignin addition.

2. More distillable liquid products are obtained from a coal-lignin mixture at lower temperature than liquids obtained from coal and lignin when they are reacted separately.

3. Liquids produced from reacting coal with lignin contain lower molecular weights than those produced when coal is reacted in the absence of lignin.

4. The mathematical analysis permits the evaluation of various rate constants for lignin-assisted coal depolymerization. The reactive intermediates produced from the lignin that are responsible for enhanced coal depolymerization are relatively short-lived.

5. The influence of recycling of the liquid product was also studied. Preliminary experiments indicate that the overall coal depolymerization yields decrease, albeit gradually.

6. The gases produced are mainly CO, CH₄, and CO₂. Total amount of gas decreased slightly by about 3% in the coal-lignin mixture, compared to gas produced by reacting coal and lignin separately.

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Nomenclature

a, b, d, f	constants
A	maximum available reactive fraction of coal molecules at reaction temperature, %
A'	maximum available reactive fraction of coal molecules at reaction temperature in presence of lignin, %
B	maximum available reaction fraction of lignin molecules at reaction temperatures, %
C	coal concentration, g/mL
C_m	coal concentration in presence of lignin, g/mL
C_0	initial coal concentration, g/mL
L	lignin concentration, g/mL
L_0	initial lignin concentration, g/mL
n	order of reaction
$K_1, K_2,$ K_3	rate constants, min^{-1} , $(\text{g/mL})^{1-n} \text{min}^{-1}$, $(\text{g/mL}\cdot\text{min})^{-1}$, respectively
$P_1, P_2,$ P_3	product concentrations, g/mL
τ	time axis whose origin corresponds to beginning of heat-up, min
t	time axis whose origin corresponds to the beginning of chemical reaction, min
t_m	time needed for P_2 to reach a maximum concentration, min
τ_0	time needed for chemical reaction to begin, min
X_C	extent of coal conversion, %
X_{Cm}	extent of coal conversion in presence of lignin, %
X_L	extent of lignin conversion, %
X_{P_2}	extent of P_2 formation, %