TECHNICAL REPORT
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Project Title: Lignin-Assisted Coal Depolymerization

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ABSTRACT

Previous research has shown that addition of lignin-derived liquids to coal stirred in tetralin under mild reaction conditions (375°C and 300-500 psig) results in a marked enhancement in the rate of coal depolymerization. A mathematical model was developed to study the kinetics of coal depolymerization in the presence of lignin-derived liquids*. In the present study, a reaction pathway was formulated to explain the enhancement in coal depolymerization due to lignin (solid) addition. The model postulated assumes that the products of lignin obtained during thermolysis interact with the reactive moieties present in coal while simultaneous depolymerization of coal occurs. A good fit between the experimental data and the kinetic model was found. The results show that in addition to the enhancement in the rate of coal depolymerization, lignin also reacts (and enhances the extent of depolymerization of coal) with those reaction sites in coal that are not susceptible to depolymerization when coal alone is reacted in tetralin under identical reaction conditions.

Additional work is being carried out to determine a thorough materials balance on the lignin-assisted coal depolymerization process. A number of liquid samples have been obtained which are being studied for their stability in various environments.

* S.B. Lalvani, C.B. Muchmore, J.A. Koropchak, B. Akash, C. Chavez and P. Rajagopal, "Coal Liquefaction in Lignin-Derived Liquids Under Low Severity Conditions," to appear in Fuel.

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EXECUTIVE SUMMARY

This research involves the substitution of expensive chemicals by lignin in coal depolymerization. The general objective of this research is to enhance the rate and extent of coal depolymerization under mild reaction conditions by addition of lignin. It was anticipated that lignin would act as a source of substituted phenoxy radicals as well as other reactive radicals at temperatures too low for significant thermolysis of the coal matrix. The two major objectives of this research are: (i) accomplishment of lignin-assisted coal depolymerization under mild reaction pressure and temperature conditions, and (ii) detailed characterization of reaction products which should result in a better understanding of the reaction chemistry involved.

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Additional work is being carried out to determine a thorough materials balance on the lignin-assisted coal depolymerization process. A number of liquid samples have been obtained which are being studied for their stability in various environments. A thorough characterization of the reaction products is underway in our laboratories.

Research is conducted according to the time schedule projected in the proposal. No materials, equipment and personnel problems are anticipated.

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OBJECTIVES

This research involves the substitution of expensive chemicals by lignin in coal depolymerization. The general objective of this research is to enhance the rate and extent of coal depolymerization under mild reaction conditions by addition of lignin. It was anticipated that lignin would act as a source of substituted phenoxy radicals as well as other reactive radicals at temperatures too low for significant thermolysis of the coal matrix. The two major objectives of this research are: (i) accomplishment of lignin-assisted coal depolymerization under mild reaction pressure and temperature conditions, and (ii) detailed characterization of reaction products which should result in a better understanding of the reaction chemistry involved.

INTRODUCTION AND BACKGROUND

It is anticipated that due to uncertain supplies of crude oil, more markets will develop for low-cost energy substitutes that take advantage of the wide distribution and renewability of lignocellulosics and other biomass resources. It has been shown by Coughlin, et al.¹ that addition of lignin to coal in the presence of a hydrogen donor solvent and high pressure (1900 psig and above) results in an enhancement in coal liquefaction. It is hypothesized that phenoxy radicals and other reactive intermediates produced from lignin at relatively low temperatures can attack the coal causing scission of aliphatic carbon-carbon bonds in the coal. Coughlin, et al.² in another study have characterized the products of coliquefaction of lignin and bituminous coal at 400°C and 1900-2400 psig. The filterable solids from coliquefaction showed enhanced solubility in benzene. In a recent study, Sato, et al.³ have reported that the influence of lignin on coal liquefaction yields is temperature dependent. In a recent paper, Lalvani, et al.⁴ have confirmed the synergistic role played by lignin in coal liquefaction, albeit under relatively mild reaction conditions (-600 psig and 375°C).

In the studies cited above, lignin (solid) was used to depolymerize coal. It was assumed that lignin conversion in the presence of coal remains unaltered, but the coal conversion is enhanced by the lignin-derived intermediates. In a recent paper⁵, we reported the enhancement in coal conversion rate when lignin-derived liquids were reacted with coal. A mathematical model was presented that described the conversion rates observed. In this study, we have developed a mathematical model that describes the enhancement in coal conversion rate and yield due to the addition of lignin (solid). Experimental conditions are described in our earlier paper⁴.

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 coal conversion rate obtained is due to reaction (3). Further improvement in the extent of coal conversion is possible by the attack of P_2 on the coal sites that are not otherwise reactive when coal alone is reacted in tetralin under identical reaction conditions. The concentration of 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 Equation 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.

During the reactor heat-up period prior to achieving the desired reaction temperature, the chemical reactions (Equations (1)-(3)) take place. In the analysis presented here, t refers to the time since the beginning of chemical reactions.

A. Coal depolymerization in tetralin

Coal conversion chemistry, as shown in Equation (1), can be modeled by the following first-order rate expression:

$$\frac{dC}{dt} = -K_1[C - (1-A)C_0] \quad (4)$$

In the above formulation, C is the coal concentration, $[C - (1-A)C_0]$ represents the number density of the reactive sites available for reaction at any time, t , C_0 represents the initial coal concentration, A is an adjustable parameter, which may be viewed as the fractional number of the total reactive sites present in the coal matrix $[(C_0 - C_{t \rightarrow \infty})/C_0]$, and K_1 is a rate constant. Both A and K_1 are expected to be dependent on temperature. The fractional conversion, X_C , is given by integration of Equation (4):

$$X_C = \frac{C_0 - C}{C_0} = A[1 - e^{-K_1 t}] \quad (4-a)$$

B. Lignin depolymerization in tetralin

Lignin conversion chemistry, as shown in Equation (2) can be modeled by the following nth-order rate expression:

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

In the above formulation, L is the lignin concentration at any time, t, and L_0 is the initial lignin concentration. The order of the reaction is n, and the fractional number of the total reactive sites present in lignin is B. Integration of Equation (5) yields the following expression:

$$[L - (1-B)L_0]^{1-n} = (BL_0)^{1-n} - K_2(1-n)t \quad n \neq 1 \quad (5-a)$$

The extent of lignin conversion, X_L is given by:

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

From the stoichiometry of Equation (2), the extent of formation of P_2 is found to be:

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

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

C. Coal depolymerization in the presence of lignin in tetralin

The rate expressions for the three reactions (Equations (1)-(3)) are given below:

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

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

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

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 enhanced from an initial value of A to A'. The subscript 'm' refers to the coal-lignin mixture.

Although an analytical solution for P_2 and hence for C is not possible, an acceptable approximate solution is deduced. In the absence of reaction (3), P_2 is given by Equation (5-c), which shows the concentration of P_2 can be approximated by the following exponential function:

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

where the various constants (a , b , d , and f) remain to be determined. The first term on the right-hand side of Equation (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 Equation (9) into Equation (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} :

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

It must also be noted that at time, $t=0$, $P_2=0$, hence from Equation (9):

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

Experimental data for coal, lignin, and coal (in coal-lignin mixture) are shown in Figures 1, 2, and 3, respectively. Plots of Equations (4-a), (5-b) and (10) permit the computation of various rate constants (shown as solid lines in Figures 1-3). Please note in Figures 1-4 that the time at which chemical reactions begin is about 58 minutes since the commencement of the experiment. Thus, conversion is zero at time corresponding to 58 minutes ($t=0$). The reactions begin after a delay because heating the reactor takes a finite time (75 minutes). The data were processed using commercially available software. The results show that the fractional number of the total reactive sites present in the coal matrix increases from an initial value of A (0.686) when it is reacted in tetralin alone to a value of A' (0.838) when coal is co-processed 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 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 Table 1. A plot of Equation (9) is shown in Figure (4). 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 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 minutes after the chemical reaction ensues.

REFERENCES

1. Coughlin, R.W. and Davoudzadeh, F., Fuel 1986, 65, 95.
2. Altieri, P. and Coughlin, R.W., Energy and Fuels 1987, 1, 253.
3. Sato, S., Murakata, T., Chiba, T., Tukakosi, M.S., and Oda, S., Proceedings, 1989 International Conference on Coal Science, Tokyo, Japan, pp. 717-720.
4. Lalvani, S.B., Muchmore, C.B., Koropchak, J., Akash, B., Chivate, P., and Chavez, C., "Lignin-Augmented Coal Depolymerization Under Mild Reaction Conditions," Energy and Fuels, 5, 347, 1991.
5. Lalvani, S.B., Muchmore, C.B., Koropchak, J.A., Akash, B., Chavez, C., and Rajagopal, P., "Coal Liquefaction in Lignin-Derived Liquids Under Low Severity Conditions," to appear in Fuel.

Table 1 Computed Rate Equations

Time, t , is measured in minutes

Coal depolymerization in tetralin

$$X_c = 0.686[1 - \exp(0.021 * t)]$$

Lignin depolymerization in tetralin

$$X_L = 0.97 - 2.26(5.35 - 0.0004t)^{-0.505}$$

$$n = 2.98$$

$$K_2 = 0.000198$$

$$L_0 = 44.215 \text{ g/l}$$

Lignin-Assisted Coal Depolymerization

$$X_{cm} = 0.838 \{1 - \exp[0.021t + 14.72(e^{-0.0921t} - 1) - 14.23(e^{-0.0953t} - 1)]\}$$

$$b = -0.0921$$

$$f = 0.0953$$

$$K_{3a} = K_{3d} = 1.356$$

Figure 1: Coal Conversion in tetralin at 375°C.
The abscissa corresponds to time since the beginning
of the experiment. The desired reaction temperature
was reached after 75 minutes.

Figure 2: Lignin Conversion in tetralin at 375°C. The abscissa corresponds to time since the beginning of the experiment. The desired reaction temperature was reached after 75 minutes.

Figure 3: 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 abscissa corresponds to the time since the beginning of the experiment. The desired reaction temperature was achieved after 75 minutes.

Figure 4: Calculated dimensionales concentration of P_2 vs. time. The abscissa corresponds to time since the beginning of the experiment. The desired reaction temperature was reached after 75 minutes.

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