Kinetics of Short Contact Time Coal Liquefaction

Part I: Effect of Operating Variables

The liquefaction kinetics of Powhatan No. 5 mine coal (Pittsburgh Seam) in the presence of SRC-II recycle solvent at short contact times (<10 min) and temperature and pressure ranges of 573–723 K and 10.3–13.8 MPa is examined in a well-mixed reactor. In the initial stages of liquefaction, while overall coal conversion (tetrahydrofuran solubles) increases with temperature, oil (pentane solubles) is lost with an increase in temperature. An increase in solvent-to-coal ratio results in an increase of conversion. The initial coal particle size distribution, total pressure, and nature of gas phase (nitrogen or hydrogen) have no significant effect on the production of any of the product of liquefaction for contact times up to 10 min. A lumped kinetic model is presented to describe the product distribution.

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SCOPE

The primary reactions in conversion of coal to liquid fuels in any coal-oil slurry liquefaction process are pyrolytic in nature and require high temperature to overcome the distribution of activation energies involved in the rupture of bond linkages in the macromolecular network of coal. It is known that when coal is contacted with a hydrogen-donor solvent, at elevated temperatures (693–733 K), much of the coal conversion to soluble products takes place in the initial 2–5 min. Hence, the preheater in the coal liquefaction process is a critical component, as it behaves as a short contact time reactor. Recently, there has been a considerable interest in the development of a short contact time two-stage process. This paper presents a short contact time (<10 min) coal liquefaction kinetic study which is carried out in a well-mixed, 1-L semibatch autoclave reactor. The experimental data are obtained for Powhatan No. 5 mine coal at various practical ranges of temperatures, pressures, solvent-to-coal ratio, and initial coal particle size. Both nitrogen and hydrogen was used as the gas phase. The data are correlated by a lumped kinetic model which would be useful in predicting the performances of a preheater or a short contact time coal liquefaction reactor.

CONCLUSIONS AND SIGNIFICANCE

The kinetics of coal liquefaction at short residence times (under 10 min) has been studied. The products of liquefaction were characterized as:

$$\text{Preasphaltenes}\left\}\begin{array}{l}\text{Soluble in Tetrahydrofuran}\\ \text{Insoluble in Toluene}\end{array}\right.$$

$$\text{Asphaltenes}\left\}\begin{array}{l}\text{Soluble in Toluene}\\ \text{Insoluble in Pentane}\end{array}\right.$$

Oils Solubles in Pentane

It is shown that initially there is an effective loss of oil, whereas the preasphaltenes and asphaltenes are rapidly formed indicating a fast dissolution of coal in the initial stages. A statistical analysis of the experiments shows that the temperature has a significant negative influence on oil concentration with a minimum at around 2–4 min of reaction time. This result indicates the occurrence of an adductive reaction between coal and oil leading to some intermediate products which in turn react to give oils. The production of toluene and tetrahydrofuran solubles is shown to be positively influenced by temperature. The solvent-to-coal ratio also significantly influences the product distribution.

An investigation of the influence of gas phase (nitrogen and hydrogen), particles size, and total pressure, at short-time liquefaction show no statistically significant effect in the range of variables studied. From a kinetic standpoint, it appears that there is no need to add hydrogen to the first stage of the short contact time two-stage processes or the preheater of other processes; however, hydrogen may be needed to prevent coke formation. A kinetic model is developed to predict the product distribution over the entire range of operating variables studied. This model should be useful in predicting the product distributions coming out of a preheater or a short contact time coal liquefaction reactor.

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INTRODUCTION

In most coal liquefaction processes, crushed coal is contacted with a hydrogen-donor solvent under elevated pressure and temperature. The solvent is usually a coal-derived liquid which is recycled through the system. The coal oil slurry is fed to a preheater where its temperature is raised to around 700 K (Shah, 1981). The slurry typically has a residence time of up to 5 min in the preheater. It is then fed into a dissolver (reactor), where the holdup time can be up to 1 h.

A model of a coal liquefaction reactor requires the knowledge of the reactor inlet conditions, i.e., preheater outlet conditions. It is, therefore, necessary to quantitatively evaluate the chemical changes occurring in the preheater. Studies on short contact time coal liquefaction have shown that coal undergoes initial reactions in the preheater, involving both chemical and physical property changes (Whitehurst et al., 1977; Wen and Han, 1978). For good design and scale-up of coal liquefaction units it is essential to obtain reliable kinetic data under conditions existing both in preheater and reactor. Most kinetic studies reported in literature have been carried out at high temperatures (>673 K) and at long residence times (10–60 min) (Cronauer et al., 1978; Shalabi et al., 1979). Studies in short contact time coal liquefaction have shown that coal is thermally fragmented into smaller molecules which are soluble in pyridine (Neavel, 1976; Whitehurst et al., 1977). In the initial stages of reaction, it is believed that a large number of free radicals are produced which are then stabilized by hydrogen abstraction from hydrogen-rich portions of coal or solvent (Curran et al., 1966; Collins et al., 1978; Petrakis and Grandy, 1980; Larsen et al., 1981), very little molecular hydrogen is consumed in this stage. This result is exploited in the short contact time two-stage process (Tarrer et al., 1981; Kleinpeter et al., 1979). Previous investigations on short contact time coal liquefaction are summarized in Table 1.

In this paper the experimental results for the effects of temperature, pressure, solvent-to-coal ratio, initial coal particle size and the nature of the gas phase (nitroen or hydrogen), on the liquefaction kinetics of Powhatan No. 5 mine Pittsburgh seam coal, for contact times up to 10 min are reported. A kinetic model is developed and the model parameters are obtained to fit the data.

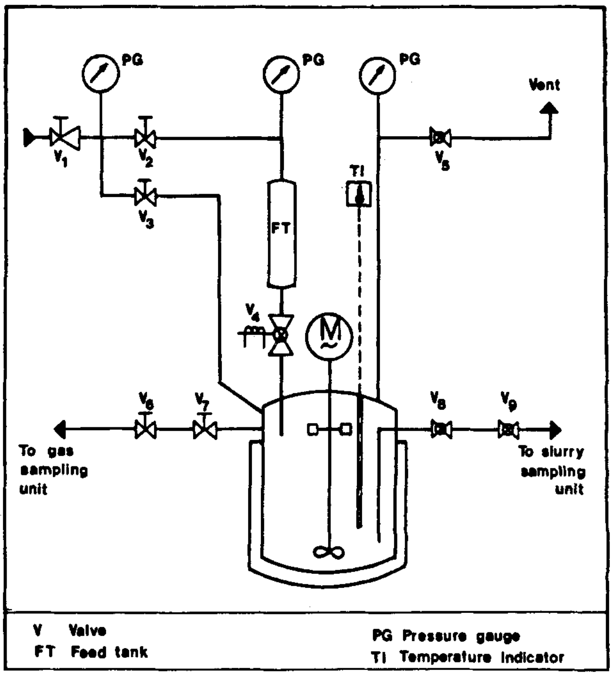

Figure 1. Batch experimental unit.

EXPERIMENTAL

Experiments were carried out in a 1-L stirred autoclave. No catalyst was used in the experiments. Figure 1 schematically illustrates the experimental setup. The autoclave was fitted to have facilities to:

1. Inject coal rapidly from the injection vessel (feed tank) into the autoclave.
2. Rapidly withdraw samples (both slurry and gas) at various reaction times.
3. Measure and control the temperature in the autoclave.

The solvent was initially preheated in the autoclave to a temperature of 15 K above the reaction temperature, and sufficient gas was charged to the head space to obtain the desired pressure. Coal was then injected in the

TABLE 1. REPORTED SHORT CONTACT TIME STUDIES

Investigators	Coal Type	Solvent Type	Reactor Type	Temp. Range (K)	Pres. Range (MPa)	Residence Time (min)
Wright et al. (1975)	Kentucky 9	Hydrogenated Anth. Oil	Coiled Preheater	473–773	6.9	2–8
Neavel (1976)	Vitrinite	Pyridine Tetralin	Tubing Bomb	673	—	0.3–5
Guin and Tarrer (1977)	Kentucky 11 Kentucky 9/14	SRC-Recycle Creosote Hydrogenated Creosote	Stirred Autoclave	683	13.8 H_2 and N_2	5–15
Whitehurst et al. (1977)	Kentucky Illinois Illinois	Synthetic Recycle Solvent	Stirred Autoclave	700–726	0–11.7 H_2	0.5–4
Longanbach et al. (1978)	Kentucky Illinois	SRC-I Recycle Solvent	Stirred Autoclave	685–727	1.2–12 N_2	1–5
Traeger et al. (1979)	Illinois Illinois	SRC-II Heavy Distillate	Coiled Preheater	673–723	13.8 H_2	0.5–8
Weber and Basu (1979)	Kentucky Illinois Indiana Kentucky	SRC Solvent	Helical Coiled Preheater	675–727	11.6–16.0 H_2	0.5–5
Pittsburg & Midway Coal Mining Co. (1981)	Kentucky Indiana Loveridge	SRC Recycle solvent	SRC Plant (Preheater & Dissolver)	723–773	13.8–20.7 H_2	1–10

TABLE 2. ANALYSIS OF POWHATAN NO. 5 MINE COAL

1. Proximate Analysis	As Rec'd	Dry
% Moisture	1.06	—
% Ash	9.58	9.68
% Volatile	39.65	40.07
% Fixed Carbon	49.71	50.25
2. Calorific Value	**As Rec'd**	**Dry**
kJ/kg	13,900	14,050
2. Ultimate Analysis		**Dry**
% Moisture		—
% Carbon		72.28
% Hydrogen		5.07
% Nitrogen		1.47
% Chlorine		0.03
% Sulfur		3.60
% Oxygen (diff)		7.87
% Ash		9.68

TABLE 3. SRC-II SOLVENT ANALYSIS

Gravity:	6.8° API
Carbon:	87.44%
Hydrogen:	8.64%
Nitrogen:	1.39%
Sulfur:	0.25%
Oxygen:	2.28%

Boiling Point Data
(Modified ASTM D-1160; Watson K = 10.0)

% Vol. Distilled	Temp. (K)
10	518
20	548
30	566
40	582
50	596
60	616
70	634
80	659
90	694
100	747

TABLE 4. FACTORIAL DESIGN OF EXPERIMENTS

Factors	Levels	
	0	1
(A) Temperature (K)	573	723
(B) Gas Phase	N_2	H_2
(C) Solvent To Coal Ratio	2.5	5
(D) Particle Size (μm)	400^-	recrushed
Avg. Vol. to Surface Dia. (μm) (See figure below.)	19.4	8.9
(E) Pressure (MPa)	10.3	13.8

autoclave by a pressure differential of 6 MPa across valve V_4, Figure 1. About 85% of coal charged in the feed tank entered the reactor. At this instant, zero time is defined. The temperature of the slurry initially dipped; however, it immediately recovered and stabilized to the reaction temperature in about 40 s. The slurry temperature was maintained at within ±2 K of the set reaction temperature. No gas was introduced during the run.

The proximate and ultimate analysis of the Powhatan No. 5 Mine coal are given in Table 2. An SRC-II recycle solvent obtained from a pilot plant at Gulf Research Center, Harmarville, PA, was used as the solvent (McIlvried et al., 1980). The solvent was derived from the liquefaction of Powhatan No. 5 mine coal at operating conditions of 728 K, 13.8 MPa, and 1 h nominal space time. Table 3 shows the analysis of this solvent.

The coal was crushed, sieved, and stored under nitrogen atmosphere. The particle size distribution was determined by an Omnicon Alpha Image Analyzer. To study the effect of particle size, a representative sample of the crushed coal was recrushed and the entire sample was used in the experiments, thereby ensuring that the coal quality did not change with the particle size.

Initial experiments were performed to determine the extent of backmixing in the reactor. The agitator used in all experiments was a propeller at 1,500 rpm. Samples of slurry were withdrawn at short times (1–10 min) and analyzed for total carbon and hydrogen contents. The total carbon and hydrogen contents of the slurry samples withdrawn at different times were almost constant, indicating that the slurry was completely backmixed in <1 min.

The slurry samples were analyzed for their solubilities in pentane, toluene and tetrahydrofuran (THF). The forward sequential technique described by Ruberto and Cronauer (1979) was used. The gas samples were analyzed on a gas chromatograph using a Poropak Q column.

RESULTS AND DISCUSSION

In the initial phase of this work, experiments were conducted to determine the effects of five reaction variables on the liquefaction behavior up to 10 min of contact time: A. temperature; B. gas phase (nitrogen or hydrogen); C. solvent-to-coal ratio; D. particle size; and E. total pressure. A two-level fraction factorial design of experiments (Walpole and Myers, 1972) was adopted by defining the ABCDE to be confounded with the blocks. Consequently, the main effects were aliased with four-factor interaction effects. Table 4 gives the levels of these factors. The 16 experiments in the principal block were performed. Error estimates were obtained by duplicating some runs.

The results of the factorial experiments are in Tables 5 to 7. Statistical F test with 95% confidence limits is used to determine the significance of the effects. The sum of squares of the main effects and that of the error term are calculated; Tables 8 to 10 show the resulting statistical F values (F_{exp}). For any effect to be statistically significant, the absolute value of F_{exp} should be greater than the F value (F_{tab}) obtained from the standard F distribution. Details of the calculation procedure for F_{exp} and tables for F_{tab} are available elsewhere (Walpole and Myers, 1972).

Results obtained from a typical experiment are shown in Figure 2. As expected, the THF insoluble portion (coal) decreases with time. A remarkable decrease in the oil (solvent) concentration is observed in the initial stage of the reaction. The oil concentration falls below the initial value of the solvent indicating an effective loss of oil. This decrease is observed up to 2 to 4 min of reaction time, and the oil fraction starts increasing thereafter. Longanbach et al. (1978), Traeger et al. (1979), and Cronauer and Ruberto (1979) have also reported similar trends. Both asphaltenes and preasphaltenes increase fairly rapidly during the first few minutes and then start decreasing. This result appears to be due to initial adductive reactions between coal liquids and components of the oil leading to some intermediate products, which are insoluble in pentane. A portion of these insolubles later undergoes dissolution to pentane-soluble products thus recovering the oil concentration. The total rate of gas formation, within the range of conditions examined here, is less than 2 wt % of feed MAF coal.

A. Effect of Temperature

Analysis of the data obtained from the factorial experiments show a negative effect on the formation of pentane-soluble products; i.e., the pentane-soluble products decreases with increase in temperature, for reaction times up to 10 min (see Table 8). This negative effect is most pronounced at 2 min of reaction time and decreases with increase in time. This effect could be attributed to the enhancement of the adductive reaction between coal and oil yielding, pentane-insoluble products. Table 9 shows that the temperature has a positive effect for the formation of toluene soluble products (i.e., increases with increase in temperature) at all times considered. (It should be noted that toluene solubles include pentane solubles, hence the temperature effect on toluene solubles becomes significant only after the oil fraction starts recovering.)

Most studies use THF solubles as a measure of coal conversion. Our results show that the temperature has a strong positive effect on the production of THF solubles (see Table 10). Whitehurst et al. (1977), Longanbach et al. (1978), and Traeger et al. (1979) have also reported a very fast increase in the formation of THF solubles for times up to 4 min.

TABLE 5. PENTANE SOLUBLES, FRACTION OF INITIAL COAL (MAF)

Reaction			Time (min)		
Conditions	2	4	6	8	10
(1)	−0.48	−0.23	−0.28	−0.16	−0.01
ab	−0.22	−0.21	−0.13	−0.10	−0.06
ac	−0.59	−1.45	−0.14	−0.41	−0.13
ad	−0.39	−0.25	−0.20	−0.07	0.13
ae	−0.24	−0.45	−0.37	−0.28	−0.24
bc	−0.10	−0.08	−0.02	−0.08	0.13
bd	−0.09	−0.16	−0.21	−0.01	0.06
be	−0.17	−0.18	−0.32	−0.19	0.02
cd	0.01	−0.44	−0.35	−0.10	0.12
ce	−0.03	−0.02	−0.13	−0.29	−0.16
de	0.09	0.02	−0.10	0.03	−0.15
abcd	−0.45	−0.28	−0.25	−0.18	−0.11
abce	−1.36	−0.17	−0.85	−0.50	−0.11
abde	−0.13	−0.06	−0.01	0.00	0.00
acde	−0.37	−0.39	−0.39	−0.38	−0.37
bcde	−0.07	−0.21	−0.11	−0.04	-0.13

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* Reactions conditions are according to statistical nomenclature; i.e., *ab* represents higher levels of *A* and *B* and lower levels of *C*, *D* and *E*. (See Table 4.)

TABLE 6. TOLUENE SOLUBLES, FRACTION OF INITIAL COAL (MAF)

Reaction			Time (min)		
Conditions*	2	4	6	8	10
(1)	0.19	0.13	0.06	0.17	0.19
ab	0.21	0.34	0.36	0.37	0.38
ac	0.22	0.22	0.39	0.35	0.47
ab	0.07	0.23	0.26	0.40	0.56
ae	0.25	0.12	0.18	0.26	0.23
bc	0.19	0.29	0.23	0.29	0.35
bd	0.12	0.10	0.02	0.20	0.22
be	0.15	0.08	0.06	0.13	0.19
cd	0.10	−0.17	0.00	0.31	0.18
ce	0.22	0.22	0.09	0.04	0.10
de	0.26	0.28	0.07	0.19	0.30
abcd	0.20	0.29	0.28	0.33	0.27
abce	0.34	0.32	0.31	0.36	0.40
abde	0.41	–	0.67	0.50	0.44
acde	0.14	0.23	0.16	0.22	0.27
bcde	0.22	0.02	0.10	0.23	0.07

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* Reaction conditions are according to statistical nomenclature; i.e., *ab* represents higher levels of *A* and *B* and lower levels of *C*, *D* and *E* (See Table 4.)

TABLE 7. TETRAHYDROFURAN SOLUBLES, FRACTION OF INITIAL COAL (MAF)

Reaction			Time (min)		
Conditions*	2	4	6	8	10
(1)	0.37	0.34	0.19	0.35	0.36
ab	0.43	0.48	0.51	0.53	0.55
ac	0.55	0.56	0.54	0.59	0.65
ad	0.47	0.53	0.49	0.54	0.69
ae	0.47	0.31	0.46	0.45	0.47
bc	0.30	0.42	0.35	0.41	0.45
bd	0.25	0.23	0.16	0.38	0.40
be	0.24	0.18	0.20	0.26	0.32
cd	0.27	0.04	0.11	0.41	0.34
ce	0.38	0.36	0.26	0.27	0.31
de	0.38	0.33	0.22	0.34	0.45
abcd	0.43	0.56	0.55	0.59	0.58
abce	0.61	0.62	0.63	0.65	0.67
abde	0.55	0.25	0.80	0.70	0.62
acde	0.54	0.50	0.48	0.52	0.56
bcde	0.33	0.19	0.23	0.38	0.25

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* Reaction conditions are according to statistical nomenclature; i.e., *ab* represents higher levels of *A* and *B* and lower levels of *C*, *D* and *E* (See Table 4.)

B. Effect of Nature of Gas Phase

For short reaction times, no significant change was observed when the gas phase was changed from nitrogen to hydrogen (see Tables 8 to 10). THF solubles at 6 min of reaction time (Table 10) do show a significant effect; however, at no other time is any significant effect seen. This appears to be an error rather than a systematic effect and hence is neglected. Apparently molecular hydrogen does not play a role in the initial stage of liquefaction. This result agrees with the initial stage mechanism proposed by collins

TABLE 8. F_{exp} FOR PENTANE SOLUBLES

Factor	Time (min) 2	4	6	8	10
A (Temp.)	−6.0	−3.5	−0.7	−1.6	−1.2
B (Gas Phase)	−0.2	−2.7	0.0	−0.2	0.0
C (S/C)	−1.0	−1.5	−0.3	−0.4	−0.1
D (Particle Size)	2.2	0.4	0.4	1.4	0.3
E (Pres.)	0.0	1.8	−0.3	−0.5	−0.3

Mean square error: 0.087.
Degrees of freedom for error: 32.
F_{tab} for 95% confidence limits: 4.15.

TABLE 9. F_{exp} FOR TOLUENE SOLUBLES

Factor	Time (min) 2	4	6	8	10
A (Temp.)	1.2	4.2	20.0	7.6	8.9
B (Gas Phase)	1.2	0.5	3.7	1.2	0.0
C (S/C)	0.7	1.7	0.0	−0.3	−0.3
D (Particle Size)	−0.6	−3.6	−0.2	−0.7	0.0
E (Pres.)	0.6	−0.5	−0.1	−2.7	−1.9

Mean square error: 0.013.
Degrees of freedom for error: 32.
F_{tab} for 95% confidence limits: 4.15.

TABLE 10. F_{exp} FOR TETRAHYDROFURAN SOLUBLES

Factor	Time (min) 2	4	6	8	10
A (Temp.)	24.9	31.2	69.0	29.9	34.7
B (Gas Phase)	−0.2	−0.1	−4.6	−2.1	0.0
C (S/C)	6.8	11.0	2.4	7.1	5.9
D (Particle Size)	−0.7	−5.6	−0.2	−0.8	0.0
E (Pres.)	0.0	−5.2	−0.1	−4.0	−3.9

Mean square error: 0.007.
Degrees of freedom for error: 32.
F_{tab} for 95% confidence limits: 4.15.

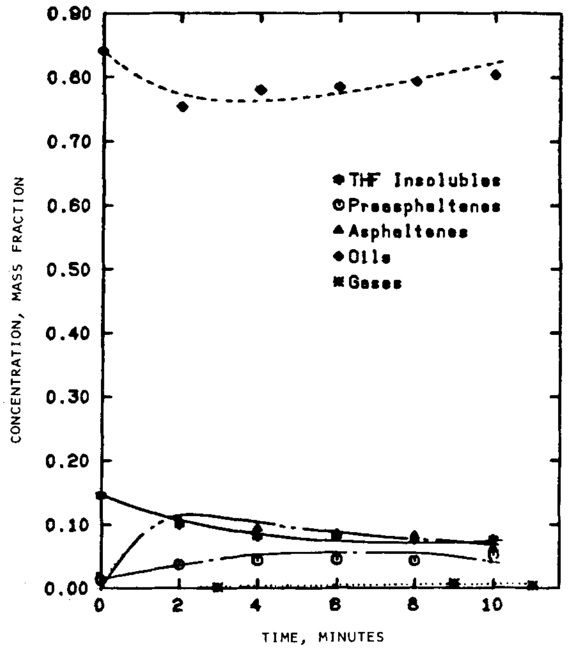

Figure 2. Product distribution for a typical experiment (conditions at high levels: 450°C, H_2, 13.8 MPa, 5/1//*S/C*, recrushed Coal).

et al. (1978) wherein free radicals formed from thermal reactions seek stabilization by abstracting hydrogen from the slurry itself by a hydrogen shuttling mechanism. They further state that molecular hydrogen is not consumed in this stage of liquefaction. Hence, from a kinetic standpoint, the presence of hydrogen is not essential in the initial stage of the reaction; however, hydrogen may be required to prohibit coke formation.

C. Effect of Solvent-to-Coal Ratio

The solvent-to-coal ratio has no significant effect on the individual yields of pentane and toluene solubles (Tables 8 and 9). However, Table 10 shows that the THF solubles are significantly increased with an increase in the solvent-to-coal ratio. This effect is most pronounced at 4 min of reaction time. It is interesting to note that around this time the oil fraction shows a minimum (Figure 2). This indicates that at least one class of the products of the adduction of coal and oils is preasphaltenes.

D. Effect of Initial Coal Particle Size

Various studies (Curran et al., 1966; Whitehurst et al., 1977) have shown that the size of the coal in the normal range of interest (1 to 1,200 μm) has a very small effect on the yields of coal liquefaction. However, in all of these studies the maceral and mineral compositions may have changed with the particle size, and hence the results obtained were not conclusive. To overcome this problem of change in coal quality with particle size, experiments were conducted by recrushing a particular particle size distribution. The results (Tables 8 to 10) indicate that within the range considered, initial coal particle size distribution has no significant effect on the yields of pentane, toluene, and THF solubles, and also that intraparticle mass transfer resistances are negligible. THF solubles at 4 min of reaction time do show a significant effect. However, as there is no systematic effect at different reaction times, this one significant effect is neglected.

E. Effect of Total Pressure

Increasing the total pressure from 10.3 to 13.8 MPa has very little effect on the yields of pentane, toluene, and THF solubles at all times up to 10 min (Tables 8 to 10), except for THF solubles at 4 min. Again, this one significant effect is neglected as there is no systematic change. The observed effect of total pressure is well within the experimental error, and hence in the present study it is concluded to have no significant effect.

The dissolution of coal is very fast in the initial stages of liquefaction, and in about 4 min of reaction time many rapid changes take place. Hence, any small inaccuracies in the time of sampling may give a large error. This could be the reason for a sigificant effect shown at 4 min for factors *D* and *E* (particle size and pressure). To check this effect, it was decided to obtain an error estimate using data obtained at 4 min of reaction time only. Such a calculation for THF solubles leads to:

$$\text{Mean square error} = 0.08$$
$$\text{Degrees of freedom for error} = 9$$
$$F_{exp} \text{ for factor } D \text{ at 4 min} = 4.9$$
$$F_{exp} \text{ for factor } E \text{ at 4 min} = 4.6$$
$$F_{tab} \text{ for 8 degrees of freedom} = 5.12$$

F_{exp} for *D* and *E* are lower than F_{tab}, hence these effects are not significant when the error estimate is obtained from replicate data at 4 min only. Based on these results, omissions of particle size and pressure effects are justified.

Two-Factor Interaction Effects

Two-factor interaction was determined. The five main effects give ten, two-factor interaction effects. All two-factor interaction effects except "*DE*" showed significant effects at all times. The interaction effect "*DE*" exhibited a significant effect only at 4 and

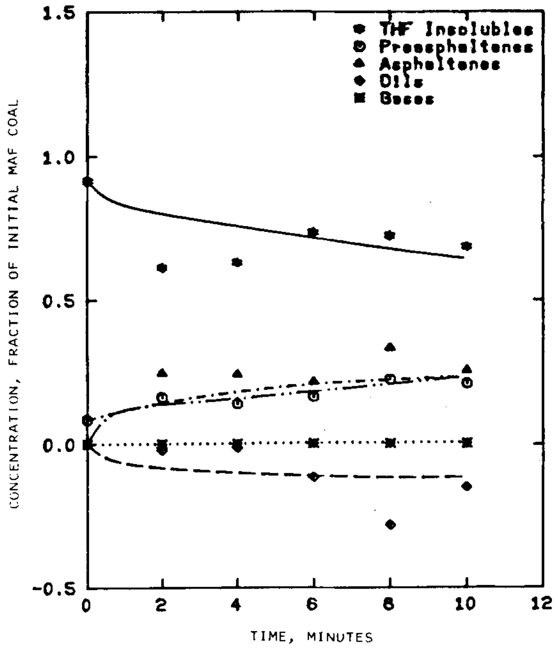

Figure 3. Product distribution and model fit at 573 K.

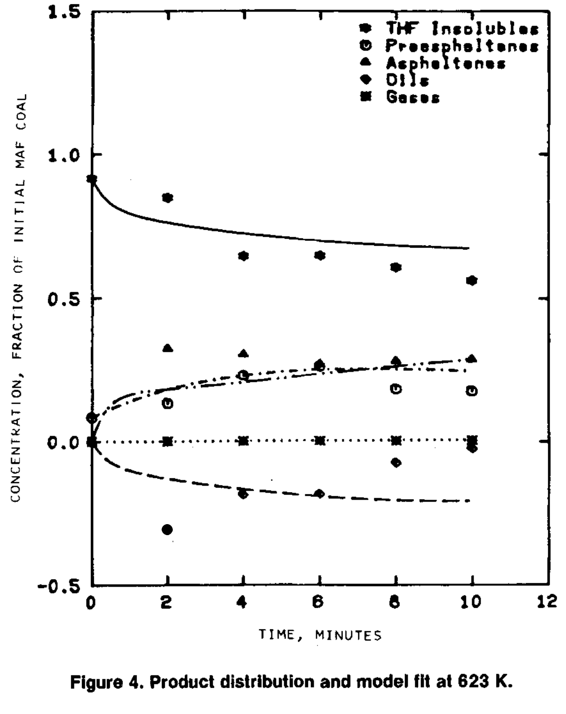

Figure 4. Product distribution and model fit at 623 K.

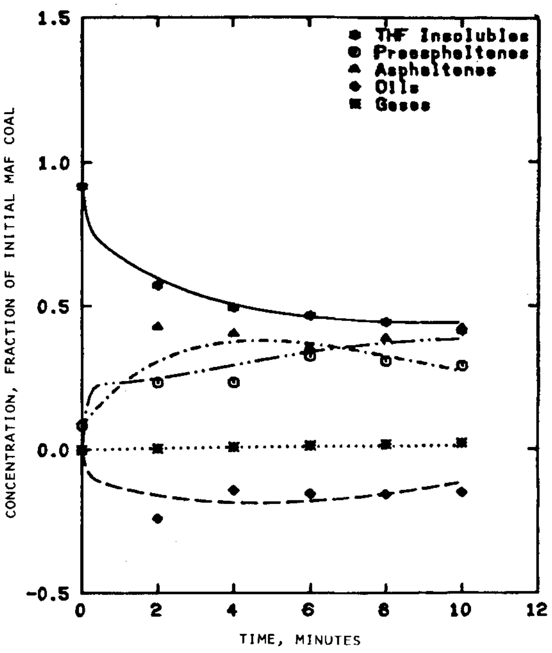

Figure 5. Product distribution and model fit at 673 K.

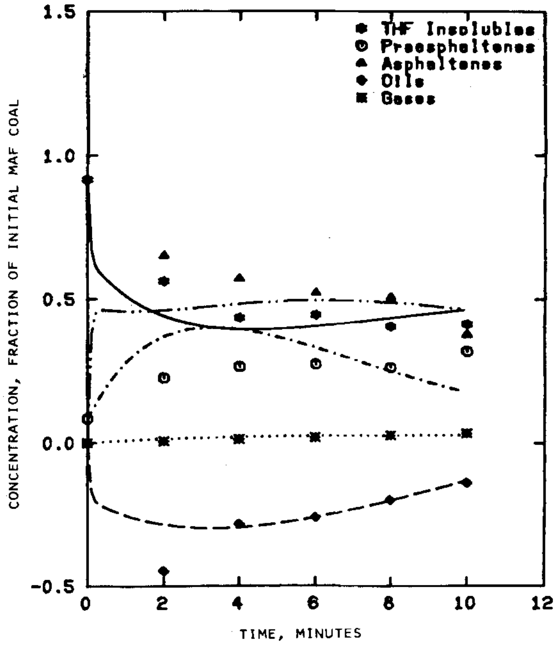

Figure 6. Product distribution and model fit at 723 K.

6 min of reaction time. We assumed it was due to errors at these reaction times and hence concluded that interactive effects were insignificant. Three and higher factor interaction effects were ignored.

Quantitative Estimation of Significant Effects

The factorial experiments show that among the five variables considered, only temperature (A) and solvent-to-coal ratio (C) have a significant effect on the product distribution at short contact time. Further experiments were performed to obtain a quantitative estimate of the effects of these two variables.

Effect of Temperature

Series of experiments was performed at temperature levels of 573, 623, 673 and 723 K. The product distributions, as fraction of initial coal, are plotted in Figures 3 through 6. The lines in these figures are predicted by the model, to be discussed later.

The negative effect of temperature on the oil concentration is clearly seen from these plots. As the temperature increases, the oil concentration goes through a minimum. The minimum in the oil concentration shifts toward shorter time as the temperature is increased. Examination of the effect of temperature on the concentration of adducts (measured as depletion of oil) indicates that at least a part of the adduction is by chemical reaction, with the adduct perhaps serving as an intermediate species. Cronauer et al. (1979) from their study with model compounds report that ad-

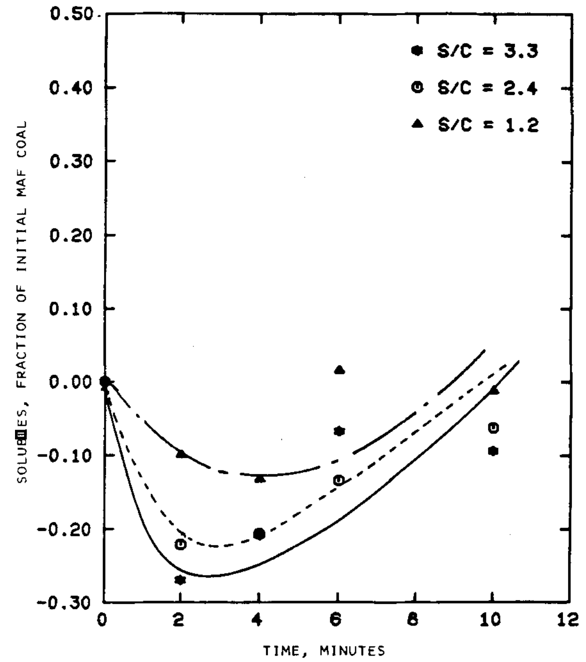

Figure 7. Effect of solvent-to-coal ratio, pentane solubles (T = 723 K).

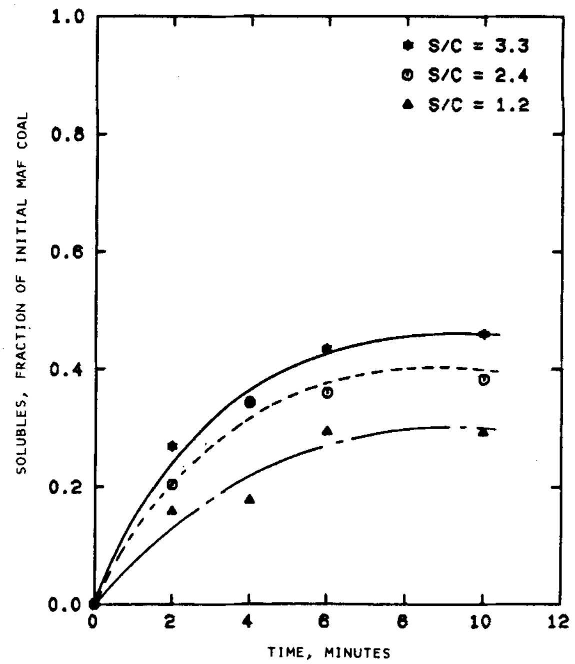

Figure 8. Effect of solvent-to-coal ratio, toluene solubles (T = 723 K).

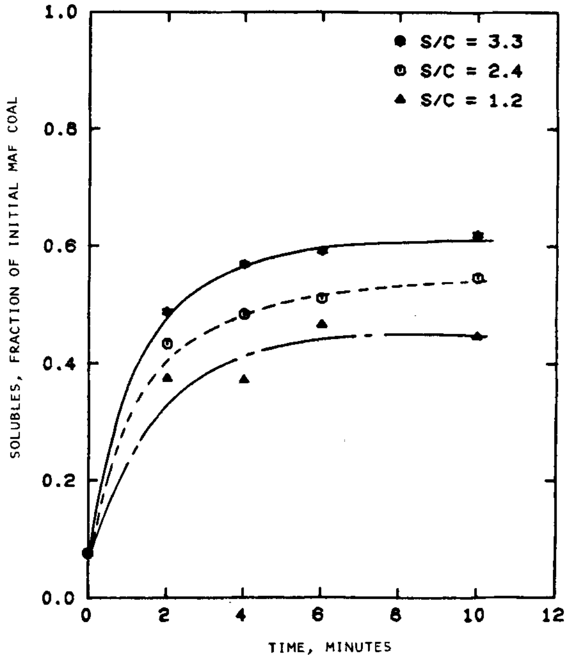

Figure 9. Effect of solvent-to-coal ratio, THF solubles (T = 723 K).

duction of some species is enhanced at low temperatures. However, their experiments were not conducted at short contact times, the shortest time being 30 min. A similar conclusion would be arrived at by examining the data at 10 min of reaction time only, as at this time the oil depletion is higher for 523 K than for 723 K (Figures 3 and 6).

The asphaltenes fraction shows a very rapid initial increase, which then starts decreasing slowly, thereby showing a maximum. This maximum increases with temperature. The preasphaltenes also show a similar trend; however, the maximum is not as pronounced as that for asphaltenes.

The overall coal conversion (obtained as 100% minus the percent recovery of THF insolubles on an MAF basis) increases with temperature. The conversion for 673 and 723 K is almost the same. Whitehurst et al. (1977) have reported that a certain amount of initially pyridine soluble coal was converted to pyridine insolubles when liquefied at high temperatures (>673 K). This was attributed to the repolymerization of preasphaltenes, giving char which no longer reacts. In the present analysis, this char is included in the THF insolubles.

With an increase of temperature, all reaction rates increase including those of coal dissolution and char formation. This fact often confounds the interpretation of the effect of temperature on coal conversion as both unconverted coal and char are inseparable, and while it may appear that the rate of coal conversion is the same at 673 and 723 K, this may only be a consequence of the above effect.

Effect of Solvent-to-Coal Ratio

To determine the effect of solvent-to-coal ratio, experiments were conducted at ratios of 1.2, 2.4, and 3.3. The results are plotted as pentene, toluene, and THF solubles in Figures 7, 8 and 9. In all the cases, initial negative yields of pentane solubles are observed (Figure 7). There is not much difference in the initial depletion of oil for solvent-to-coal ratios of 2.4 and 3.3. For solvent-to-coal ratio of 1.2, the oil depletion is less. This could be due to insufficient oil for the adductive reaction. As shown in Figure 8, while there is a marginal difference between the toluene solubles obtained at solvent-to-coal ratio of 2.4 and 3.3, in general, less toluene solubles are formed at the lower level of solvent-to-coal ratio. It may be expected that an increase in the solvent-to-coal ratio has a stabilizing effect on soluble products due to greater availability of hydrogen. However, once a certain minimum amount of solvent is available, any additional increase would hae a marginal effect. For Powhatan coal and SRC recycle solvent, this minimum solvent-to-coal ratio appears to lie between 1.2 and 2.4.

As shown in Figure 9, the THF solubles show a gradual increase with greater availability of the solvent. This was also shown by the factorial experiments which indicate that the oils concentration does take part in the intrinsic kinetics of coal liquefaction.

Kinetic Model

A lumped parameter kinetic model is developed to predict the product distribution. The assumptions made in the development of this kinetic model are briefly summarized below:

TABLE 11. MODEL PARAMETERS FOR POWHATAN COAL WITH SRC RECYCLE SOLVENT

Parameters (min^{-1})	Temperature (K) 723	673	623	573	Activation Energy (kcal/gmol)
$k_1\ (C_1 + O \rightarrow P)$	0.31	0.16	0.07	0.04	12.2
$k_2\ (C_2 + O \rightarrow A)$	17.49	8.22	2.85	2.28	11.6
$k_3\ (C_1 \rightarrow O)$	0.05	0.04	0.00	0.00	41.4
$k_4\ (C_2 \rightarrow O)$	2.58	1.48	0.63	0.50	14.3
$k_5\ (C_1 + C_2 \rightarrow G)$	0.016	0.004	0.001	0.001	15.3
$k_6\ (P \rightarrow A)$	0.14	0.14	0.13	0.13	0.5
$k_7\ (A \rightarrow O)$	0.09	0.09	0.08	0.08	0.4
$k_8\ (P \rightarrow \text{char})$	0.12	0.08	0.08	0.0	34.0
C_1 as Fraction of Initial Coal	0.62	0.77	0.82	0.85	

1. Coal fragments into smaller species when contacted with a solvent at high temperatures. This process is instantaneous.

2. Coal and oil undergo adductive reactions to give pentane insoluble products. These products could be asphaltenes or preasphaltenes.

3. Asphaltenes and preasphaltenes concentrations show maxima, indicating that they are intermediate products.

4. The oil fraction increases after certain reaction times, indicating that the intermediates are eventually converted to oils.

5. Whitehurst et al. (1977) have reported that a certain amount of initially pyridine-soluble coal was converted to pyridine insolubles when liquefied at high temperatures (>673 K). This was attributed to the repolymerization of preasphaltenes at this temperature, giving char which no longer reacts. In the present study, due to the analysis technique, this char is included in the unreated part of coal.

Based on the above assumptions, the kinetic model can be expressed as:

$$C \rightarrow C_1 + C_2(\text{Instantaneous}) \tag{1}$$

$$C_1 + O \xrightarrow{k_1} P \tag{2}$$

$$C_2 + O \xrightarrow{k_2} A \tag{3}$$

$$C_1 \xrightarrow{k_3} O \tag{4}$$

$$C_2 \xrightarrow{k_4} O \tag{5}$$

$$(C_1 + C_2) \xrightarrow{k_5} G \tag{6}$$

$$P \xrightarrow{k_6} A \tag{7}$$

$$A \xrightarrow{k_7} O \tag{8}$$

$$P \xrightarrow{k_8} \text{char} \tag{9}$$

where the symbols are defined in the Notation section.

The model assumes that coal (C) fragments into two broad categories, C_1 and C_2. The relative amount of C_1 and C_2 is a function of the reaction temperature. C_1 and C_2 form adducts with oils to give preasphaltenes (P) and asphaltenes (A), respectively, which in turn give oils (O). C_1 and C_2 also directly give oils and gases. Char is formed from preasphaltenes. All reaction rates are assumed to be of first order with respect to each of the reacting species.

For a gradient-less batch reactor, the material balance equations can be expressed as

$$\frac{dC_1}{dt} = -k_1C_1O - k_3C_1 - k_5C_1 \tag{10}$$

$$\frac{dC_2}{dt} = -k_2C_2O - k_4C_2 - k_5C_2 \tag{11}$$

$$\frac{dP}{dt} = 2k_1C_1O - k_6P - k_8P \tag{12}$$

$$\frac{dA}{dt} = 2k_2C_2O + k_6P - k_7A \tag{13}$$

$$\frac{dO}{dt} = k_1C_1O - k_2C_2O + k_3C_1 + k_4C_2 + k_7A \tag{14}$$

$$\frac{dG}{dt} = k_5(C_1 + C_2) \tag{15}$$

$$\frac{d_{\text{char}}}{dt} = k_8P \tag{16}$$

$$C = C_1 + C_2 + \text{char} \tag{17}$$

In order to integrate the above equations, the initial conditions for all the species need to be known. The initial concentrations for coal and oils can be obtained from the solvent-to-coal ratio. The initial conditions for asphaltenes and preasphaltenes can be obtained from the solubility of fresh coal in toluene and THF. There are no gases at the start of the reaction. The initial condition for char was obtained from the petrographic composition of coal. It was assumed that fusinite, semifusinite, macrinite, and micrinite portions of coal are unreactive (Given et al., 1975). These fractions accounted for 8.2% of Powhatan coal.

The model parameters were fitted to the experimental data by a computer code developed for solving nonlinear continuous optimization problems. The minimum sum of absolute values of deviations criterion was used to determine the model constants. An average deviation of 4.0% between the experimental and model-predicted levels of conversion were obtained. The experimental data were not smoothed and were used as obtained; hence a 4.0% difference between the model-predicted and experimental data represents a good fit.

The model constants obtained for the liquefaction of Powhatan coal in SRC recycle solvent are given in Table 11. Activation energies for the rate constants are also included in this table. Each pseudocomponent (preasphaltenes, asphaltenes, and oils) contains many chemical species. Therefore, the activation energies obtained from the model represent a lower average of the activation energies of many chemical species reacting to given many "other" chemical species. Several of these values are quite low indicating a possible diffusion effect. Figure 10 shows the Arrhenius fits for the rate constants. Figures 3 through 6 show the comparison between the model-predicted and the experimental results. As seen from these plots, the model adequately represents the product distribution for all conditions examined in the present study.

The previously discussed model (Abichandani et al., 1982) containing 15 parameters was also tested against the present data. This model gave a marginally better fit (average error = 3.2%) over the model presented above. This was expected due to a greater number of parameters available for optimization. However, some

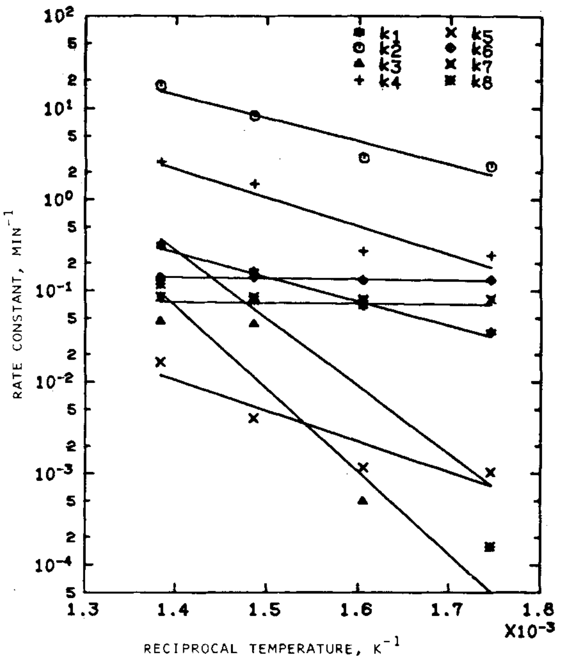

Figure 10. Arrhenius fits for the rate constants (high levels: 450°C, H_2, 13.8 MPa, 5/1//*S/C*, recrushed coal).

of the rate constants did not show Arrhenius law dependency, and hence the model was rejected. It appears that a direct comparison between CSTR results and those from a batch-mixed tank cannot be effectively made in the case of coal liquefaction.

NOTATION

A = asphaltenes, fractional
C = coal, fractional
C_1 = part of coal, fractional, defined in Eq. 1
C_2 = part of coal, fractional, defined in Eq. 1
G = gases, fractional
k = reaction rate constant, min^{-1}
O = oils (solvent), fractional
P = preasphaltenes, fractional
S/C = solvent-to-coal ratio, dimensionless
t = time, min
T = temperature, K
THF = tetrahydrofuran

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