

KINETICS AND MECHANISMS OF THE HYDROLIQUEFACTION OF COAL:  
ILLINOIS NO. 6, BURNING STAR COAL IN SRC-II HEAVY DISTILLATE\*

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Introduction

Four major industrial processes are currently being applied to coal liquefaction at the demonstration level, H-Coal<sup>1</sup>, Exxon Donor Solvent (EDS)<sup>2</sup>, Solvent Refined Coal I (SRC-I) and Solvent Refined Coal II (SRC-II)<sup>3</sup>. One of the reasons for parallel development of these processes is the lack of basic understanding of the reaction mechanisms, activation energies, and rates of reaction of coal liquefaction. We have begun a multifaceted program to delineate information on a number of coal-solvent combinations in order to develop a process kinetic model for coal liquefaction that will better enable process designers to make sound technical decisions.<sup>4</sup>

The present study has been conducted to obtain rates of reaction and activation energies for one coal--Illinois No. 6, Burning Star high volatile bituminous coal--and one solvent--coal-process derived SRC-II Heavy Distillate (450-850°F distillation range). Coal to solvent ratio, reaction time, temperature, and pressure are variables in a parametric study between 275°C and 475°C. Two different types of reactors were employed, a microreactor system for screening and a continuous flow reactor for the derivation of kinetic data. No attempt to generalize the results is made; although the authors believe that the descriptions contained are applicable to other systems. Generalizations will be attempted as the overall study continues.

Experimental

Illinois No. 6, Burning Star Mine coal was used in all experiments. The coal was ground to -45 mesh and riffled into 1 gallon containers. Proximate and ultimate analyses are provided in Table I. The liquefaction solvent used was untreated SRC-II heavy distillate received from the Ft. Lewis, Washington Pilot Plant. Elemental analysis, gravity, and boiling range is provided in Table II. Although the solvent was a 450-850°F cut, it contained ~ 5-10% pentane insoluble material. The solvent was received in 55 gallon drums, rolled, and transferred to 5 gallon cans from where it was sampled.

Microreactors were used to study the initial dissolution of coal and the effects of solvent/coal ratio on conversion. The microreactors have a total volume of ~ 20 cm<sup>3</sup>, and are designed to operate between 0-2000 psi hydrogen and 25-500°C. The total mass of the reactors is 0.6 Kg. A Tecann fluidized bed sand bath is used for rapid reactor heating and provides a 2-2.5 minute heat-up time. A water quench provides a 90 sec quench between 400° and 50°C. Wrist-action shaking, ~ 300 cpm, with a 2-inch stroke, is used for mixing. Mass balances are routinely within 1% based upon total reactor charge.

Data for the rates of reaction and activation energies were obtained using a non-recycle continuous flow tubular reactor, Figure 1. The reactor consists of 4 independently heated stages (.203" ID helical coils) and was operated isothermally at 400°, 425°, 450°, and 475°C,

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Table I. Proximate and Ultimate Analysis of Illinois No. 6 Burning Star Coal

<u>Proximate Analysis Wt %</u>	
Moisture	3.41
Ash	10.39
Volatile	36.70
Fixed Carbon	49.50

<u>Ultimate Analysis Wt %</u>	
Moisture	3.41
Carbon	69.90
Hydrogen	4.59
Nitrogen	1.15
Chlorine	0.07
Sulfur	3.06
Ash	10.39
Oxygen (diff)	9.43
	<u>100.00</u>

<u>Sulfur Form Wt %</u>	
Pyritic	1.11
Sulfide	0.09
Organic (diff)	<u>1.86</u>
Total Sulfur	3.06

Table II. Analysis of SRC-II Heavy Distillate

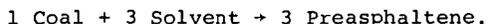
Ash (%)	0.05
Carbon (%)	89.8
Hydrogen (%)	7.6
Nitrogen (%)	1.4
Sulfur (%)	0.4
Oxygen (%)	1.8
Pentane Insols	6%
Distillate	86.5 850°F
Yield	

at coal plus solvent mass flowrates of 0.7 to 6 lb/h, hydrogen pressure of 2000 psi, and gas flowrates of 10-200 MSCF per ton of coal. Reaction temperatures are predicted to be attained within 6.5 ft of the reactor inlet and the total length of the reactor was varied between 10-83.5 ft. Liquid and gas samples are obtained separately at atmospheric pressure. Data reported are obtained from analyses of samples withdrawn at steady state conditions; i.e., after 1.5 h at fixed reactor operating conditions. The coal derived products, obtained at the conclusions of the runs, were extracted exhaustively into pentane-soluble (oil), benzene-soluble pentane-insoluble (asphaltene), THF-soluble benzene-insoluble (preasphaltene), and THF-insoluble (inorganics + IOM) fractions. Elemental analyses were provided

by Huffman Laboratories. Viscosities were measured with a Brookfield model LVT viscometer. Gas samples were obtained at all conditions and analyzed with an HP 5840 gas chromatograph equipped with a TC detector. The columns are teflon-lined aluminum packed with 800-100 mesh Poropak Q.<sup>5</sup>

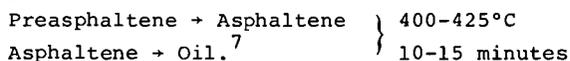
### Results and Discussion

In order to establish a kinetic model for coal liquefaction, we have endeavored to determine a stepwise reaction mechanism. The proposed first step is the dissolution of coal. Data from microreactor runs in the temperature range 275°-375°C--below typical liquefaction temperatures--are presented in Table III. There is a small solubility of coal in the solvent at low temperatures, and marked increases at temperatures between 275°C and 350°C. Equilibrium in terms of gas make and solubility are attained rapidly. Up to 350°C, the SRC-II solvent is depleted. Solvent is a reactant with coal.<sup>4</sup> The stoichiometry of the coal-solvent reaction can be estimated by weight loss of solvent and net THF sols. Based upon these data, it appears that the reaction can be represented as

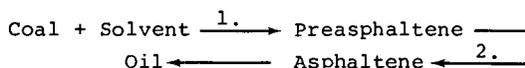


This stoichiometry is also consistent with published values for molecular weights of solvent (250), preasphaltene (1000), and coal (2250)<sup>6</sup>. The stoichiometry and approximate molecular weights establish a mass balance for the initial dissolution step. It is also seen that it is primarily the pentane insoluble fraction of the initial solvent--the heavier, more functional portion--that reacts with coal in this initial reaction.

The second reaction step appears to be the decomposition of preasphaltene. In a recent study, reactions of preasphaltene and asphaltene obtained from liquefaction experiments with another Illinois No. 6 coal, River King, were shown to react thermally



Both coal-derived substrates appear to react in a series reaction path, ultimately producing oil. Thus, the mechanistic reaction path used for subsequent kinetic analysis is



Although the production of gas accompanies each step, the primary gas production occurs at short time and is primarily (in terms of mass) associated with coal.

### Kinetics Treatment

The coal liquefaction reaction kinetics were determined using data from a non-recycle continuous tubular flow reactor (Figure 1). The reaction mechanisms were the result of the microreactor experiments previously described. The scale-up to the continuous flow reactor is necessary for reaction kinetics in order for industrial application of the results because the microreactor eliminated aspects of the overall reaction scheme such as hydrogen mass transfer, and multiphase flow regimes, and mixing.

Table III. Microreactor Data from Liquefaction Runs Between 275-375°C

Run No.	Run Parameters		Gas Make		Liquid Product, Wt				Conversion	
	Temp °C	Time	CO <sub>2</sub>	C <sub>1</sub> -C <sub>4</sub>	PreA	THF Insols	Asph	Oil	Toluene	THF
1	275	6.5 min	1.49	-	.36	2.3	-	-	-	15
2	300	6.5 min	1.25	-	.50	2.1	.46	4.7	-7	24
3	300	26 min	1.85	.04	.59	2.1	.31	5.0	-1	24
4	325	6.5 min	1.32	.03	.47	1.7	.48	5.2	15	40
5	325	26 min	1.83	.09	.60	1.6	.38	5.2	11	44
6	350	6.5 min	1.84	.17	.65	1.5	.61	5.1	16	44
7	375	6.5 min	2.30	.47	.92	1.2	-	-	-	61
8	375	26 min	2.72	1.29	.90	1.0	-	-	-	70
9	Blank	-	-	-	0	2.67	.58	4.8	-	-

Because of the complicated multiphase flow in the reactor, we are unable (at this time) to quantitatively determine the residence time of each reactant phase in the reactor. As a consequence, reaction times are expressed as space time,  $\theta$ , i.e.,

$$\theta = \frac{\text{Volume of Reactor}}{\text{Coal/Solvent Slurry Mass Flowrate}} \left( \frac{\text{ft}^3\text{-hr}}{\text{lb}_m} \right)$$

It is possible to determine the activation energy of the various liquefaction reactions, but the pre-exponential multiplier (frequency factor) in the Arrhenius type rate constant will be a function of the spacetime and therefore is questionable when used in other reactor systems.

The data obtained using the flow reactor were analyzed as previously described. The product slate from the reactor was found to be independent of the gas flowrate over the range used (10-200 MSCF/ton coal). Thus, hydrogen transfer from the vapor phase to the liquid phase was insignificant for this work and was eliminated from the further consideration. The kinetic parameters were estimated using a non-linear minimization algorithm (Powell's conjugate gradient method<sup>8</sup>) in conjunction with a Runga Khulta 7/8 numerical integrator. Based upon the reaction mechanism and stoichiometry determined from the microreactors, a component mass balance can be written for the system:

$$\frac{d[C]}{dt} = -0.8 k_1 [C][S] + k_2 [P] - k_7 [C] \quad 1)$$

$$\frac{d[P]}{dt} = k_1 [C][S] - k_2 [P] - k_3 [P] + k_4 [A][S] \quad 2)$$

$$\frac{d[A]}{dt} = 0.8 k_3 [P] - 0.8 k_4 [A][S] - k_5 [A] + k_6 [S]^3 \quad 3)$$

$$\frac{d[S]}{dt} = -0.2 k_1 [C][S] + 0.2 k_3 [P] - 0.2 k_4 [A][S] + k_5 [A] - k_6 [S]^3 \quad 4)$$

$$\frac{d[G]}{dt} = k_7 [C] \quad 5)$$

where: [C] = weight fraction in whole liquid product (WLP) of coal

[P] = weight fraction in WLP of preasphaltene

[A] = weight fraction in WLP of asphaltene

[S] = weight fraction in WLP of solvent

[G] = weight fraction gas ( $C_1$ - $C_4$ , CO, CO<sub>2</sub>, H<sub>2</sub>S)

t = space time (hr ft<sup>3</sup>/lb<sub>m</sub>)

$k_1$ - $k_7$  = Arrhenius rate constants.

The reaction rate constants  $k_1$ - $k_7$  were determined numerically using the data obtained from the tubular flow reactor at a given reactor isothermal operating condition (i.e., Figure 2 as an example). For a given set of  $k_1$ - $k_7$ , the concentration profiles as a function of space time of [C], [P], [A], [S], and [G] can be obtained by numerically integrating the mass balance equation (eqns 1-5) using the concentration profiles. By using the deviation between the calculated and experimental concentration profiles as the objective function of an unconstrained minimization algorithm, e.g.,

$$\text{minimize } f(k_1, k_2, \dots, k_7) = \sum_{j=1}^n \sum_{i=1}^m \text{abs} \frac{(C_{ij}^* - C_j(t_i))}{\bar{C}_i}$$

$$\bar{C}_i = \begin{cases} C_{ij}^* & \text{if } C_{ij}^* \geq 1.0 \times 10^{-6} \\ 1 & \text{otherwise} \end{cases}$$

where:  $C_{ij}^*$  = weight fraction of component j at space time  $t_i$

$C_j(t_i)$  = calculated weight fraction of component j at time  $t_i$

n = number of components (n = 5)

m = number of experimental data points

an optimal set of reaction rate constants  $k_1$ - $k_7$  can be obtained. The technique in effect chooses the best set of  $k_1$ - $k_7$  in order that the deviation between the experimental and calculated concentration profiles is minimized. A set of optimal reaction rate constants is obtained for each isothermal reactor data set. Shown in Figure 2 are the experimental data and the calculated concentration profiles of the



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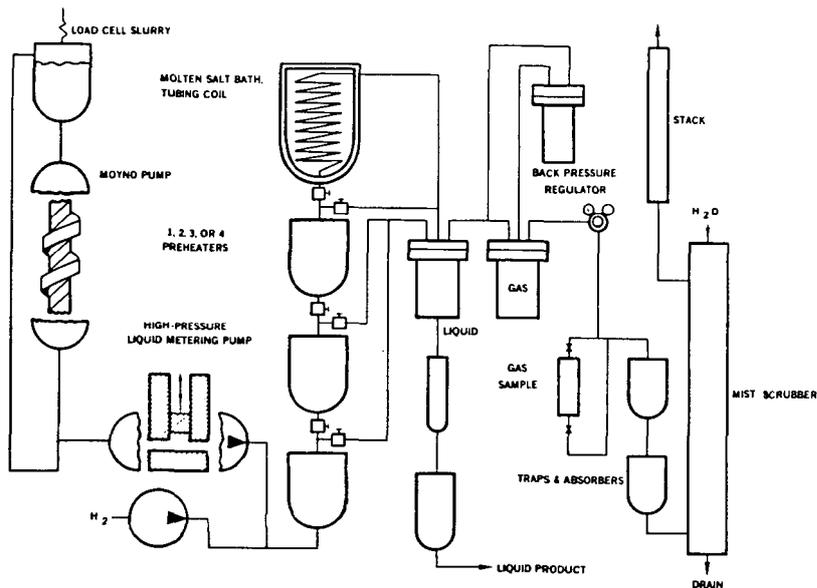


Figure 1. Continuous Coal Liquefaction Reactor

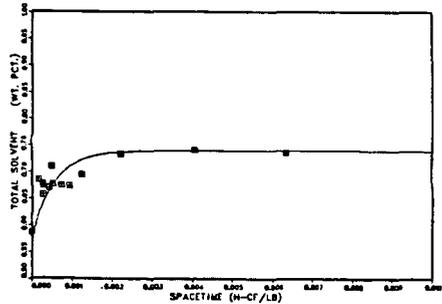
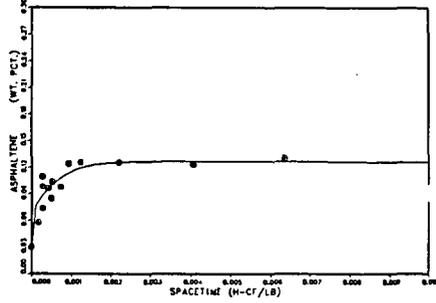
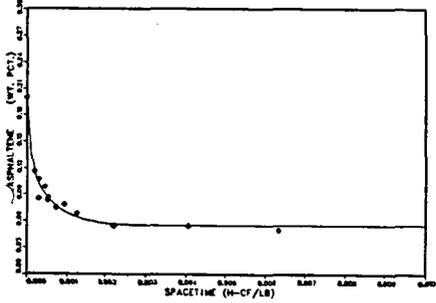
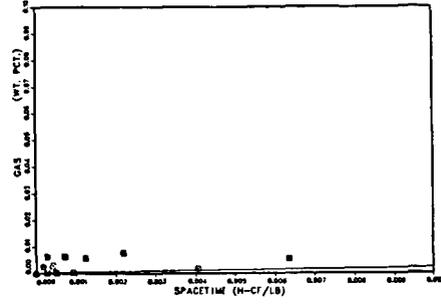
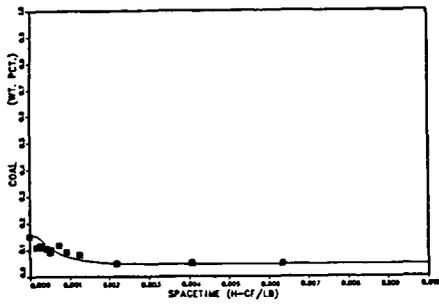


Figure 2. Experimental data and model predictions of Concentrations as a function of time.