

KINETICS OF COAL HYDRODESULFURIZATION IN A BATCH REACTOR

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Background

In recent years there has been a renewed interest in developing this nation's coal reserves because of our growing reliance on foreign oil sources. Due to the stringent air quality standards set by the Environmental Protection Agency, however, the burning of coals with sulfur contents of greater than one percent has been essentially prohibited.

An alternative to the production of low-sulfur coal reserves exists in the desulfurization of high-sulfur coal reserves by the techniques of solvent refining and hydrogenation. It is generally accepted (1) that sulfur occurs in coal in three forms: organic, pyritic, and sulfate. These forms vary in concentration and ease of removal from one coal to another. The purpose of this paper is to develop a kinetic model that will represent the rate of removal of sulfur for all three forms simultaneously. Since several different sulfur reactions occur at the same time it is feasible to consider a model in which the reaction rate appears to vary as a function of conversion. Such models were successfully applied by Hill, et al. (2) to the dissolution of coal in tetralin and by Lessley, et al. (3) to thermal cracking of shale gas oil under a hydrogen atmosphere.

Much of the earlier work done on coal desulfurization took the form of carbonization studies in which coal or coal char was heated in the presence of various gas streams and the percent removal of total sulfur from the coal was determined. A good review of the work done on this subject prior to 1932 is given by Snow (4).

In 1960 Batchelor, et al. (5) published an article describing a method in which a bed of char was fluidized with a known mixture of hydrogen and hydrogen sulfide to establish the equilibrium distribution of sulfur between gas and char. He also developed an equation for calculating the maximum amount of desulfurization that could be achieved.

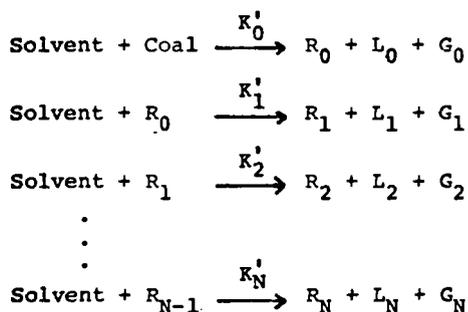
In more recent years a non-isothermal method for determining the kinetics of coal desulfurization has been developed in which the sample is subjected to a constant rate of heat. Vestal, et al. (6) suggests that this method is superior to isothermal methods since it avoids the uncontrolled occurrence of chemical reactions during the time that the sample is being heated to reaction temperature. A good review of this method, complete with theory, experimental procedure and apparatus, results, and discussion, is given by Yergey, et al. (1). The study reveals that in most cases the kinetics of hydrogen sulfide removal can be described by five processes. These processes are directly related to the five forms of sulfur present in the coal which are designated as Organic I,

Organic II, Pyrite, Sulfide, and Organic III. With each of the processes there is an associated activation energy, reaction order, and rate constant.

Another kinetic model for desulfurization is given by Qader, et al. (7). This article discusses the hydroremoval of sulfur from coal tars and concludes that the reaction is first order with respect to heterocyclic molecules. The experimental results also show that sulfur removal follows a true Arrhenius temperature dependence.

To date no articles dealing with the kinetics of hydrodesulfurization of coal in liquid phase have appeared, but several articles have been published on coal dissolution kinetics.

Hill (8) proposed a model for coal dissolution in which a series of reactions take place between the solvent and the coal residue. The model is given as follows:



where

- R_i is the solid coal residue
- L_i is the extract in solution
- G_i is the gaseous products.

In another article Hill, et al. (2) develops a model in which the first-order reaction velocity constant varies with the fraction of coal extracted. This model fits the kinetic data in the range of 350° to 450°C quite well. Plots of the Arrhenius energy of activation and the Eyring enthalpy of activation are included in the article and both plots exhibit straight line relationships.

Wen, et al. (9) have proposed a rate equation for the dissolution of coal under hydrogen pressure which describes fairly closely the experimental data reported from two independent sources. Wen's equation describes the rate of dissolution as a function of the fraction of undissolved solid organics and the coal-solvent ratio. It also incorporates an Arrhenius temperature dependence and an exponential dependence on the hydrogen partial pressure.

Another semi-empirical correlation which adequately represents coal dissolution data is discussed by Curran, et al. (10). This

correlation deals more specifically with the mechanism of hydrogen transfer and does not lend itself to the application of conventional kinetic data analysis techniques.

Experimental Design

The purpose of this study was to determine the effects of temperature and time on the desulfurization of coal and to develop a kinetic model that can satisfactorily represent the rate of total sulfur removal.

The coal used in this study was a bituminous coal from the Madisonville No. 9 seam, Fies Mine, in Kentucky. The proximate and ultimate analyses for the coal are given in Table 1. This coal was selected because it is currently being used in the start up of the Fort Lewis ERDA solvent refining plant. Coal of minus 200 mesh size fraction was used for this study.

The solvent used was straight run anthracene oil purchased from the Reilley Tar and Chemical Company. The raw solvent was vacuum distilled at an absolute pressure of 2-3 mm of mercury and the cut between 125°-250°C was saved. This cut is similar to the cut used in the Pittsburgh and Midway Solvent Refined Coal Process (11). Hydrogen gas for this study was 3500 psig grade with a purity of 99.95%. The gas was manufactured by the Linde division of the Union Carbide Corporation.

The temperatures chosen for this study were 360°, 390°, and 420°C. The lower temperature was selected since literature (12) indicates that at temperatures below 350°C the dissolution of coal in the solvent is incomplete. The upper temperature was selected because at temperatures of greater than 450°C coking occurs.

Studies on the kinetics of dissolution of coal (2) indicate that at times of greater than 4 hours the percent dissolution does not significantly increase. For this reason reaction times of 1/2, 1, 2, and 4 hours were selected. The lower limit was selected because the 10 minutes required for heating up the injected slurry would interfere with runs of less than 30 minutes.

Initial pressures of 750, 785, and 820 psig were used for runs at 420°, 390°, and 360° respectively. These initial pressures resulted in a reaction pressure of approximately 1900 psig.

The solvent-to-coal weight ratio was set at 10 to 1. This ratio was chosen because it kept the amount of slurry injected into the reactor at a minimum.

The determination of the percent of sulfur remaining in the solvent refined coal was done by an ASTM total sulfur method. This number was then corrected to give the amount of sulfur remaining in the coal on a solvent free basis. Sulfur analyses were also made on the reclaimed solvent and the reaction off gas. Based on these analyses and the analysis of the original coal and solvent a sulfur balance was completed for each run.

Experimental Equipment

All experimental runs in this study were carried out in a 300 cc Magnedrive batch autoclave, manufactured by Autoclave Engineers of Erie, Pennsylvania. A manual Ruska piston pump (250 ml capacity) was used for injection of slurry into the autoclave. An equipment flow sheet is presented in Figure 1.

Experimental Procedure

One hundred eighty milliliters of vacuum distilled solvent were added to the reactor and the head sealed. The reactor was then purged with helium and pressurized with hydrogen to the desired initial (cold) pressure, and the jacket heater turned on. One hundred grams of a thick paste (1:1 ratio by weight) of 200 mesh coal and solvent was then charged to the Ruska pump and all air bled from the system. The reactor was allowed to heat (with constant stirring) to reaction temperature, at which time exactly 40 ml of slurry were charged to the hot reactor via the Ruska pump. At the conclusion of the reaction, the reactor was quenched by dropping the heating jacket and cooling the autoclave vessel with a high speed fan. Product gas was analyzed on a gas chromatograph and solvent recovered by vacuum distillation of the resulting liquid product.

Run Conditions

Table 2 shows the run numbers and the corresponding reaction conditions. Runs 1-11 were all performed using the same coal. Different samples of coal were used for runs 12-14 and 15-17 because an insufficient quantity was prepared initially.

Percent Desulfurization of the Coal

A plot of sulfur conversion for each temperature level as a function of time is given in Figure 2. The data points for 360°C were fit by the method of least squares for a straight line. The data points for 390° and 420° were fit with a flexible curve. Attempts to fit these data points with second and higher order polynomials proved unsuccessful and there was no theoretical basis for trying to fit the data with other mathematical models.

Correlation of the Data

Initial attempts to plot the data according to a rate equation of nth-order proved unsuccessful. Although the data at 360°C fit a first-order model quite well the data at the higher temperatures would not yield straight lines for any simple rate expression. The fact that a constant value could not be obtained for the rate constant suggested that the rate constant might be a function of some other variable such as the fractional conversion of the sulfur compounds to hydrogen sulfide and desulfurized products. This would seem feasible since several sulfur reactions are occurring simultaneously (1) with different rate constants and activation energies for each reaction. The idea of the reaction rate varying as a

function of conversion is not a new one and has found application in several areas. Hill, et al. (2) developed a model which successfully described the rate of dissolution of coal in tetralin and Lessley, et al. (3) developed a similar model for the thermal cracking of shale gas oil under a hydrogen atmosphere. Other applications are described by Fabuss, et al. (15) to the thermal decomposition rates of saturated cyclic hydrocarbons and Buekens, et al. (16) to the thermal cracking of propane.

The model of Hill, et al. (2) proved successful in representing the data taken in this study and is developed below.

Rearranging the rate expression for a simple first-order irreversible reaction yields the equation

$$\frac{dx/dt}{1-x} = k.$$

For each temperature level the value of dx/dt was evaluated at several different times by using the method of "Equal Area Graphical Differentiation" as described by Fogler (17). A plot of $(dx/dt)/(1-x)$ vs. x was then made (see Figure 3), and the data exhibited a linear relationship. The best fit straight line through each data set was determined by a least squares fit.

The linear change of the rate constant, k , with x , the fraction converted can be expressed as

$$k = C_1 - C_2 x$$

$$k = C_1 \left(1 - \frac{C_2}{C_1} x \right)$$

If $C_1 = k_0$ and $C_2/C_1 = a$

then $k = k_0 (1-ax)$ (1)

The values of k_0 and a were found by rearranging the coefficients of the best fit straight line to the form of equation (1).

Substituting equation (1) into the first-order rate expression gives:

$$\frac{dx}{dt} = k_0 (1-ax) (1-x)$$

where k_0 is a pseudo second-order rate constant.

Separating the variables and integrating gives:

$$\frac{dx}{(1-ax)(1-x)} = k_0 dt \quad \text{and}$$

$$\ln \left(\frac{1-x}{1-ax} \right) = (k_0 t + C) (a-1)$$

Using the boundary condition: $t = 0, x = 0$, the value of C is found to equal 0. Therefore, the final equation becomes

$$\ln\left(\frac{1-x}{1-ax}\right) = k_0 t(a-1)$$

The values of k_0 and a for this equation are listed in Table 3 as a function of temperature.

Arrhenius Activation Energy

Based on the values of k_0 given in Table 3 a plot of $\ln k_0$ vs. $1/T$ was made to determine the Arrhenius energy of activation. This plot is shown in Figure 4. The linear relationship indicates that the desulfurization reactions follow a true Arrhenius temperature dependence at low conversions. The value of the activation energy obtained from this graph is 33.04 Kcal/mol. This value is within the range of reported values for hydrodesulfurization reactions (1).

Reproducibility

Runs 15, 16, and 17 were carried out under the same set of conditions to serve as a check on the reproducibility of the data. The conditions chosen were a temperature of 360°C and a reaction time of 1/2 hour. This set of conditions represents an extreme that should give the maximum variance in the results. At the other extreme the large reaction time would tend to minimize the effect of the temperature drop after injecting the slurry. The percentage of desulfurization for these three runs are shown in Table 4 along with the mean and standard deviation.

Sulfur Balances

A sulfur balance was completed for each run based on the weights and sulfur contents of the reactants and products. In no case was the weight of the sulfur in the products more than 0.4 grams less than the weight of the sulfur in the reactants. It is quite probable that these sulfur losses can be attributed to the volatilization of sulfur-containing compounds during the vacuum distillation. The results of the sulfur balances, expressed as percent recovery are shown in Table 5.

Conclusions

The following conclusions can be made from this study.

(1) The percent desulfurization of coal is a function of both time and temperature. Increasing either of these variables within the range of conditions for this study will cause the conversion to increase.

(2) The reaction rate constant appears to be a variable of conversion as well as temperature. The relationship between these variables can be adequately described by an equation of the form

$$k = k_0(1-ax)$$

where k_0 and a are constants.

The general expression showing conversion as a function of time is then given by

$$\ln\left(\frac{1-x}{1-ax}\right) = k_0 t(a-1).$$

This expression represents the kinetic data taken in this study quite well.

(3) At low values of conversion the reaction rate constant shows a true Arrhenius temperature dependence. The value of the activation energy as calculated from the Arrhenius plot is 33.04 Kcal/mole.

(4) The desulfurization of coal is affected to a large extent by the nature of the coal. Even coal taken from the same sample will give large variations in the percent of desulfurization if it is not carefully mixed.

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Table 1

Proximate and Ultimate Analyses of Coal Used

Coal: Fics Mine
Source: Kentucky
Rank: Bituminous

(A) Runs 1-11

<u>Proximate Analysis</u>	<u>As Received</u>	<u>Dry Basis</u>
% Moisture	6.00	-
% Ash	16.20	17.20
% Volatile	32.80	34.90
% Fixed Carbon	45.00	47.90
	100.00	100.00
<u>Ultimate Analysis</u>		
% Carbon	62.90	66.90
% Hydrogen	4.60	4.89
% Nitrogen	1.10	1.17
% Sulfur	2.86	3.04
% Oxygen	11.34	6.80
% Ash	17.20	17.20
	100.00	100.00

(B) Runs 12-14

<u>Ultimate Analysis</u>		
% Carbon	64.50	65.70
% Hydrogen	4.41	4.49
% Nitrogen	1.33	1.35
% Sulfur	3.40	3.46
% Oxygen	9.56	7.90
% Ash	16.80	17.10
	100.00	100.00

(C) Runs 15-17

<u>Ultimate Analysis</u>		
% Carbon	61.00	63.50
% Hydrogen	3.88	4.04
% Nitrogen	1.34	1.39
% Sulfur	3.66	3.81
% Oxygen	11.60	7.96
% Ash	18.50	19.30
	99.98	100.00

Table 2

Run Conditions

<u>Run No.</u>	<u>Reaction Temperature (°C)</u>	<u>Reaction Time (min)</u>
1	420	120
2	420	30
3	420	60
4	360	60
5	390	240
6	360	30
7	390	120
8	360	240
9	390	30
10	390	60
11	420	240
12	360	120
13	390	60
14	420	120
15	360	30
16	360	30
17	360	30

Table 3
Values for the Parameters k_0 and a

<u>Temperature (°C)</u>	<u>k_0</u>	<u>a</u>
360	0.03544	-1.165
390	0.1166	3.373
420	0.3454	2.787

Table 4
Reproducibility Results

<u>Run Number</u>	<u>Percent Desulfurization</u>
15	19.42
16	21.26
17	20.21
Mean	20.30
Standard Deviation	0.92

Table 5
Sulfur Balance Results

<u>Run No.</u>	<u>Percent Recovery</u>
1	91
2	91
3	95
4	97
5	91
6	97
7	93
8	97
9	99
10	93
11	79
12	83
13	83
14	77
15	95
16	93
17	91

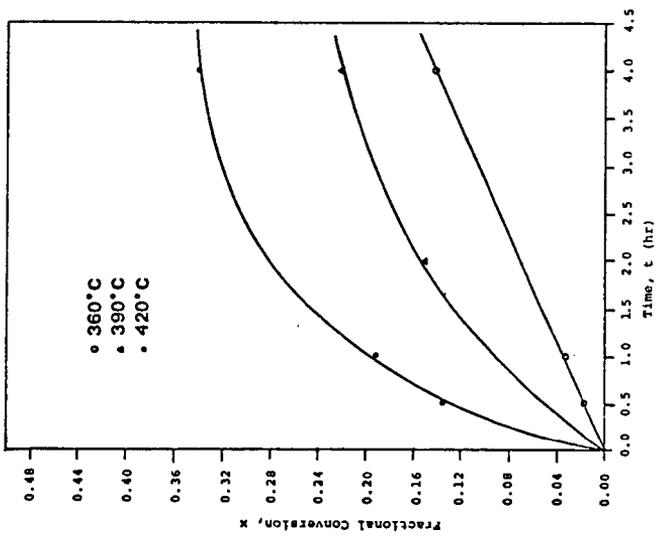


Figure 2: Fractional Conversion

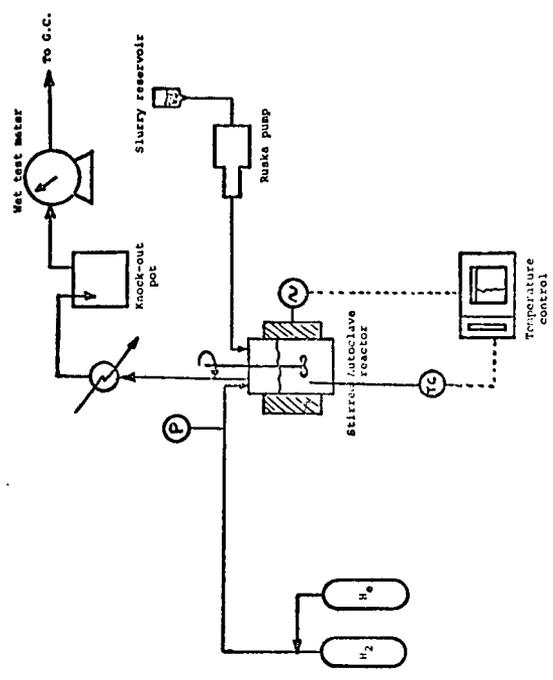


Figure 1: Experimental Apparatus

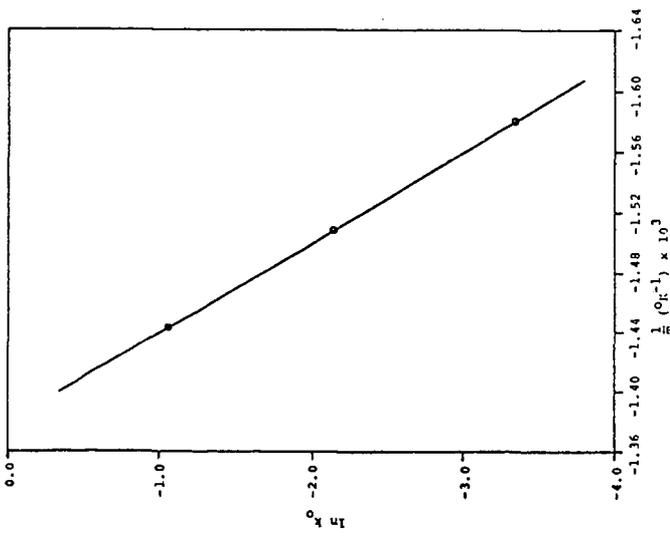


Figure 4: Arrhenius Plot

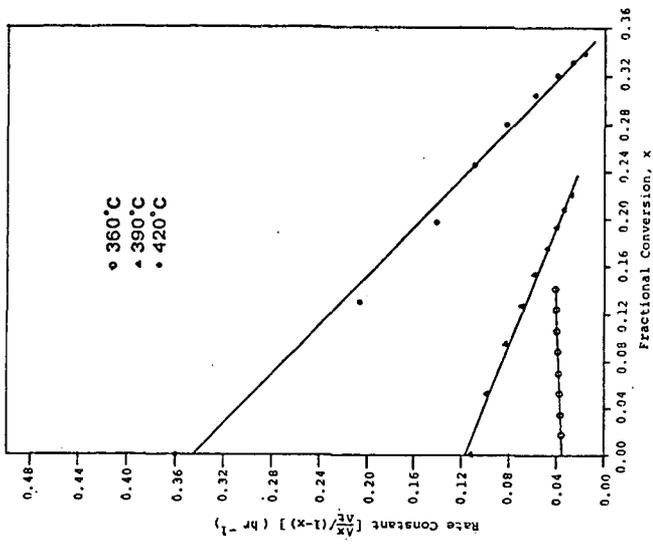


Figure 3: Rate constant vs. Fractional Conversion