KINETICS OF HYDRODESULFURIZATION OF COAL IN A BATCH REACTOR

by

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DEDICATION

This thesis is dedicated to

my Father and Mother

ABSTRACT

The kinetics of hydrodesulfurization of coal was studied at the Colorado School of Mines under contract from the Energy Research and Development Administration, Fossil Energy, University Relations Division. The purpose of the study was to develop a model for the overall rate of sulfur removal from coal.

Experimentation was done in a 300 cc Magnedrive reactor. Reaction temperatures of 360°, 390°, and 420°C were studied at times of 1/2, 1, 2, and 4 hours. Fixed operating variables were: reaction pressure, solvent type, coal type, and solvent-to-coal ratio. The effects of heat-up time were minimized by heating the bulk of the solvent to reaction temperature and then injecting a small sample of coal-solvent slurry. Total sulfur analyses were performed on the liquid and solid products and the gaseous products were analyzed with a gas chromatograph.

The results indicate that the desulfurization of coal increases with an increase in either the reaction temperature or the reaction time. The results also indicate that the reaction rate constant appears to be a function of conversion as well as temperature. The type of model which successfully described the data taken in this study is given by an equation of the form

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

where k_o and a are constants, and

x is the fractional desulfurization.

An Arrhenius plot of ln k_o vs 1/T for each of the reaction temperatures showed that the rate constant follows a true Arrhenius temperature dependence for low values of conversion. The activation energy for the desulfurization reaction as determined from this plot was 33.04 Kcal/mole.

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INTRODUCTION

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 thesis 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.

All of the experimental runs were carried out in a 300 cc Magnedrive autoclave. Reaction temperatures of 360^{o},

390°, and 420°C were studied at times of 30, 60, 120, and 240 minutes. Fixed operating variables were: solvent-to-coal ratio, reaction pressure, coal type, and solvent type.

The coal was injected in a coal-solvent slurry by means of a Ruska pump. The purpose of injecting the coal in this manner was to minimize the effects of heat-up time; namely the occurrence of undesired hydrodesulfurization reactions at temperatures less than the operating temperature. For each run the solvent was recovered from the liquid product by means of vacuum distillation and analyzed for total sulfur by an induction furnace method. The solid product was analyzed by an ASTM total sulfur method and the reaction gases were analyzed with a gas chromatograph. Based on these analyses and the analysis of the original coal and solvent a sulfur balance was completed for each run.

LITERATURE SURVEY

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 is 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:

$$\text{Solvent} + \text{Coal} \xrightarrow{K_0'} R_0 + L_0 + G_0$$

$$\text{Solvent} + R_0 \xrightarrow{K_1'} R_1 + L_1 + G_1$$

$$\text{Solvent} + R_1 \xrightarrow{K_2'} R_2 + L_2 + G_2$$

$$\vdots$$

$$\text{Solvent} + R_{N-1} \xrightarrow{K_N'} R_N + L_N + G_N$$

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 I. This coal was selected because it is currently being used in the start up of the Fort Lewis ERDA solvent refining plant.

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.

Table 1

Proximate and Ultimate Analyses of Coal Used

Coal: Fies Mine
Source: Kentucky
Rank: Bituminous

(A) Runs 1-11

Proximate Analysis	As Received	Dry Basis
% Moisture	6.00	-
% Ash	16.20	17.20
% Volatile	32.80	34.90
% Fixed Carbon	45.00	47.90
	100.00	100.00
Ultimate Analysis		
% 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

Ultimate Analysis		
% 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

Ultimate Analysis		
% 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

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. The fractional conversion was calculated by dividing the difference in the sulfur contents of the raw and refined coals by the sulfur content of the raw coal. The fractional conversion is therefore strictly a function of the sulfur in the coal and not in the solvent or the gas.

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.

EQUIPMENT

The reactor system used in this study consisted of a batch stirred autoclave, a slurry pump, and a gas delivery system.

The batch stirred autoclave, as shown in Figure 1, was manufactured by Autoclave Engineers, Inc. of Erie, Pennsylvania. Both the reactor and the stirring head were fabricated from 316 stainless steel with a pressure rating for the reactor of 5400 psig at 650°F. The reactor had an inside diameter of 1 3/16 inches and a depth of 7 inches resulting in an effective volume of 300 ml. A 1200-watt, 115-volt heating jacket was used for heating. It was capable of heating the reactor from room temperature to 800°F in about 45 minutes. The stirring head assembly was driven by a 1/4 horsepower variable speed D.C. motor. A 1/4 inch valve with soft-sealing stem was used for the gas inlet line and a 1/4 inch metal tip throttling valve was used for the slurry line. Both valves were Hoke 316 stainless steel valves with a pressure rating of 5000 psig at 70°F.

A Leeds and Northrup Series 60 controller with a Model 11906-223 SCR final control element was used for temperature control. Temperatures were recorded on a Speedomax continuous recorder. The input to the controller was from a chromel-alumel (Type K) thermocouple.

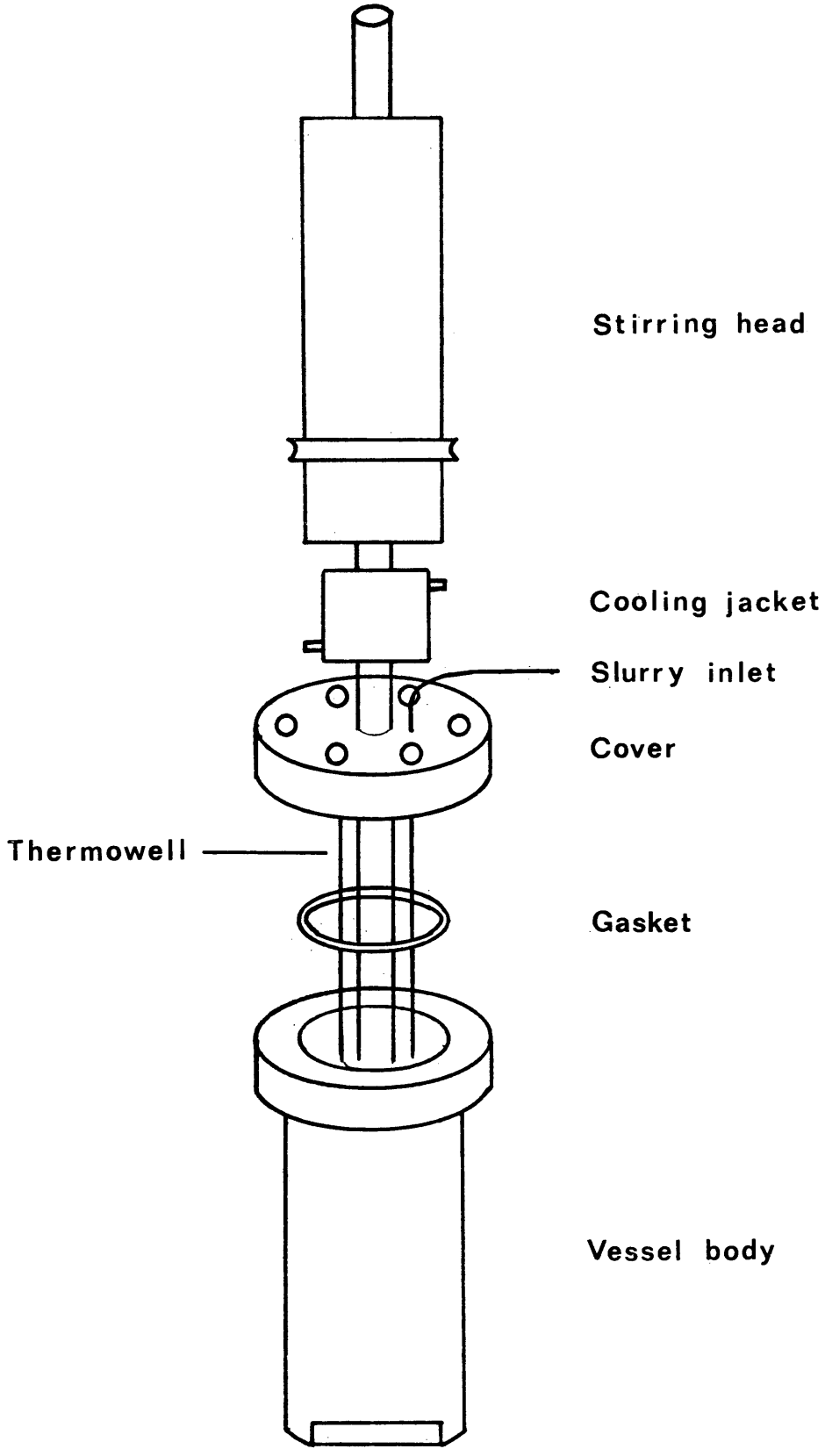


Figure 1 Reactor and stirring head assembly

The slurry pump used in this study was a manually-operated 250 ml piston pump manufactured by the Ruska Instrument Corporation of Houston, Texas. Both the inlet and outlet lines were fitted with 1/4 inch, 316 stainless steel Hoke valves with soft sealing stems.

A complete diagram of the gas delivery system is shown in Figure 2. The system consisted of a hydrogen cylinder, a helium cylinder, two pressure regulators, three pressure gauges, two gas reservoirs, a reducing valve, eleven shut-off and regulating valves, and other connecting parts such as tees and tubing. The two pressure regulators were manufactured by Hoke, Inc. of Cresskill, New Jersey and were rated at 5000 psig on both the inlet and outlet. The pressure gauges were Ashcroft Maxisafe gauges with a pressure range of 0 to 5000 psig.

A reducing valve was incorporated into the system to provide for the option of maintaining a constant pressure. The valve was capable of controlling the system pressure in the range of 0 to 3000 psig and it was manufactured by the Grove Valve and Regulator Co. of Oakland, California. All of the shut-off and regulating valves were made by Autoclave Engineers, Inc. of Erie, Pennsylvania, and had a pressure rating of 30,000 psig with the exception of the reservoir and regulator inlet valves and the system vent valve. These three valves were 1/4 inch, 316 stainless steel Hoke valves with soft sealing stems and a pressure rating of 5000 psig

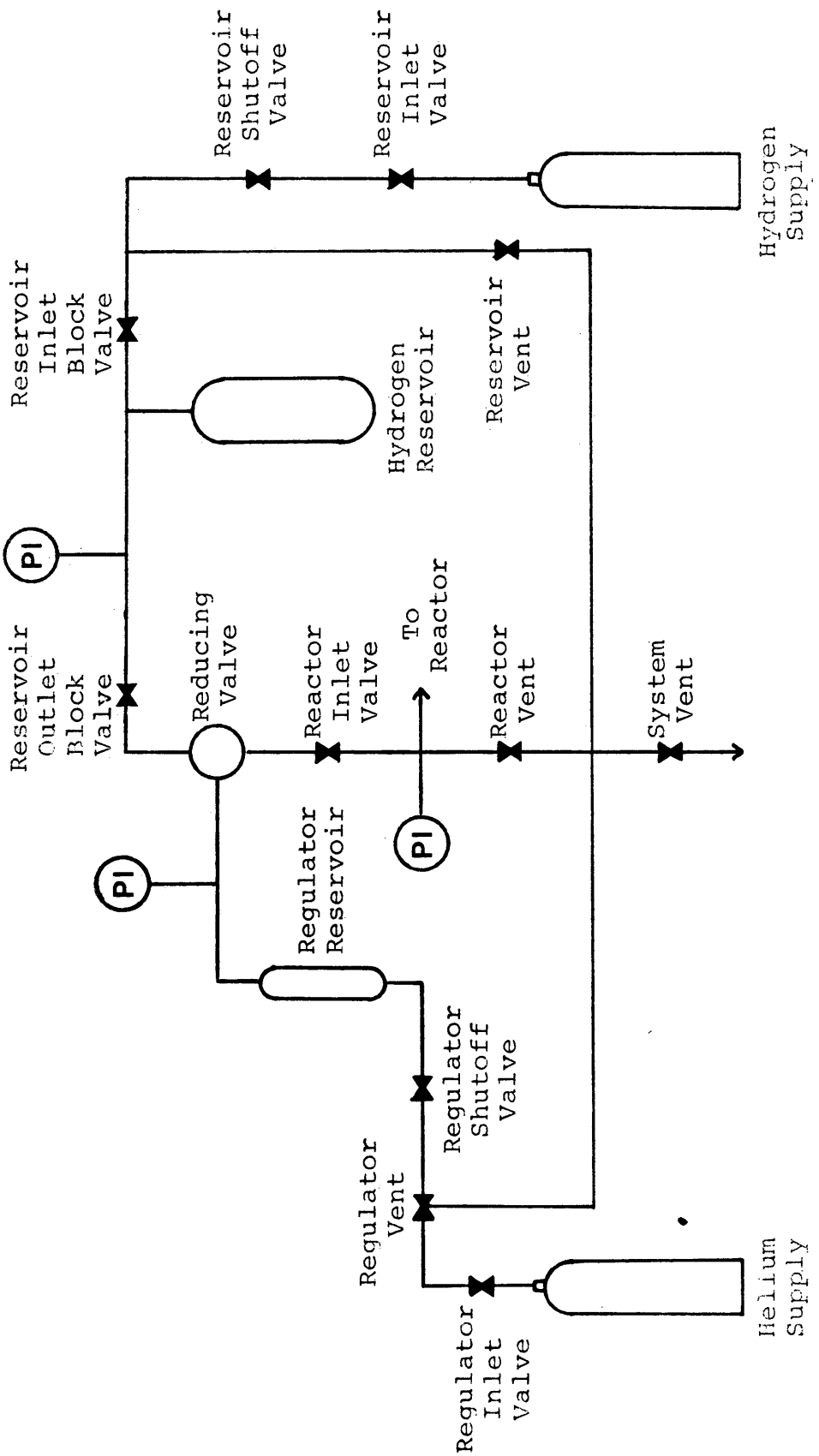


Figure 2. Gas Delivery System.

at 70°F. The tubing used for this system was of 2 types: 316 stainless steel, 1/4 inch o.d. tubing with a pressure rating of 12,000 psi was used for the vent lines and the lines between the gas cylinders and the inlet valves. All other tubing was 304 stainless steel, 1/4 inch o.d. with a pressure rating of 100,000 psi.

EXPERIMENTAL PROCEDURE

The following procedures are listed in the order in which they were performed (see Figure 3) All experimental runs were done in a random order.

Coal Preparation

Raw coal from the mine was pulverized in a ball mill and screened. All the coal which passed through a 200 mesh screen was saved. It was necessary to repeat this procedure a second and third time in order to have sufficient coal for runs 12-14 and 15-17 respectively.

Solvent Preparation

Solvent for each run was prepared ahead of time by vacuum distillation of anthracene oil. All material with a boiling point of less than 125^{o}C was discarded and the fraction with a boiling range of 125^{o}-250^{o}C was saved. The initial batches of solvent were distilled in 500 ml Hempel flasks but the latter batches were distilled in 2 liter flasks to save time. The absolute pressure during each distillation was 2-3 mm of mercury.

Slurry Preparation

Prior to each run a slurry was prepared by thoroughly mixing 50.0 grams of coal with 50.0 ml of solvent.

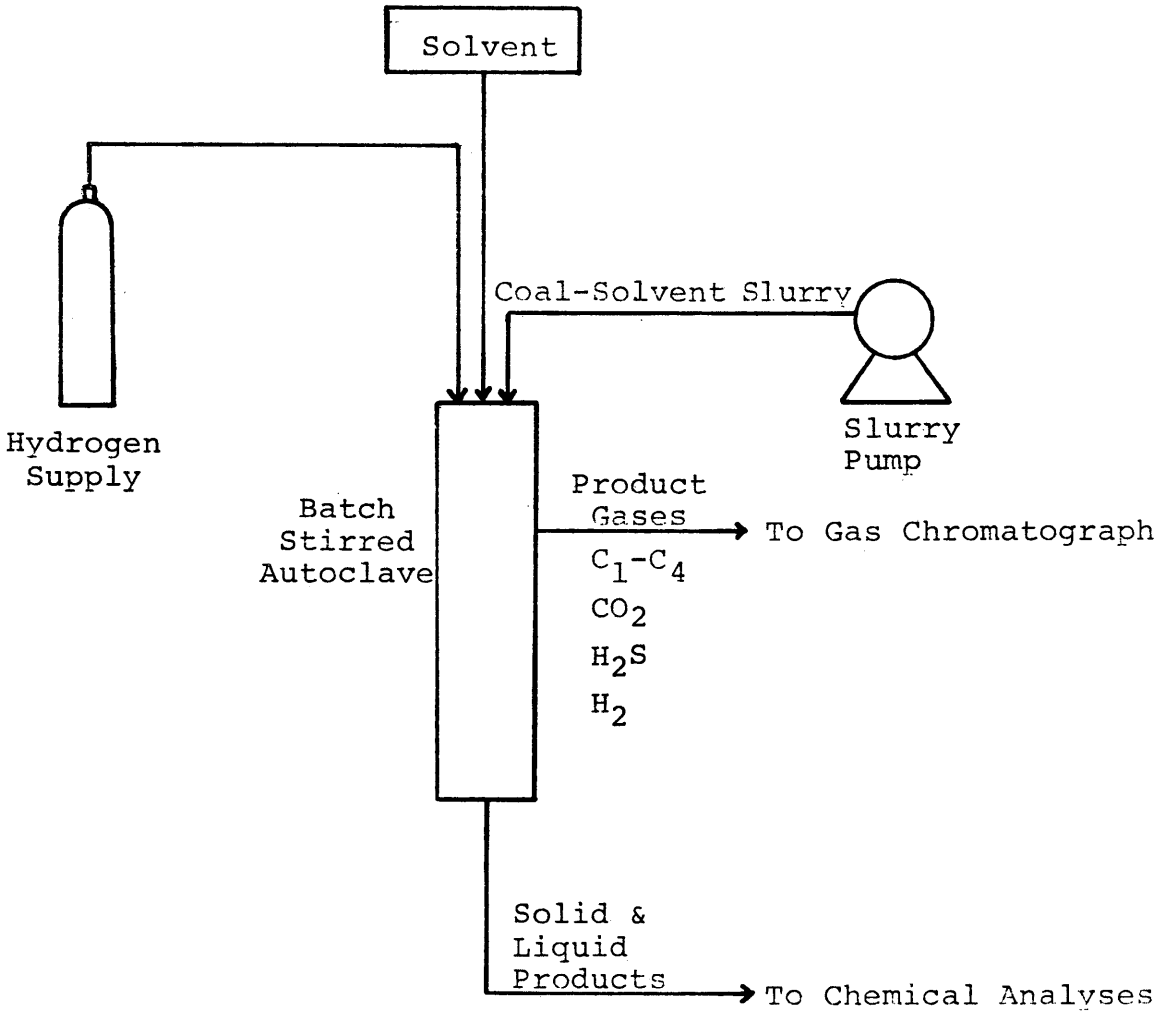


Figure 3. Simplified Process Flow Diagram, Hydrodesulfurization of Coal.

Processing

The procedure for each run is given below. All valves are closed unless otherwise noted.

1) The reactor assembly is weighed clean and empty.

2) 180 ml of solvent are added to the reactor and the cover is secured by applying 60 ft-lb of force to each cap screw.

3) The reactor assembly is reweighed.

4) The system is purged with helium as follows:

   a) The reactor is connected to the gas delivery system and the gas inlet valve on the reactor is opened.

   b) The regulator reservoir is filled to 1500 psig by adjusting the helium regulator and opening the regulator inlet and regulator shut off valves.

   c) The regulator inlet valve is closed and the regulator and reactor vents are opened slowly to allow the reactor pressure to increase to 500 psig.

   d) The regulator shut off and regulator vent valves are closed and the system vent is opened slowly to allow the reactor to return to atmospheric pressure. The reactor and system vents are then closed.

5) The reactor assembly is pressurized with hydrogen to the desired initial pressure as follows:

a) The hydrogen reservoir is filled to 1200 psig by adjusting the hydrogen regulator and opening the reservoir inlet, reservoir shut off, and reservoir inlet block valves. These three valves are then closed.

b) The reactor is filled with hydrogen to the desired initial pressure by slowly opening the reservoir outlet block valve and the reactor inlet valve. These two valves are then closed and the gas inlet valve on the reactor is also closed.

c) The pressure in the lines is relieved by slowly opening the reactor and system vents. These valves are then closed and the reactor is disconnected from the gas delivery system.

6) The reactor assembly is reweighed and reconnected to the gas delivery system.

7) The slurry pump is charged with fresh slurry and all air is bled from the pump. This procedure is given as follows:

a) The top valve on the pump is opened and the piston is moved forward until it will go no further.

b) The top valve is closed and the bottom valve is opened. The slurry is then injected by bringing the piston back to a setting of 145.

c) After the slurry has all been drawn into the pump the bottom valve is closed and the top valve is opened. Air is removed from the pump by moving the piston forward until slurry comes out.

d) The top valve is closed and the remaining air is removed from the top of the pump by removing the plug and bringing the piston forward until slurry appears in the opening. The plug is replaced using a fresh piece of Teflon tape.

8) The outlet line is connected to the pump and filled with slurry by bringing the piston slowly forward.

9) The outlet line is connected to the reactor and the outlet valve on the reactor is opened to equalize the pressure between the pump and the reactor.

10) The system pressure is brought back to the initial value by adding hydrogen as necessary. This is done by opening the gas inlet valve on the reactor and then slowly opening the reservoir outlet block valve and the reactor inlet valve. The latter two valves are then closed.

11) The water lines are connected to the cooling jacket on the stirring head and the water supply is opened.

12) The fan belt is connected between the motor and the stirring head and the motor is turned on.

13) The temperature controller is set at the desired temperature and the power is turned on.

14) The reactor is brought up to the reaction temperature and the pressure at this temperature is recorded.

15) Exactly 40 ml of slurry are injected into the reactor and the pressure and temperature are recorded.

16) The outlet valve on the reactor is closed.

17) The system is allowed to react for the specified length of time.

18) After the reaction is over the heating jacket is removed and a high speed blower is turned on to cool the reactor quickly.

19) When the temperature has dropped below 400^{o}F the stirring motor is turned off and the cooling water is stopped.

20) When the reactor is cool the pressure on the pump is reduced by moving the piston backward and the top valve on the pump is opened to the atmosphere.

21) The line between the pump and the reactor is disconnected and cleaned.

22) The reactor assembly is reweighed and carried to the gas analysis system.

23) After completion of the gas analysis the reactor is vented to atmospheric pressure and reweighed.

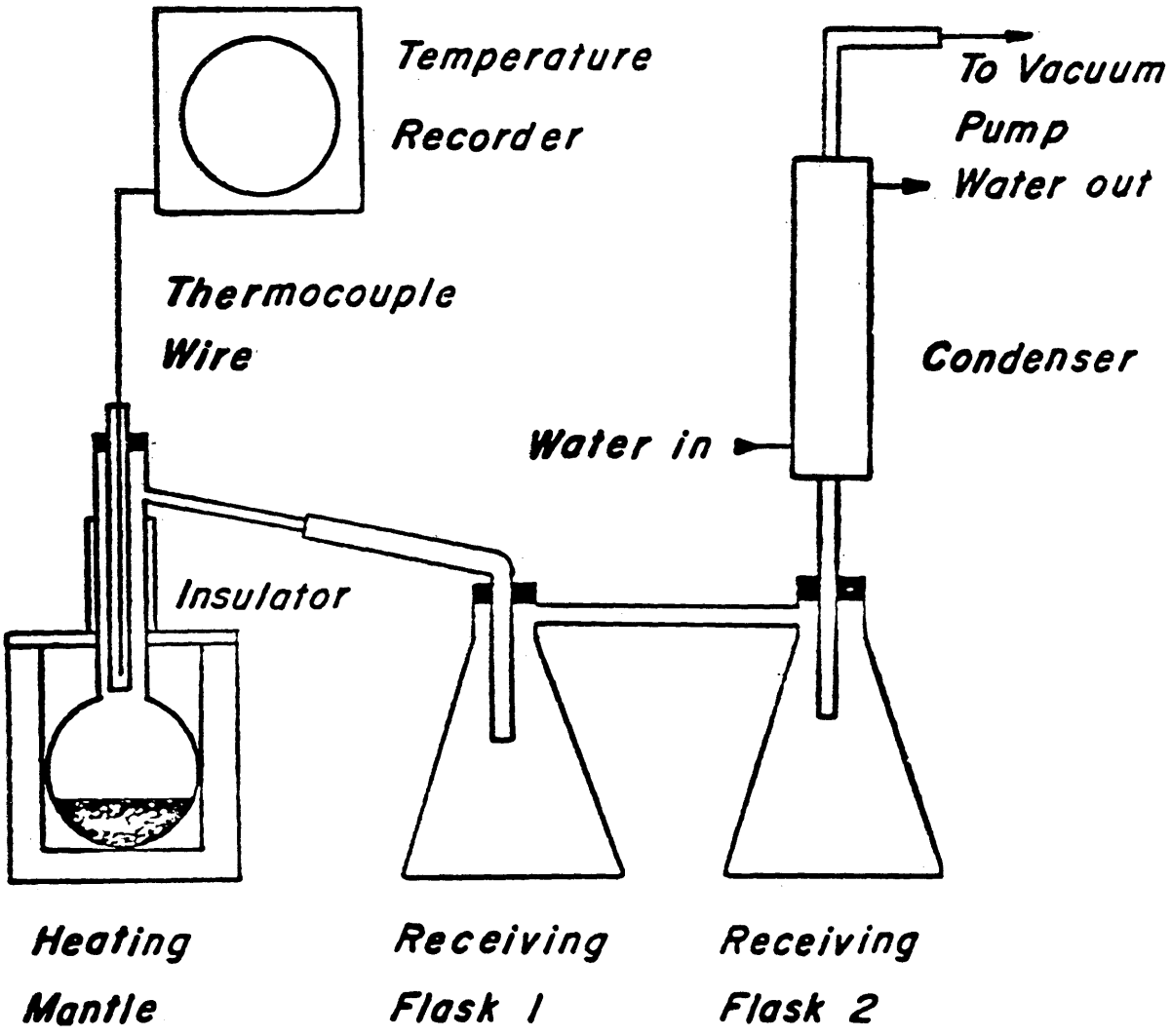
24) The liquid product is mixed well and poured from the reactor into a weighed distilling flask. The reactor is then cleaned with acetone and made ready for the next run.

Solvent Recovery

After each run it was necessary to separate the desulfurized coal from the solvent. This was done by means of a vacuum distillation. The apparatus used for this process is shown in Figure 4. The liquid product from each run was placed in a weighed distillation flask and the flask was then reweighed. The weight of the empty receiving flasks was also recorded. The distillation was carried out under a vacuum of 3 mm of mercury and a final temperature of 250°C. After the distillation the distilling flask and the receiving flasks were then reweighed and the weights of the desulfurized coal and the reclaimed solvent were determined by difference.

FIGURE 4

SOLVENT RECOVERY SYSTEM



ANALYTICAL PROCEDURES

The analytical methods used for analyzing the reaction products are given below. With the exception of the ultimate analyses of the raw coal all of the analyses were performed in the coal lab of the Colorado School of Mines Chemical and Petroleum-Refining Engineering Department. The ultimate analyses were done by the Colorado School of Mines Research Institute.

Total Sulfur Content of the Solid Product

The total sulfur content of the solid product was determined by the Eschka method as described by ASTM D271-68 (13). The following changes were made to Section 20(c):

1) Instead of digesting, heat gently with 100 ml of water for 1/2 hour.

2) After treating with bromine water, acidify the filtrate with 4 ml of 1:1 HCl.

3) The absence of bromine in the boiling solution is indicated by the color change of methyl orange to pink.

4) Use boiling water to accelerate the washing of excess chloride ions from the $BaSO_4$ precipitate.

5) Smoke off the filter paper below 500^{o}C for about 1 1/2 hour.

Total Sulfur Content of the Liquid Product

To analyze for the total sulfur content of the liquid product the Leco induction furnace technique, ASTM

D1552-64 (14) was used with the following changes:

1) Section 3(a) 1 -- Replace Figure 1, Combustion Tube, with Leco "L" Modification of the Combustion Tube assembly.

2) Section 7(a) -- Add 500-800 mg of solid sodium azide to the titration vessel to inhibit any interference of chlorine or nitrogen in the determination.

3) Section 8(a) -- Replace the entire section with the following procedure. Add approximately 0.15 g of chemically pure MgO to a sample crucible and weigh the crucible to 0.1 mg. Add approximately 50 mg of sample to the crucible and weigh to 0.1 mg. Add about 0.15 g more MgO to the crucible. Add about 2.3 g of low-sulfur iron accelerator to the geometric center of the crucible. Sprinkle about 0.6 g of tin accelerator on the mound of iron accelerator. Cover the crucible with a porous lid and place on the furnace pedestal.

4) Section 8(b) -- Add the following procedure: Combustion time, defined as the period during which plate current is greater than 350 ma, must be three to five minutes. When combustion is completed, add KIO_3 titrant until the reading on the millivolt meter of the titrator returns to its original position (10 mv)

The analysis system consisted of a purification train, an induction furnace and a semi-automatic titrator. The gas purifying train contained an acid tower, a dry reagent tower, and a rotameter, and was used to measure and scrub any residual sulfur from the entering oxygen. The induction furnace was a Leco model 521, equipped with the "L" modifica-

tion on the combustion chamber. A special feature of the "L" modification was the inclusion of a high temperature igniter in the combustion chamber. The exhaust gases from the induction furnace combustion chamber were sent through a glass delivery tube and into the Leco semi-automatic titrator model 518. The semi-automatic titrator used an idiometric reaction with a color change endpoint to analyze the combustion gases. This method proved to be both rapid and reliable for analyzing the liquid products for total sulfur. The reported accuracy of the test is ±0.01 weight percent sulfur.

Gas Analysis

The analysis of the reaction product gas was accomplished by gas chromatography. The gas chromatograph was fitted with an external valve oven, two eight-foot Porapak Q columns, and one six-foot molecular sieve column in a series by-pass arrangement. The columns were heated to 170°C. The chromatograph used helium carrier gas. A heated thermal conductivity detector was used.

The following components could be quantitatively determined:

1) H_2
2) CH_4
3) CO_2
4) C_2H_6
5) H_2S

6) C_3H_8

7) $i\text{-}C_4H_{10}$

8) $n\text{-}C_4H_{10}$

Calibration of the gas chromatograph was accomplished by determining an average response factor for pure components relative to carbon monoxide and an average retention time for each component was established. The results of this calibration procedure are given in Table 2.

Table 2

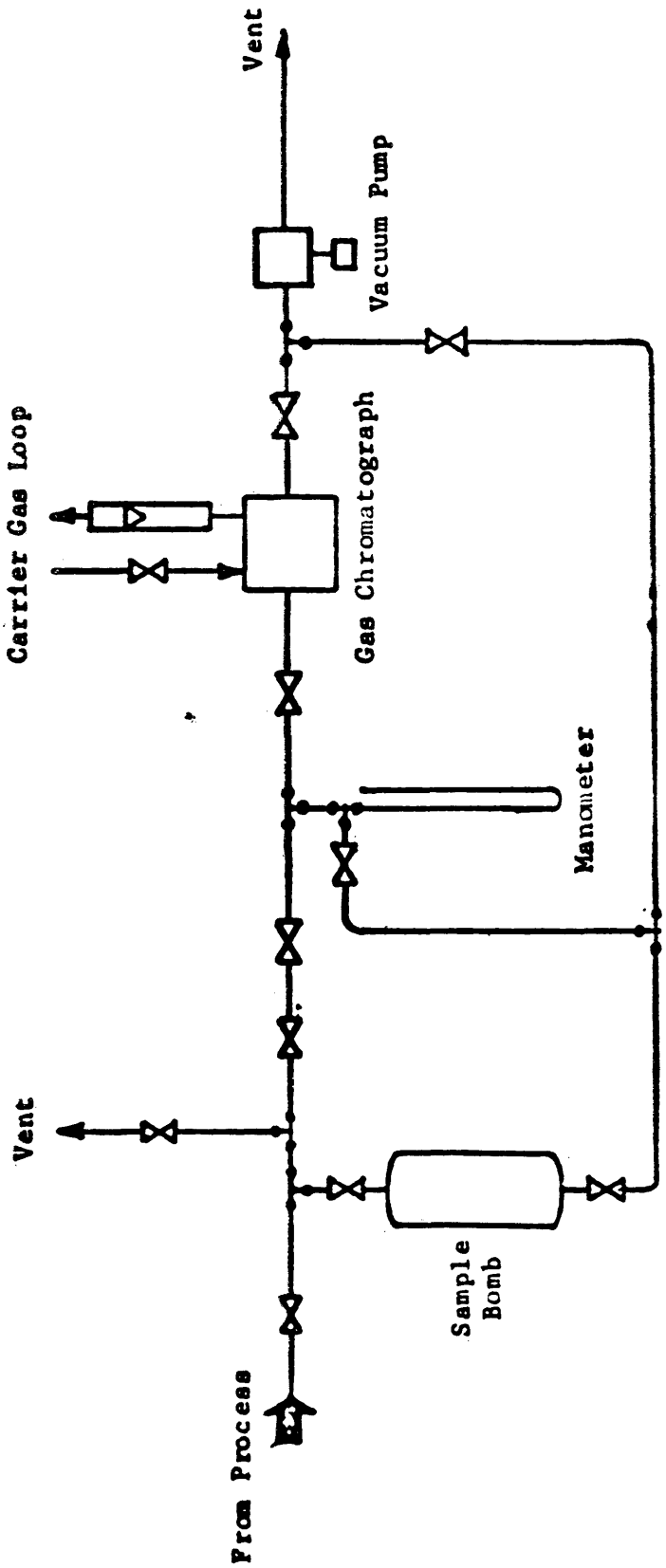
Chromatograph Calibration Results

Gas	Avg. Relative Response Factor
1) Hydrogen	16.3124
2) Methane	1.1628
3) Carbon Dioxide	0.7743
4) Ethane	0.8213
5) Hydrogen Sulfide	0.8201
6) Propane	0.5963
7) Iso-Butane	0.4962
8) Normal-Butane	0.4273

The procedure used to analyze the gaseous products is given as follows:

1) The weighed reactor assembly is attached to the gas analyzing system shown in Figure 5 by a short length of 1/4 in. stainless steel tubing.

FIGURE 5



Gas Sampling System, Gas Chromatograph

2) The total system is evacuated and the sample cylinder is filled by slowly opening the bleed valve on the reaction vessel.

3) The system pressure is brought to 20 psig by slowly opening the valve between the sample cylinder and the gas chromatograph.

4) A gas sample is injected into the gas chromatograph and the attenuation control is set at the proper level for each component.

RESULTS

The following section contains the results and a discussion of their significance.

The subjects contained in this section are listed below.

1) Run Conditions
2) Percent Desulfurization of the Coal
3) Correlation of the Data
4) Arrhenius Activation Energy
5) Reproducibility
6) Sulfur Balances
7) Error Analysis

Run Conditions

Table 3 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

The percent desulfurization of the coal for each run is shown in Table 4. A plot of these conversions for each temperature level as a function of time is given in Figure 6. Runs 12-14 and 15-17 are not included in this plot because they were performed using different samples of coal. Run 1 is also excluded because a significantly smaller volume of

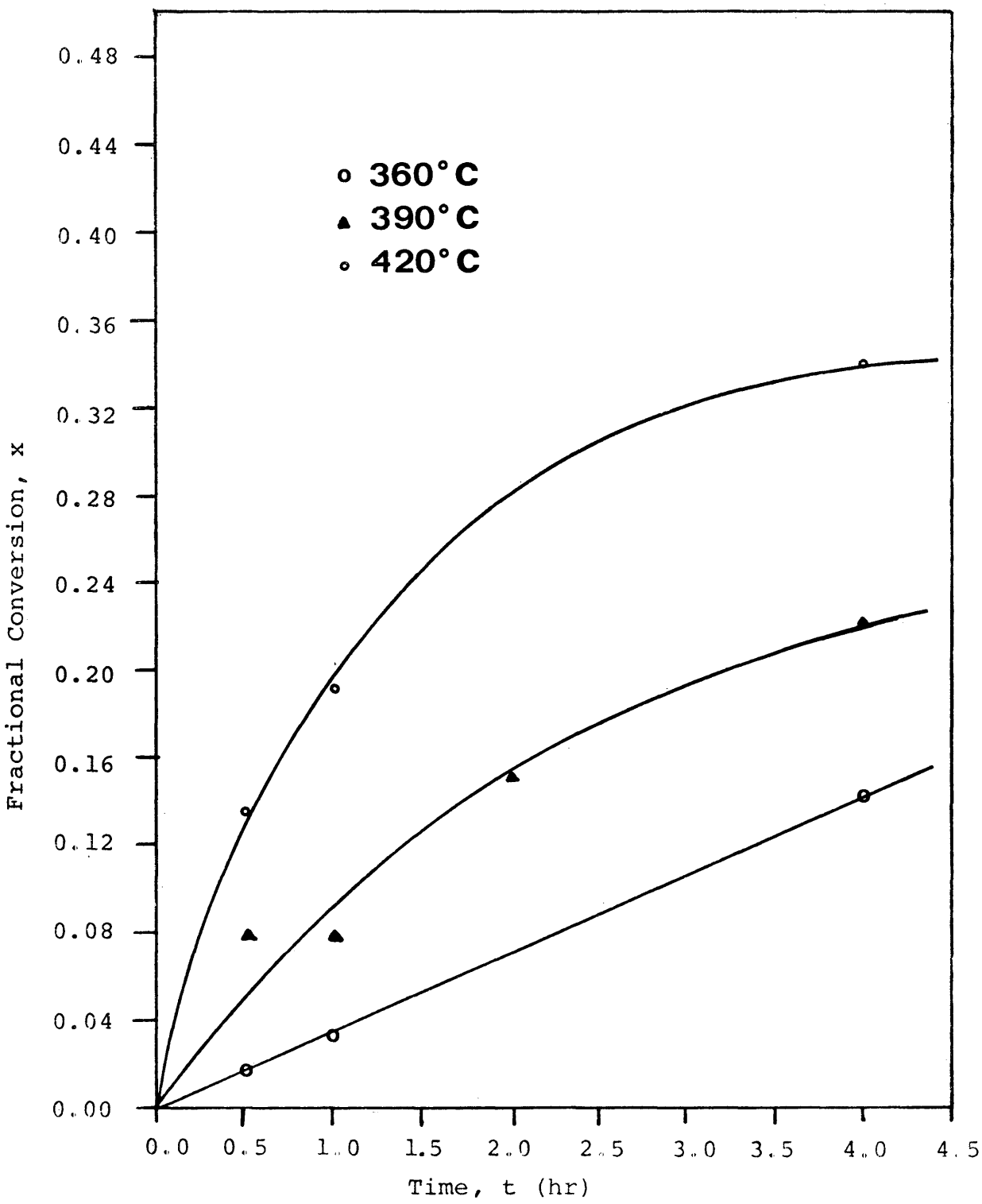


Figure 6. Fractional Conversion vs Time

Table 3

Run Conditions

Run No.	Reaction Temperature (°C)	Reaction Time (min)
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 4

Percent Desulfurization of the Coal

Run No.	Percent Desulfurization
1	12.50
2	13.49
3	19.08
4	3.29
5	22.04
6	1.64
7	15.13
8	14.14
9	7.89
10	7.89
11	33.88
12	28.32
13	37.28
14	41.91
15	19.42
16	21.26
17	20.21

slurry was injected. 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°C 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 n^{th}-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 $\frac{dx/dt}{1-x}$ vs x was then made (see Figure 7), 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 $C_1 = k_o$ and $C_2/C_1 = a$

then $$k = k_o (1-ax) \qquad (1)$$

The values of k_o and a were found by rearranging the coefficients of the best fit straight line to the form of

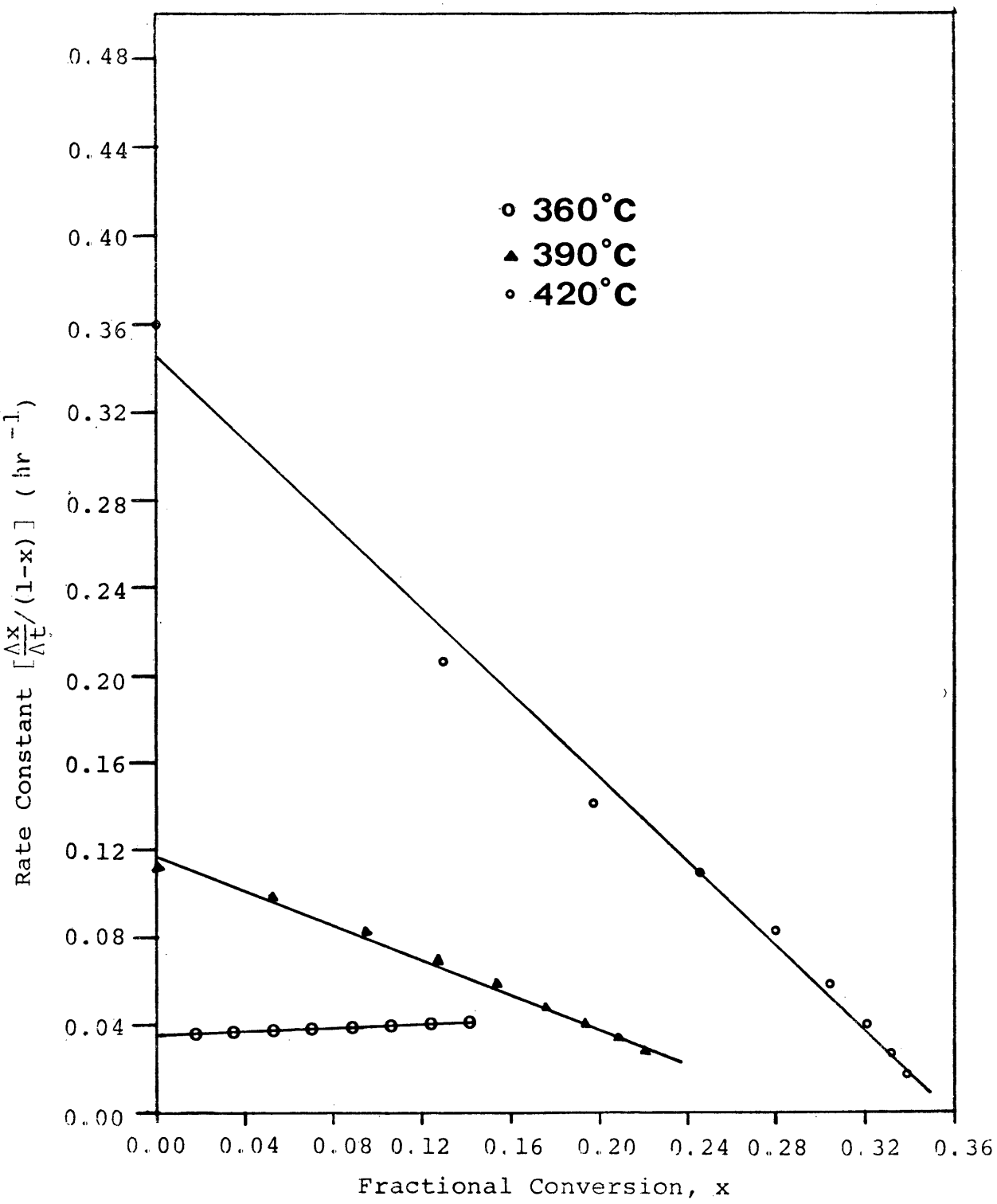


Figure 7. Rate Constant vs Fractional Conversion

equation (1).

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

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

where k_o is a pseudo second-order rate constant.

Separating the variables and integrating gives:

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

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

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

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

The values of k_o and a for this equation are listed in Table 5 as a function of temperature.

Table 5

Values for the Parameters k_o and a

Temperature (^oC)	k_o	a
360	0.03544	-1.165
390	0.1166	3.373
420	0.3454	2.787

Arrhenius Activation Energy

Based on the values of k_o given in Table 5 a plot of $\ln k_o$ vs $1/T$ was made to determine the Arrhenius energy of activation. This plot is shown in Figure 8. The linear

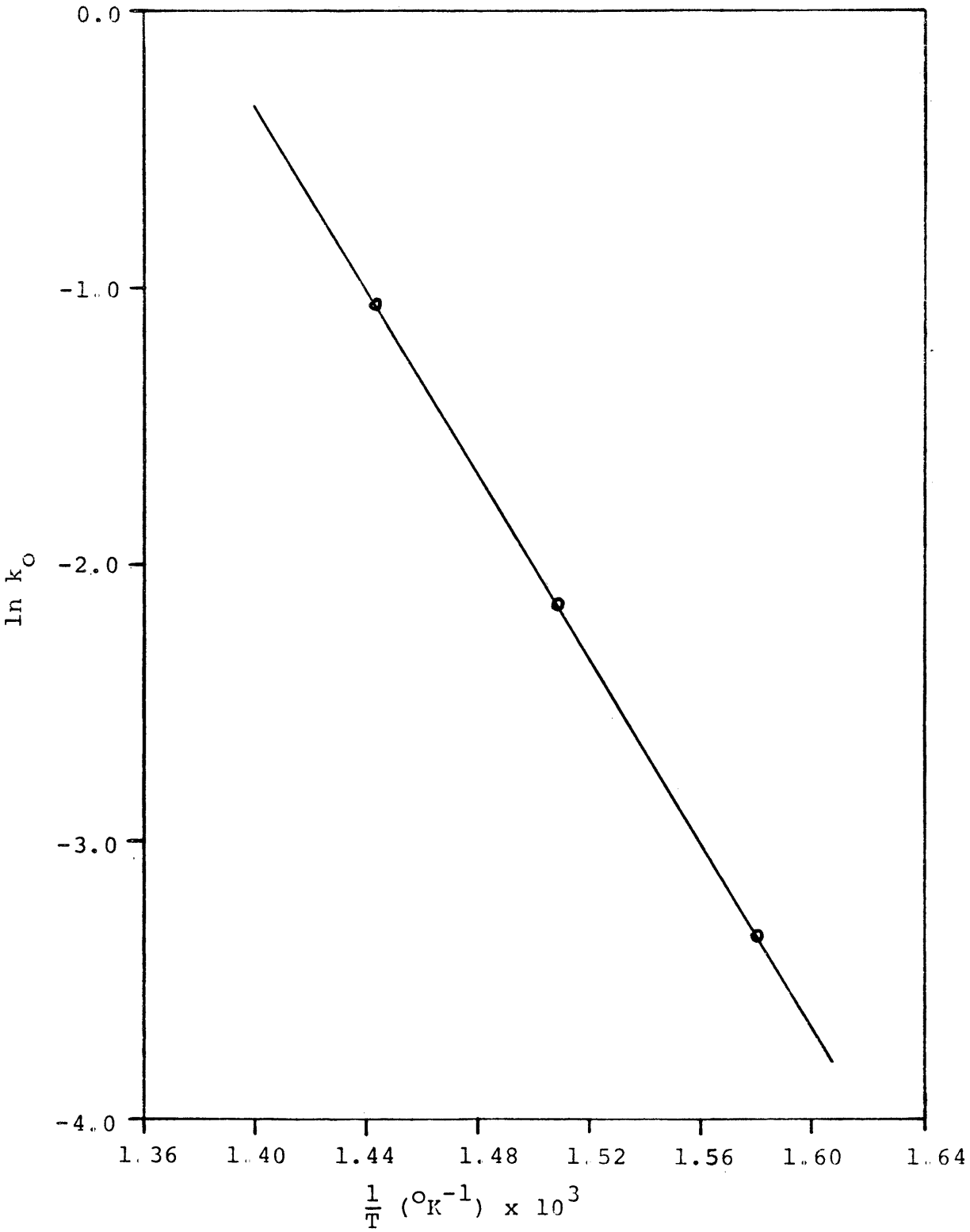


Figure 8. Arrhenius Plot.

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 6 along with the mean and standard deviation.

Table 6

Reproducibility Results

Run Number	Percent Desulfurization
15	19.42
16	21.26
17	20.21
Mean	20.30
Standard Deviation	0.92

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 7. The errors associated with these numbers represent errors arising from analytical techniques only and do not include experimental errors. Low recoveries indicate that a portion of the sulfur in the products is unaccounted for but do not in themselves give sufficient grounds for rejecting data since the data points are based strictly on the analyses of the coal and not on the analyses of the liquid and gas. Of the three analyses performed it was found that the reproducibility of the Eschka method was the best. For this reason discrepancies in the sulfur balances are most likely attributable to the analyses of the liquid and gas. Furthermore, a significant error exists in the estimation of the amount of dissolved hydrogen sulfide. The equation used for calculating this quantity was intended for use with heavy naphtha and its validity for use with coal-derived solvents is uncertain.

The Eschka results of Run 11, which had a low percent recovery, are shown on the next page.

Analysis Number	Weight Percent Sulfur
1	1.3
2	1.1
3	1.3
4	1.2

Table 7

Sulfur Balance Results

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

Error Analysis

In order to estimate the cumulative effect of analytical errors an error analysis was performed on each sulfur balance. These errors are given in Table 7 along with the percent recovery. The reported errors for the ASTM Leco method and the ASTM total sulfur method are ±0.01 weight percent and ±0.1 weight percent respectively. The error for the gas chromatograph was found to be ±5% by running several samples of the same gas and determining a mean value and a standard deviation. The error in the determination of the quantity of hydrogen sulfide dissolved in the liquid is an unknown error because the correlation was developed for use with heavy naphtha and not coal-derived solvents. The error was estimated to be ±20%. The actual development of the error analysis is given in Appendix A.

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

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

where k_o and a are constants.

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

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

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.

RECOMMENDATIONS FOR FURTHER STUDY

In order to gain a better insight into the kinetics of the removal of sulfur from coal it would be helpful to study the removal of the various sulfur forms. Knowing the kinetics for the removal of each form would provide a basis for predicting the ease of desulfurization for an unknown coal. Another area that would merit further study is determining whether or not the model developed here would apply in a system using carbon monoxide and water instead of hydrogen. Also the effect of pressure could be studied and an economic analysis could be made to determine the optimum conditions for operation. Other possibilities for further study would include determining the effect of changes in the solvent type, the coal type, and the solvent-to-coal ratio.

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APPENDIX A

SAMPLE CALCULATIONS

Note: All sample calculations are for Run 1 unless specified otherwise

(1) Reaction Gas Compositions

Component	(1)	(2)	(3)	(4)	(5)
H_2	9991.34	58.85	2.016	118.64	12.42
CH_4	5488.42	32.33	16.043	518.67	54.29
CO_2	439.80	2.59	44.010	113.99	11.93
C_2H_6	808.16	4.76	30.070	143.13	14.98
H_2S	85.50	0.50	34.080	17.04	1.78
C_3H_8	151.46	0.89	44.097	39.25	4.11
$i\text{-}C_4H_{10}$	3.60	0.02	58.124	1.16	0.12
$n\text{-}C_4H_{10}$	10.26	0.06	58.124	3.49	0.37
Sum	16978.54	100.00		955.37	100.00

(1) Product of attenuation, peak area, and response factor for each component
(2) Mole percent of each component
(3) Mole weight of each component
(4) Product of columns (2) and (3)
(5) Weight percent of each component

(2) Weight of Sulfur in Reaction Gas

$$\text{Wt of sulfur} = \text{wt of gas} \times \text{wt \% } H_2S \times \frac{32}{34}$$

$$= 1.404 \times .0178 \times \frac{32}{34}$$

$$= .024 \text{ g S}$$

(3) Sulfur Content of the Product Coal

Since several grams of solvent often remained in the solid products after distillation it was necessary to calculate the sulfur content of the product coal on a solvent free basis. The correction was made by using this expression

$$\%S \text{ in coal} = \frac{(\%S \text{ in solid} \times \text{wt of solid}) - (\%S \text{ in liquid} \times \text{wt of liquid})}{\text{wt of coal}}$$

where:

$$\text{wt of coal} = \text{wt of slurry} \times 0.4793 \times \left(\frac{\text{wt 1}}{\text{wt 2}}\right)$$

$$\text{wt of solvent} = \text{wt of solid} - \text{wt of coal}$$

wt 1 = wt of combined solid and liquid products after distillation

wt 2 = wt of solid and liquid products before being transferred from the reactor.

The number 0.4793 represents the weight fraction of coal in the slurry as determined by accurately weighing 25 grams of coal and 25 ml of solvent.

$$\text{wt of coal} = 34.425 \times .4793 \times \frac{215.5}{233.263} = 15.24 \text{ g}$$

$$\text{wt of solvent} = 29.7 - 15.24 = 14.46 \text{ g}$$

$$\%S \text{ in coal} = \frac{1.544(29.7) - 0.3668(14.46)}{15.24} = 2.66$$

(4) Percent Desulfurization of the Coal

The percent desulfurization of the coal in each case was calculated as follows:

$$\% \text{ Desulfurization} = \frac{\%S \text{ in raw coal} - \%S \text{ in product coal}}{\%S \text{ in raw coal}}$$

$$= \frac{3.04 - 2.66}{3.04}$$

$$= 0.125 = 12.5\%$$

(5) Percent Recovery of Sulfur

For each run a sulfur balance was made to determine the percent recovery of sulfur.

Sulfur In

Wt of S in coal = wt of slurry x 0.4793 x wt fraction of S in coal.

Wt of S in solvent = [Wt of solvent + (wt of slurry x 0.5207)] x wt fraction of S in solvent.

Sulfur Out

Wt of S in solid product = wt of solid product x $(\frac{\text{wt 1}}{\text{wt 2}})$ x wt fraction of S in solid product.

Wt of S in liquid product = wt of liquid product x $(\frac{\text{wt 1}}{\text{wt 2}})$ x wt fraction of S in liquid product.

Wt of S in gases.

Wt of S in dissolved H_2S where

wt 1 = wt of liquid + solid products before being transferred from the reactor

wt 2 = wt of combined liquid and solid products after distillation.

The numbers 0.4793 and 0.5207 represent the weight fractions, in the slurry, of the coal and the solvent respectively.

The weight of sulfur dissolved in the solvent as H_2S was approximated using the following method described by Frolich, et al. (18):

$$y = 5.5\ x$$

where y = volume of gas at 25°C, 1 atm, per volume of liquid

and x = absolute pressure in atmospheres.

Sulfur In

Wt of S in coal = 34.425 x 0.4793 x .0304 = 0.502

Wt of S in solvent = [198.52+(34.425x0.5207)]x.00426 = 0.922

Total 1.424

Sulfur Out

Wt of S in solid product = $29.7 \times (\frac{233.263}{215.5}) \times 0.01544$ = 0.496

Wt of S in liquid product = $185.8 \times (\frac{233.263}{215.5}) \times 0.003668$ = 0.738

Wt of S in gases = 0.024

Wt of S in dissolved H_2S = 0.035

Total 1.293

$$\% \text{ Recovery of S} = \frac{\text{Sulfur Out}}{\text{Sulfur In}} \times 100$$

$$= \frac{1.293}{1.424} \times 100$$

$$= 91\%.$$

(6) Method of Equal Area Graphical Differentiation

The method of equal area graphical differentiation discussed by Fogler (17) was used to evaluate dx/dt from the plots given in Figure 6. Figure 9 shows the graph that was used to calculate dx/dt at 390°C. The numbers associated with this method are given on the next page.

(7) Error Analysis

Based on the errors associated with each analytical method the total error was calculated as follows.

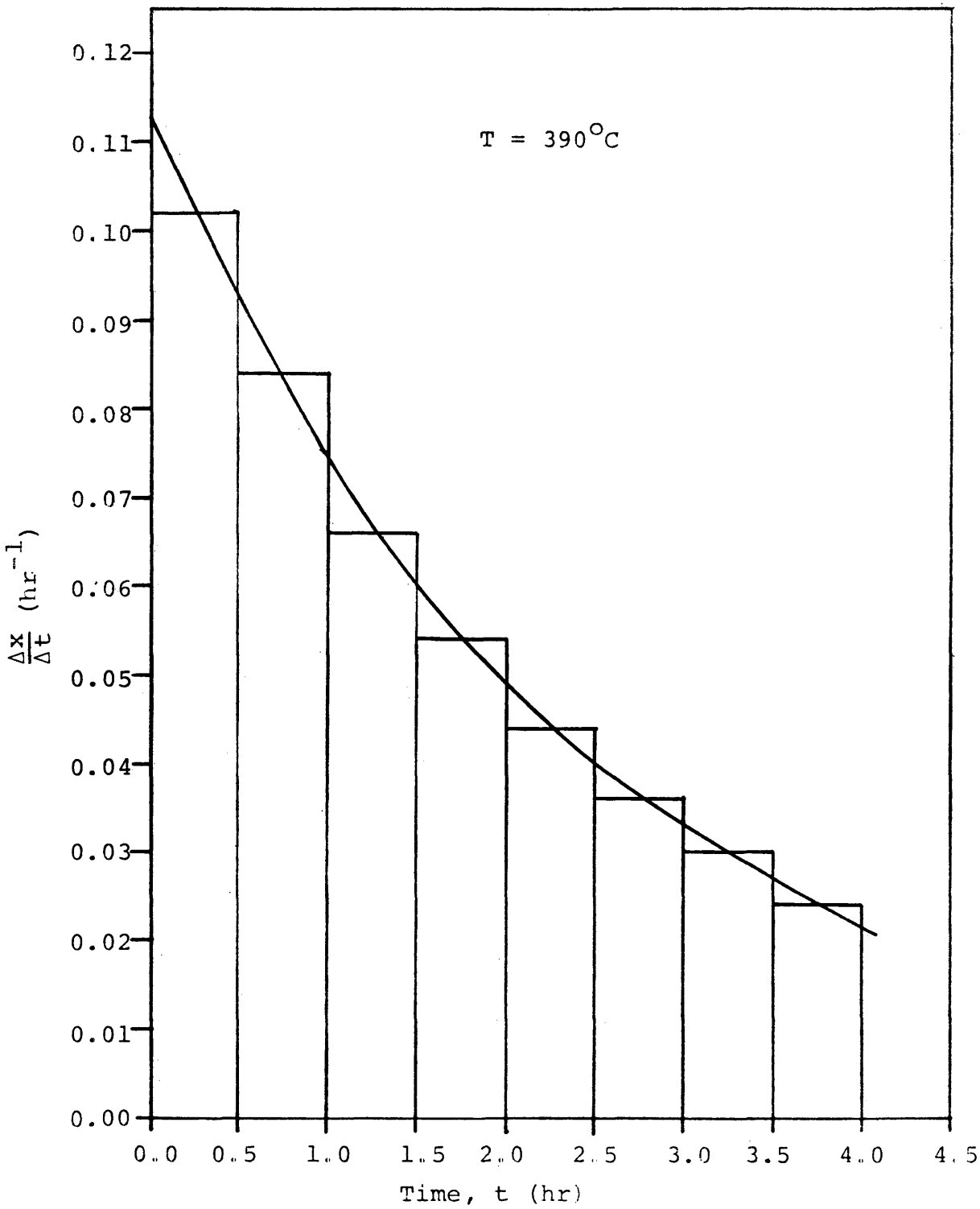

Figure 9. Method of Equal Area Differentiation.

t	x	$\frac{\Delta x}{\Delta t}$	$\frac{dx}{dt}$	$\frac{dx}{dt}/(1-x)$
0.0	0	-	0.113	0.113
0.5	0.051	0.102	0.093	0.098
1.0	0.093	0.084	0.074	0.082
1.5	0.126	0.066	0.060	0.069
2.0	0.153	0.054	0.049	0.058
2.5	0.175	0.044	0.040	0.048
3.0	0.193	0.036	0.033	0.041
3.5	0.208	0.030	0.027	0.034
4.0	0.220	0.024	0.021	0.027

Let X = the total Sulfur In (as calculated in (5) of Appendix A)

ΔX = the error associated with X

= [wt of slurry x .4793 x .001]

+ [wt of solvent + (wt of slurry x .5207)] x .0001

Y = the total Sulfur Out (as calculated in (5) of Appendix A)

ΔY = the error associated with Y

= [wt of solid product x $(\frac{\text{wt 1}}{\text{wt 2}})$ x .001]

+ [wt of liquid product x $(\frac{\text{wt 1}}{\text{wt 2}})$ x .0001]

+ [wt of S in gases] x .05

+ [wt of S in dissolved H_2S] x .20

where wt 1 = wt of liquid + solid products before being transferred from the reactor

wt 2 = wt of combined liquid and solid products after distillation.

The fractional recovery of sulfur is given by

$$Z = \frac{Y}{X}$$

and the error associated with Z can be approximated by

$$\Delta Z = \frac{Y}{X^2} \Delta X + \frac{1}{X} \Delta Y.$$

X = 1.424 (as given in (5) of Appendix A)

ΔX = (34.425 x .4793 x .001) + (198.52 + (34.425 x 5207)) x .0001 = .0381

$$Y = 1.293 \text{ (as given in (5) of Appendix A)}$$

$$\Delta Y = \left(29.7 \times \left(\frac{233.263}{215.5}\right) \times .001\right) + \left(185.8 \times \left(\frac{233.263}{215.5}\right) \times .0001\right) + (.024) \times .05 + (.035) \times .20 = .0605$$

$$\Delta Z = \frac{1.293}{(1.424)^2} \times (.0381) + \frac{1}{1.424} \times (.0605) = .07 = 7\%.$$

APPENDIX B

RAW DATA

Table 8

Reaction Gas Compositions

Component Mole Percent

Run No.	H_2	C_1	CO_2	C_2	H_2S	C_3	i-C_4	n-C_4
1	58.84	32.33	2.59	4.76	0.50	0.89	0.02	0.06
2	90.02	6.68	1.37	1.22	0.22	0.41	0.06	0.02
3	74.77	18.14	2.49	3.20	0.50	0.82	0.02	0.04
4	97.27	1.13	1.10	0.22	0.20	0.07	0.00	0.00
5	69.54	20.84	3.70	3.93	0.73	1.19	0.03	0.05
6	98.63	0.37	0.77	0.07	0.13	0.03	0.00	0.00
7	80.12	13.87	3.01	1.99	0.47	0.50	0.01	0.03
8	88.25	6.00	2.83	1.61	0.81	0.47	0.01	0.03
9	95.20	2.70	1.28	0.45	0.23	0.15	0.00	0.00
10	92.71	4.68	1.39	0.78	0.23	0.19	0.01	0.01
11	58.59	32.50	2.40	5.05	0.38	0.95	0.05	0.08
12	97.44	1.30	0.81	0.26	0.12	0.07	0.00	0.00
13	93.81	4.00	1.16	0.69	0.19	0.15	0.01	0.01
14	68.28	23.89	2.74	3.73	0.52	0.74	0.04	0.08
15	99.18	0.24	0.46	0.05	0.06	0.02	0.00	0.00
16	99.06	0.25	0.54	0.06	0.08	0.02	0.00	0.00
17	99.18	0.24	0.46	0.05	0.06	0.02	0.00	0.00

Table 9

Reaction Gas Compositions

Component Weight Percent

Run No.	H_2	C_1	CO_2	C_2	H_2S	C_3	i-C_4	n-C_4
1	12.41	54.29	11.93	14.98	1.78	4.11	0.12	0.37
2	43.64	25.77	14.50	8.82	1.80	4.35	0.84	0.28
3	21.40	41.32	15.56	13.66	2.42	5.13	0.17	0.33
4	66.95	6.19	15.03	2.26	2.33	1.05	0.00	0.00
5	16.79	40.06	19.51	14.16	2.97	6.29	0.21	0.35
6	80.66	2.41	13.75	0.85	1.80	0.54	0.00	0.00
7	26.19	36.08	21.48	9.70	2.60	3.58	0.09	0.28
8	35.78	19.37	25.02	9.72	5.59	4.13	0.10	0.30
9	59.99	13.54	17.61	4.23	2.45	2.07	0.05	0.05
10	51.39	20.65	16.82	6.45	2.16	2.30	0.10	0.13
11	12.31	54.33	11.02	15.84	1.36	4.36	0.29	0.50
12	73.28	7.78	13.37	2.89	1.56	1.12	0.00	0.00
13	55.86	18.95	15.04	6.14	1.86	1.89	0.12	0.14
14	16.98	47.28	14.87	13.84	2.17	4.03	0.29	0.54
15	87.56	1.65	8.87	0.63	0.93	0.37	0.00	0.00
16	85.83	1.70	10.23	0.72	1.11	0.40	0.00	0.00
17	87.71	1.68	8.79	0.62	0.85	0.35	0.00	0.00

Table 10

Total Sulfur Analysis on Solvent and Liquid Product

Run No.	Weight Percent Sulfur*
Solvent (Runs 1-14)	0.43 ± .01
1	0.37 ± .01
2	0.38 ± .01
3	0.42 ± .01
4	0.40 ± .01
5	0.35 ± .01
6	0.40 ± .01
7	0.41 ± .01
8	0.42 ± .01
9	0.43 ± .01
10	0.39 ± .01
11	0.35 ± .01
12	0.37 ± .01
13	0.40 ± .01
14	0.36 ± .01
Solvent (Runs 15-17)	0.42 ± .01
15	0.43 ± .01
16	0.43 ± .01
17	0.42 ± .01

*The values listed are an average of two readings and are multiplied by the furnace constant.

Table 11

Total Sulfur Analysis on Solid Product and Raw Coal

Run No.	Weight Percent Sulfur
1	1.5 ± .1
2	2.3 ± .1
3	2.0 ± .1
4	2.1 ± .1
5	1.8 ± .1
6	2.7 ± .1
7	1.9 ± .1
8	2.4 ± .1
9	2.0 ± .1
10	2.1 ± .1
11	1.2 ± .1
Raw Coal (Runs 12-14)	3.3 ± .1
12	2.4 ± .1
13	1.8 ± .1
14	1.1 ± .1
Raw Coal (Runs 15-17)	3.7 ± .1
15	2.8 ± .1
16	3.0 ± .1
17	3.0 ± .1

Table 12

Weights of Products and Reactants

Run No.	Wt. of Solvent	Wt. of H_2	Wt. of Slurry	Wt. of Product Gases	Wt. of Liquid & Solid Products
1	198.520	0.318	34.425	1.404	233.263
2	198.835	0.402	48.342	0.788	246.791
3	200.325	0.450	44.970	1.040	244.705
4	199.795	0.566	49.949	0.457	249.853
5	199.559	0.496	48.034	1.090	246.999
6	199.082	0.462	49.435	0.494	248.485
7	200.481	0.440	50.854	0.660	251.115
8	199.153	0.449	49.587	0.429	248.760
9	200.526	0.434	50.418	0.530	250.848
10	198.918	0.452	48.713	0.539	247.544
11	200.214	0.507	48.068	2.779	246.010
12	200.701	0.465	48.992	0.428	249.730
13	200.128	0.472	48.380	0.578	248.402
14	200.105	0.420	47.762	1.742	246.545
15	199.991	0.404	48.134	0.518	248.011
16	200.973	0.501	47.915	0.538	248.851
17	201.590	0.441	47.045	0.509	248.567

Note: All weights are in grams.

Table 13

Weights of Distilled Products

Run No.	Wt. of Solid Product	Wt. of Liquid Product
1	29.7	185.8
2	23.7	196.7
3	26.7	203.3
4	33.0	198.4
5	28.7	198.6
6	25.1	206.5
7	32.7	203.2
8	25.3	209.4
9	34.3	205.0
10	31.3	204.9
11	40.1	180.7
12	23.3	214.9
13	30.9	205.1
14	43.1	190.9
15	24.4	214.4
16	21.6	216.2
17	20.4	217.4

Note: All weights are in grams