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THE EFFECTS OF PROCESS VARIABLES ON COAL CHAR  
DESULFURIZATION USING THE SOLVENT REFINING PROCESS

by

Richard J Long

1974

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Chemical and Petroleum-Refining Engineering.

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ABSTRACT

The purpose of this investigation was to determine which, if any, of the following process variables had a significant effect on the desulfurization of coal char by solvent treatment in the presence of hydrogen:

- 1) reaction temperature (T)
- 2) hydrogen partial pressure (P)
- 3) solvent-to-char ratio (SCR), and
- 4) solvent type (ST).

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The process under consideration consisted of reacting a char-solvent slurry with hydrogen at elevated temperatures and pressures in a batch autoclave rocking bomb reactor. Vacuum distillation was used to recover the solvent from the treated char product. Analyses for total sulfur content, organic sulfur content, inorganic sulfur content (sulfate and pyritic), sulfur content of the solvent, hydrogen content of the solvent, and heating value of the treated char were made on the various samples. A  $2^4$  full factorial, doubly replicated experimental design plus 4 supplemental high temperature runs required a total of 36 experimental runs.

Pressure, temperature, and solvent-to-char ratio were very highly significant variables (99.9% confidence level) for the desulfurization of char in the process. A combination of high pressure, high temperature, high solvent-to-

char ratio, and anthracene oil solvent allowed a maximum of 38 percent desulfurization of the char. Anthracene oil was found to be a better solvent than tetralin, but the char was only partially soluble in the anthracene oil solvent. The heating value of the treated char was up to 10 percent greater than that of the original char.

A multiple linear regression technique was used to formulate the following empirical mathematical model of residual total sulfur content of the char in this process:

$$S_{TOT} = 4.901 - 0.003 T - 0.0003 P - 0.097 SCR$$

where  $S_{TOT}$  = total residual sulfur content

$T$  = reaction temperature, °C

$P$  = hydrogen partial pressure, psig

$SCR$  = anthracene-to-char ratio.

The mathematical model is equilibrium limited, since a batch reactor was used, and does not represent maximum desulfurization. Also, the model should not be used outside of the range of process variables investigated in this study.

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DEDICATION

This thesis is dedicated to my wife, Mia, whose love, encouragement, and support throughout this period has made this effort possible, and to my parents, Alexander and Regina, who provided the initial guidance, means, and incentive for my education.

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INTRODUCTION COLORADO SCHOOL OF MINES  
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A significant number of processes for converting coal to synthetic fuels produce coal char as a by-product or co-product. These chars have been looked upon as a fuel source for the generation of electric power in conventional power plants. The chars can also be used in further processing to produce synthetic natural gas (SNG) or low-Btu gases. Other important uses of coal char include: a reductant in metallurgical processes, a blend component for coking coals, a raw material for making carbonized briquettes and activated carbon, or a carbonaceous filter aid.

The current and emerging air quality standards, as set by the Environmental Protection Agency and adopted by the metropolitan areas of the United States, set very low levels for permissible emissions of sulfur oxide gaseous pollutants. The Clean Air Act Amendments of 1970 provided for the establishment of national ambient air quality standards, and set a target date of July 1, 1975 for their implementation by the states. The national sulfur oxide standards set a limit of 0.03 ppm for an annual arithmetic mean concentration with an allowable 24 hour maximum of 0.14 ppm, not to be exceeded more than once per year. This means that the utilization of chars with sulfur contents greater than one percent will be essentially prohibited by law in the larger

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urban centers. Metropolitan areas faced with the problem of fueling char-fired power plants as well as satisfying air quality standards will limit the sulfur content of the chars used. Low sulfur coal reserves (1 percent or less total sulfur), from which the char is derived, are generally found in areas where production is costly or not environmentally feasible. To prevent this potential pollution problem, either coal or the product char will have to be desulfurized or the oxides of sulfur will have to be removed from the flue gases, or a combination of all approaches will be necessary. Efforts to secure pollution abatement from all approaches are underway.

One method of reducing the total sulfur content of coal has been studied at the Colorado School of Mines. The technique under investigation was coal desulfurization by solvent refining in the presence of hydrogen. This research was designed to determine how the solvent refining process affects the coal char sulfur content and heating value, and the change in hydrogen content of the solvent. The experimental data for the analysis were obtained by a full-factorial experimental design for 4 operating variables, each investigated at 2 levels. The process variables studied were temperature, hydrogen partial pressure, solvent-type, and solvent-to-char ratio. Statistical means were used to reduce the data and to examine the significance of



the operating variables.

This study was part of Phase 2 of a research contract granted by the Office of Coal Research of the United States Department of the Interior (1), and was patterned after previous coal desulfurization research at CSM (1,2,3,4,5)

## LITERATURE SURVEY

### Formation of Coal Char

Char is the carbonaceous solid product derived from the low-temperature ( $900^{\circ}$  to  $1200^{\circ}$ F) devolatilization and carbonization of coal (6). Char contains 60 to 80 percent of the original coal and has characteristics making it, in certain respects, superior to the original coal for use as a boiler fuel or for power generation. Char may actually be higher in heating value than the original coal, particularly if wet, lower-rank coals are used. If dryer high-rank coals are used, the char will generally be lower in heating value than the original coal.

The mineral matter (ash) in coal is almost completely retained as mineral matter in char. Bowling and Waters (7) reported coals of 20 to 50 percent volatile matter changing to 14 to 21 percent and 10 to 13 percent volatile matter in the chars formed at  $500^{\circ}$ C and  $600^{\circ}$ C, respectively

A number of processes have been studied to derive char from raw coal. The Char Oil Energy Development (COED) process (8,9,10), developed by the FMC Corp., pyrolyzes coal in a multistage, fluidized-bed to yield a synthetic crude oil, a char, and a gaseous product. When using an Illinois No. 6 seam coal, this process reduced the sulfur content from more than 3 wt percent in the coal to as low as 0.3 wt

percent in the char (11). The University of Utah (12) has studied the one-step hydrogenation of coal to synthetic crude oil, solid char fuel, and fuel gases. Fields and Wyse (13) have simultaneously carbonized and desulfurized coal into char in a non-catalytic process. Using a cyclone reactor, the reaction temperature can be varied to 816°F under a gas blanket of 21 atm or less and containing 20 percent or more hydrogen. A coal with 1.9 percent original total sulfur content heated to 621°F under 34 mole percent hydrogen at 6.7 atm of total pressure formed a char of 59 percent of the original coal mass and had a 0.64 percent sulfur content. Curran et al. (14,15) have studied a 2-stage combustion, CO<sub>2</sub> acceptor process to produce a low-sulfur boiler fuel, a low-sulfur char, and a low-sulfur gas.

#### Processing of Coal Char into Synthetic Fuels

In recent years a number of pilot scale operations have been developed to process coal char into synthetic fuels. The gasification of coal char with steam in electrofluid reactors has been carried out at the Institute of Gas Technology (16,17) and at the Iowa State University (12,18, 19,20,21). The reactors at Iowa State University have operated over a temperature range of 1500° to 1900°F at atmospheric pressure, while the reactors at the Institute of Gas Technology have operated over a similar temperature range,

but at pressures up to 1000 psig. The product gas was used as feed gas for the HYGAS conversion of coal to pipeline gas (12,22)

Singh (23) has patented a low-sulfur fuel system utilizing coal char and petroleum coke. Granular coal is devolatilized at 150 psig and the reaction by-products are separated from the char. Preheated oil is coked at 150 psig and the reaction products are separately withdrawn. The char from the coal devolatilization and coke from the oil fluid-coker are passed into a heat generator, where partial burning with air occurs. The by-products are separately processed to recover sulfur and fuel gases.

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#### Desulfurization by Other Methods

Many processes are under study for the removal of sulfur from coal and may be analogous to the desulfurization of coal char. Sinha and Walker (24) have studied sulfur removal from coal by air oxidation at temperatures from 350° to 450°C. The efficiency of sulfur removal is controlled by diffusion of oxygen into coal and its pyrite. The rate of sulfur removal increased with increasing temperatures but was unaffected by the SO<sub>2</sub> concentration buildup in the air stream up to 10 percent. Desulfurization of coal was studied by Batelle Memorial Institute (10) using a hydrothermal technique. Eighty percent total sulfur reduction with 50 percent organic sulfur removal was realized. A carbonization

process was used by Van Hoessle and Quadri (25) to produce a smokeless fuel from subbituminous coal and resulted in a 95 percent reduction in pyritic sulfur content and 60 to 70 percent reduction in both organic and sulfate sulfur contents. A process has been patented by Lefrancois et al. (26) in which coal is mixed with a sodium carbonate melt, which leaches the sulfur content. Sacks et al. (27) reported that the sulfur content of char could be reduced from 3 percent to less than 0.6 percent by reaction with hydrogen in the presence of calcined dolomite, which acted as an  $H_2S$  acceptor. The optimum conditions for the acceptance reaction of calcined dolomite were studied by Pell et al. (28)

The Atlantic Richfield Company (29) was granted a patent for a process which could simultaneously deash and desulfurize coal. The total sulfur content was reduced by 54 percent and the ash content was reduced by 27 percent by simply treating the coal in a batch reactor with water at  $650^{\circ}F$  and a nitrogen pressure of 2350 psig for one hour. Flotation methods have been examined and developed by Miller and Baker (30), Galiguzov (31), Leonard and Cockrell (32), Terchik (33), and Aplan (34). Deurbrouck (35) has an extensive computer study of the removal of pyritic sulfur by flotation methods. Alkali metal hydroxides have been used by Murphy and Messman (36) in a patented process that reduces the total sulfur content by 35-50 percent. The sulfur-

containing impurities were volatilized at elevated temperatures in a fluidized-bed system. Akhtar et al. (37) and Yavorsky et al. (38) have developed a continuous process for the hydrodesulfurization of coals in a turbulent flow, fixed-bed reactor. From coal having 3.0 percent sulfur content and a 9.4 percent ash content, the totally coal-derived synthetic fuel oil, produced at 2000 psig and 450°C, had 0.31 percent sulfur content and 1.3 percent ash content.

#### The Solvent Refining Process

Several methods have been studied to desulfurize coal using organic solvents. Dreyfus (39) has patented a process to obtain a coal extract using tetrahydronaphthalene, anthracene oils, phenols, and a number of other hydrocarbon solvents. The desulfurization was extended by treating the extract with an alkali solution and then heating the extract with a metal oxide on a carrier. Lowry and Rose (40) have developed the Pott-Broche coal extraction process in Germany. By mixing ground coal in a 1:2 ratio with a middle oil and heating the mixture to 400°-420°C under a pressure of 100 atmospheres, an ash-free coal slurry could be filtered to remove ash and undissolved coal and readily hydrogenated to liquid hydrocarbons. A de-ashed low sulfur coal was produced by a continuous solvent refined process developed by Kloepper et al. (41). The reaction was carried out under a hydrogen atmosphere and the sulfur and ash compounds were

filtered from the product coal. The total sulfur content was reduced from 1.4 percent to 0.5 percent and an ash content of 0.2 percent resulted from the original 12 percent in the raw coal. Jameson (42) studied the economics of a solvent refining process that could reduce a coal's total sulfur content from 3.27 percent to 0.95 percent by weight. Cudmore and Guyot (43) studied the effects of coal type, coal particle size, solvent characteristics, solvent-to-coal ratio, gas type, pressure, temperature, and reaction time on the desulfurization of raw coal using an anthracene oil solvent in the presence of hydrogen. A coal with an original total sulfur content of 1.1 percent was reduced to a product containing a 0.4 percent total sulfur content.

The Pittsburgh and Midway Coal Mining Company (44,45,46, 47,48) developed a solvent refining process using an internally generated solvent to dissolve the raw coal. The process involves mixing pulverized raw coal with a coal-based solvent and pumping the slurry at 1000 psig through preheaters which heat the mixture to 800°F. Hydrogen is added prior to entering the preheaters and separated, with other gases, in the pressure letdown. After the pressure is reduced, the coal slurry is passed through a rotary filter from which the slurry is pumped to a vacuum flash evaporator to remove the solvent for recycling. The product is a liquid at higher temperatures or may be cooled and formed into prills or lumps of pitch-like material for fuel. A continuous pilot plant is

currently under operation to further test this process.

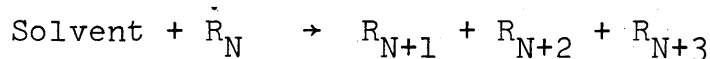
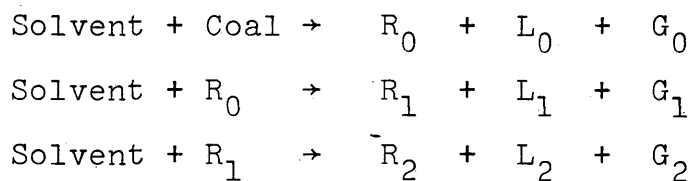
Desulfurization of coal using the solvent refining process has been studied at the Colorado School of Mines using batch autoclave rocking bomb reactors. Ferrall (2) concluded that hydrogen partial pressure and temperature were statistically significant variables in the solvent refining process, but that reaction times in excess of 15 minutes were not statistically significant. Kirchner (3) designed a set of experiments to determine the effects of solvent type, solvent-to-coal ratio, and coal rank on the removal of total sulfur, organic sulfur, and inorganic sulfur (sulfate and pyritic) from 2 bituminous and 2 subbituminous coals. Solvent type and coal rank were found to be statistically significant at the 95 percent confidence level, and the maximum removal of total, organic, and inorganic sulfur contents that resulted was 74.0, 70.2, and 98.6 percent, respectively. Gary et al. (1) studied the effects of reaction temperature, hydrogen partial pressure, reaction time, solvent type, and solvent-to-coal ratio on 2 bituminous and 2 subbituminous coals using the solvent refining technique. Both solvent type and temperature were found to be very highly significant variables (99 percent confidence level) for all the coals studied, while some significance (90 percent confidence level) of the solvent-to-coal ratio was demonstrated for the subbituminous coals. Anthracene oil was found to be a better



solvent for the process than tetralin. Results showed that 98 percent of the inorganic sulfur content and 81 percent of the organic sulfur content could be removed by this process. Bao (4) studied the effect of temperature and pressure on coal desulfurization in a statistically designed set of experiments on one bituminous and one subbituminous coal. Using an analysis of variance test at a 90 percent confidence level, pressure (linear) and the temperature-pressure interaction were significant for the subbituminous coal, while temperature (linear and quadratic) was significant for the bituminous coal. Approximately 50 percent maximum sulfur removal was achieved. A surface response study indicated that a combination of low pressure and high temperature improved desulfurization on both of the coals. Empirical mathematical models of percent sulfur removed were also formulated. Gary et al. (5) reported no trend in sulfate sulfur or pyritic sulfur removal could be statistically determined as a function of temperature, hydrogen partial pressure, or solvent-to-coal ratio, although considerable sulfate and pyritic sulfur content reduction was realized.

#### Mechanistic and Kinetic Considerations

A series reaction mechanism was proposed by Hill (49) for the dissolution of coal in a solvent. The insoluble fraction from the previous step becomes the reactant in the following step as follows:



where R refers to the solid coal residue, L to the coal dissolved or in solution, and G to the gaseous products. The sum of the individual rates for each step totaled the overall rate of reaction. The kinetics of the dissolution of coal in tetralin (1, 2, 3, 4 tetrahydronaphthalene) has been studied by Hill (49) and Charlot (50), who applied the Eyring Absolute Rate theory to the reaction and derived values for the heat of activation ( $\Delta H$ ) and entropy of activation ( $\Delta S$ ) by examining the temperature dependency of the rate of dissolution. The parameters ( $\Delta H$  and  $\Delta S$ ) varied with the fraction of coal dissolved. The entropy of reaction ( $\Delta S$ ) was shown by Hill to be dependent upon the position of the activated complex, and therefore was a function of the extent of dissolution, as shown in Table 1. This apparent increase in the entropy of reaction is consistent with theory in that highly dissolved species exhibit more active sites for reaction.

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Table 1

Heats and Entropies of Activation as a Function  
of Fraction of Coal Dissolved in a Solvent

<u>Fraction Extracted</u>	<u><math>\Delta H</math></u> (Kcal/mole)	<u><math>\Delta S</math></u> (e.u./gram)
0.0	31	-21.0
0.1	37	-19.5
0.5	36	-15.0
0.8	40	- 9.0
0.9	70	+36.0

Kloepper et al. (41) concluded that the transfer of hydrogen from the solvent phase was the most important mechanism of free radical termination for the dissolved coal. The presence of a solvent which can transfer hydrogen or a high activity of hydrogen gas in the reaction atmosphere favors the formation of low molecular weight compounds during the dissolution of coal at high temperatures. The application of heat and solvent was found to be sufficient to remove low molecular weight compounds from the coal matrix. The rupture of bonds and free radical formation become the important kinetic factors at higher temperatures. A study of the kinetics of the reactions involved in the gasification, pyrolysis, and desulfurization of coal was conducted by Vestal et al. (51), Vestal and Johnson (52), and Juntgen et al. (53). In the desulfurization section of their study, they reported that the volatile organic sulfur content reacted readily with hydrogen, the sulfate and pyritic sulfur

contents reacted with hydrogen to produce a sulfide, which was converted to  $H_2S$ , and the organic sulfur content associated with the carbon reacted slowly with the hydrogen. A two-stage gaseous desulfurization mechanism was derived by Cindeu-Munteau (54). The porosity of the material increased during the first step while the actual attack upon the sulfur-bearing constituents occurs during the second step.

Feldkirchner and Linden (55) investigated the reaction rate characteristics of coal char hydrogasification in a semiflow system. They concluded that the initial high-rate period was proportional to the hydrogen partial pressure without equilibrium hindrance. The final stages of the reaction included pyrolysis of the char, hydrogenolysis of the intermediates that are derived from essentially aliphatic hydrocarbon side chains and oxygenated functional groups, and the slow conversion into methane according to the carbon-hydrogen reaction. These results were supported by the work of Wen and Huebler (56).

Bruk et al. (57) reported that the effect of reducing the heating rates (decreasing the rate of temperature increase) increased desulfurization up to  $600^\circ C$ , then no effect was observed. Best desulfurization results were obtained between  $500^\circ$  and  $600^\circ C$ .

### The Effect of Hydrogen

Sinha and Walter (58) have studied the desulfurization of coals and chars under various atmospheres between 400° and 600°C. The low rate of desulfurization by hydrogen at low temperatures was thought to be due to either a low rate of sulfur release from the decomposition of sulfur-bearing species present in the coal matrix or to a low rate of dissociation of hydrogen, or to both. The reaction of coal and hydrogen was considered to be a two-stage process by Blackwood and McCarthy (59), where a very rapid hydrogenation of the oxygen-containing functional groups of the coal was the first step, followed by a slow reaction between the hydrogen and the residual char. These conclusions were also reported by Chermin and Van Krevelen (60), Van Krevelen et al. (61), Pitt (62), and Linden (63). The hydrogen also served to saturate the solvents used and reacted with the sulfur compounds present to form H<sub>2</sub>S. The kinetics of the transfer of hydrogen in the coal-air-hydrogen-tetralin system was studied by Curran et al. (64). They proposed a pseudo-first-order reaction involving the decomposition of the coal into free-radical components. Very little hydrogen transfer was necessary to dissolve the first 50 percent of the coal, but the next 40 percent of the coal required 7 times the hydrogen transfer of the initial 50 percent to effect dissolution. Kloepper et al. (41) found a significant increase in the amount of coal dissolved as the partial pressure of

hydrogen was increased in a batch autoclave system. These results are given in Table 2.

Table 2

Effect of Partial Pressure of Hydrogen on  
Dissolution of Coal in Anthracene Oil

Run No.	Initial H <sub>2</sub> Partial Pressure (psig)	Pyridene Insolubles (%)	Coal Dissolved (% Moisture-Ash Free)
B-18	0	12.46	53
B-25	100	11.98	55
B-26	500	8.66	70
B-27	1000	5.43	85
B-33	1500	2.52	97

Kirk and Seitzer (65) reported on the hydrogenation of coal process at 750<sup>o</sup>-840<sup>o</sup>F and 2500 psig, with a liquid product resulting. Potzieter (66) and Liebeuberg and Potzieter (67) studied the hydrogenation of coal in a tetralin solvent.

#### Thermodynamic Considerations

Kloepper et al. (41) indicated an overall 20 percent improvement in the heating value of the solvent refined coal, compared to the parent coal. They attributed this effect to the departure of oxygen and sulfur atoms from the coal matrix during the treatment, which left polynuclear aromatic products in the solvent refined coal product. These compounds have very high resonance energies and therefore a high heat of

combustion. Cudmore and Guyot (43) also noted that the overall heat of combustion of the products exceeded the heat of combustion of the reactants in their study of the dissolution of coal in anthracene oil. An enrichment in polycyclic aromatic compounds was observed in the solvent refined product and a corresponding increase in the heating value of the treated coal.

#### Organic Sulfur Removal

In a patented process for a pebble-heated gasification unit, Mayland (68) observed that a significant amount of the organic sulfur content in the coal was converted to  $H_2S$ . Mukai et al. (69) found that a room temperature treatment of a bituminous coal with a 3 percent solution of hydrogen peroxide removed 100 percent of the organic sulfur content. The process was able to oxidize all of the organic sulfur content without changing the properties affecting the coal's coking ability. Meyers, Land, and Flegal (70) used a weak organic acid to leach 45 to 80 percent of the organic sulfur content in several coals. They reported that phenyl-nitrate was the most efficient solvent for organic sulfur content removal. Meyers (71) later received a patent for this process.

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Pyritic Sulfur Removal

McKinley and Henke (72) patented a process using hydrogen contacting to desulfurize coal with a high pyritic sulfur content. Meyers et al. (73,74) have developed a process to remove pyrites from coal using an aqueous ferric sulfate solution at 50°-130°C. The pyritic sulfur content is selectively oxidized to form free sulfur. Meyers (75) was later issued a patent for this process. Flotation-gravity separation methods have been used extensively to desulfurize coals with high pyritic sulfur contents (30,31, 32,33,34,35) Blum and Cindeu-Munteau (76) reported that coal containing less than 2.5 percent total sulfur could have 90 to 95 percent of its total sulfur content removed in 30 to 60 minutes using an air-stream fluidized-bed process. By electrostatically separating the pyrite and hematite particles in a magnetic separator, Tarts and Andreeva (77) reduced the total sulfur content of a lignite coal, which was previously heated to 600°F, from 7.6 percent to 2.8 percent. Abel et al. (78) also used a centrifugal-electrostatic method to remove 50 to 70 percent of the pyritic sulfur content and 30 to 50 percent of the total sulfur content from a finely ground Pittsburgh seam coal

Given and Jones (79) concluded that although several reactions were capable of removing the pyritic sulfur content of coal, the rates of reaction were too low for practical use. This is because the pyrite is finely dispersed and



embedded in the coal matrix with little surface exposure. They also found in their study that some of the released pyritic sulfur content becomes fixed in the organic matter of the coal, thus raising the organic sulfur content of the coal. Smith (80) also reported similar results.

### Application of Catalysts

Wrinkler (81) found that activated iron powder mixed with finely ground bituminous coal dissolved in a highly aromatic solvent can reduce the coal's total sulfur content by 56 percent upon application of heat. Samoilenko et al. (82), using a Raney nickel catalyst, achieved a maximum of 55 percent total sulfur content reduction for a soft coal, but realized only 7 to 26 percent sulfur content reduction in most of the coals studied. A French patent granted to Fohler (83) used oxides and salts of calcium, magnesium, lead, copper, zinc, and molybdenum as catalysts to split organic sulfur bonds before a desulfurizing treatment. Manmohan and Goswami (84) reported that carbonizing coal for six hours with sodium chloride gave 80 percent total sulfur content removal. The addition of aluminum chloride ( $AlCl_3$ ) was the most effective method of desulfurizing coke, according to Krasnyukov et al. (85). However, the ash content of the coke was increased 7 to 9 times and practical application of the process was impossible due to rapid corrosion of the equipment by the aluminum chloride.

Akhtar et al. (37) demonstrated that a bituminous coal containing 3.4 percent total sulfur content can be catalytically hydrodesulfurized at 4000 psig and 450°C in a tar slurry to a product that yielded 91 percent fuel oil having only 0.09 percent sulfur content after removal of solids residue. Ouchi, Imuta, and Yamashita (86) have studied depolymerization catalysts for coal.

#### Choice of Organic Solvent

Orechkin (87) found that the absence of hydrogen in the reaction atmosphere may still allow an effective extraction. Solvents of sufficiently high hydrogen content may effectively dissolve the coal. However, the average molecular weight of the product was high due to the fact that hydrogen required to reduce the coal to low molecular weight compounds was supplied entirely by the solvent, and this quantity was limited by the solvent characteristics and degree of unsaturation. Gary et al. (1,5) found that anthracene oil, having a higher hydrogen-to-carbon ratio than tetralin, was a significantly better solvent for the dissolution and desulfurization of coal.

EXPERIMENTAL APPROACHARTHUR LAKES LIBRARY  
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The importance of four operating variables, temperature (T), hydrogen partial pressure (P), solvent-to-char ratio (SCR), and solvent type (ST) was investigated in this research study. A full-factorial, doubly replicated experimental design employing each of the process variables at two levels required 32 experimental runs in the batch rocking-bomb autoclave. Each process variable was given a high value and a low value in the run design matrix and four separate responses were determined in the final product for each combination of the variables. The responses measured with the appropriate method of analysis are listed in Table 3.

Table 3

## Responses and Methods of Analysis

Total Residual Sulfur Content	-	ASTM D271-68
Organic Residual Sulfur Content	-	by difference
Inorganic Residual Sulfur Content (pyritic + sulfate)	-	ASTM D2492-68
Hydrogen Content of the Solvent	-	Infrared Spectrophotometric Analysis

In addition, a singly replicated data set for the heating value of the treated char was obtained by bomb calorimetry techniques. Thus, 5 run matrix tables were constructed listing the response as a function of the operating variables

at their appropriate levels. The matrix table format is shown in Table 4.

Table 4

Run Design Matrix-Coal Char Desulfurization

Factors:

1. Temperature
2. Hydrogen Partial Pressure
3. Solvent-to-Char Ratio
4. Solvent Type

Tabular Designators:

$R_1$  = 2.0/1 Solvent-to-Char Ratio

$R_2$  = 5.0/1 Solvent-to-Char Ratio

$T_1$  = 325°C

$T_2$  = 425°C

$P_1$  = 1000 psig Hydrogen Partial Pressure

$P_2$  = 2000 psig Hydrogen Partial Pressure

$S_1$  = Tetralin Solvent (C/H = 10/1 by weight)

$S_2$  = Anthracene Oil Solvent (C/H = 17/1 by weight)

The table below is the run matrix for each response studied, and consists of 4 factors at 2 levels ( $2^4$ ), or 16 experimental runs. Reaction conditions for each result are designated by the row and column position of the response. The order of experimental run conditions was determined from a random number generation table.

Table 4 (Cont.)

		T <sub>1</sub>		T <sub>2</sub>	
		P <sub>1</sub>	P <sub>2</sub>	P <sub>1</sub>	P <sub>2</sub>
S <sub>1</sub>	R <sub>1</sub>	8	10	6	4
	R <sub>2</sub>	15	1	7	9
S <sub>2</sub>	R <sub>1</sub>	5	12	11	16
	R <sub>2</sub>	13	2	14	3

A statistical factorial design using an analysis of variance of the data generated is a frequently used method for determining the effect of process variables on a given response, since main effects alone as well as all possible interactions of the main effects may be examined and tested for significance separately (1,2,3,4,5). In this study Yates' technique was used to calculate an "F" statistic, which was compared against tabular values to affix importance of the main effect or interaction at any desired level of significance. The "F" statistic used was the ratio of the sum of squares for each effect and interaction divided by the residual sum of squares for all effects and interactions. This technique was applied to the solvent refining process in order to assign confidence levels of 95, 99, and 99.9 percent to main effects and important interactions.

Since the heating value analysis was singly replicated, an alternate method of determining the residual sum of squares for the "F" ratio was used. The sum of squares for the four factor interaction gave an estimate of the residual sum of squares associated with the data set. Thus, the sum of squares for each of the main effects and interactions (through the third order) was divided by the residual sum of squares as obtained from the fourth order interaction.

Two further tests were performed in an attempt to establish the linearity of the experimental data points. A series of 4 runs were made at a third temperature level (475°C) with a fixed solvent (anthracene oil) and both levels of pressure and solvent-to-char ratio being investigated. This allowed plots of isotherms and isobars relating the total residual sulfur content and the process variables to be drawn. A hypothesis testing technique (89) was used to confirm the independence of the population sets. Also an empirical mathematical model was derived for the residual sulfur level of the char using a multiple linear regression technique (90)

Two Fortran IV computer programs were written to calculate the analysis of variance (ANOVA) table for the doubly replicated and singly replicated run matrices, while the regression model was solved by a Fortran IV matrix multiple linear regression computer program.

## EQUIPMENT

Three major equipment systems were employed in this study: 1) Reactor system, 2) Scrubber system, and 3) Solvent recovery system. A description of the components of each system is given below, along with graphical illustrations of the important sections of each system. A process equipment flow sheet is given in Figure 1.

### Reactor System

Three reactor systems of the batch autoclave generic type were used in this study. A gas delivery system, a reaction vessel, and a shaking assembly were the functional parts of the reactor systems.

The reaction vessels, as shown in Figure 2, were manufactured by the American Instrument Company (AMINCO) of Silver Spring, Maryland, and were from the 4 3/8-in. series. All three reaction vessels had inside depths of 10 in., inside diam. of 3-5/16 in., and approximate weights of 50 lbs. One vessel was fabricated from AISI 316 stainless steel, while the other two were made of AISI 347 stainless steel. The vessels had a working pressure rating of 5,050 psi at 100°F and had an effective volume of 1410 ml.

Three shaking assemblies were used in the reactor system. One of the assemblies was manufactured by High Pressure Equipment Company, Inc. (HIP) of Erie, Pa., and

FIGURE 1

PROCESS EQUIPMENT FLOWSHEET-COAL CHAR DESULFURIZATION

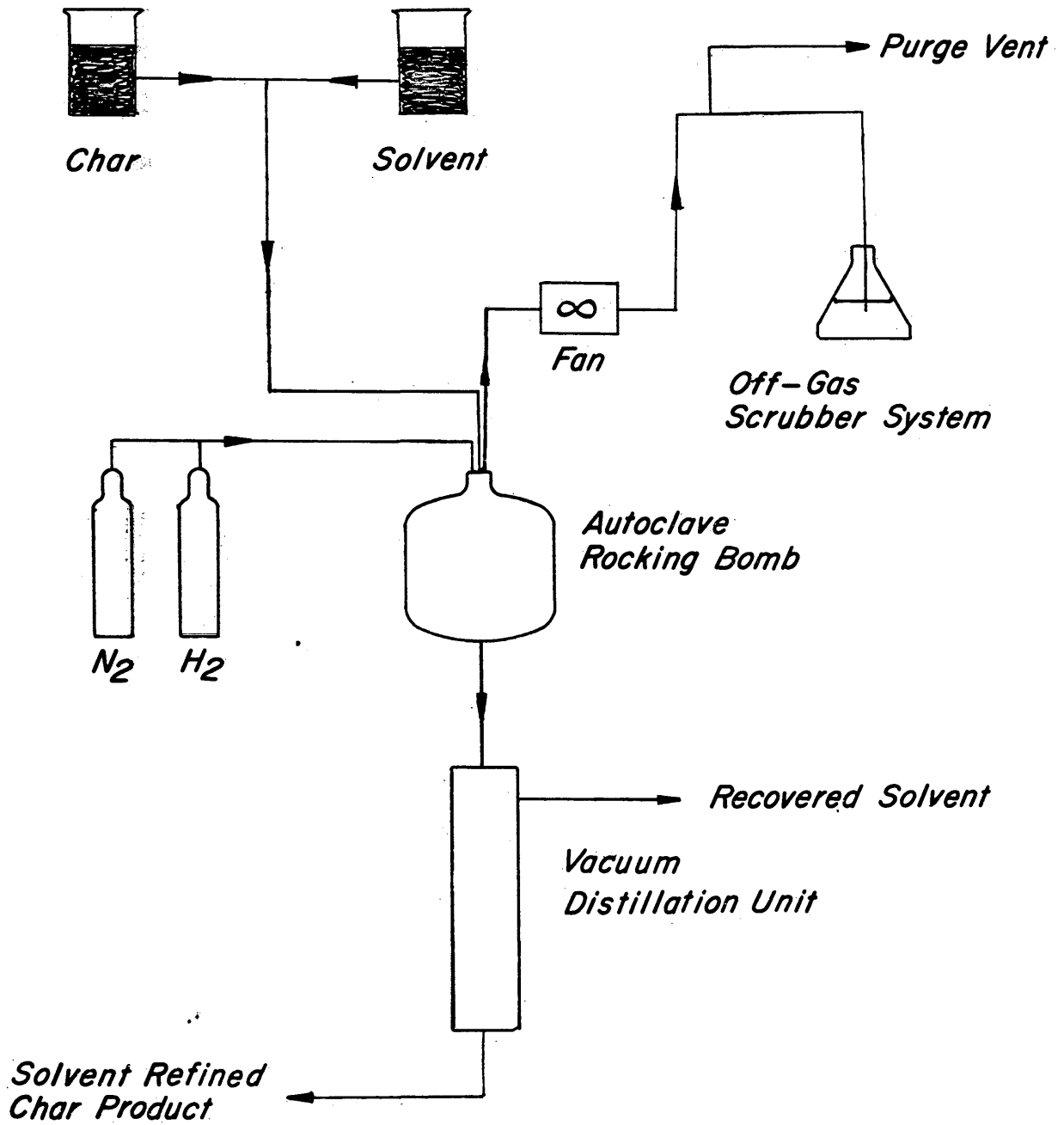
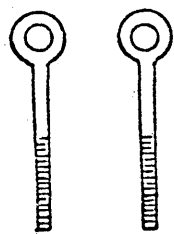


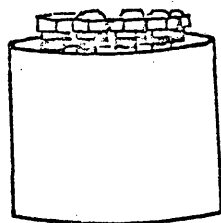


FIGURE 2

REACTION VESSEL ASSEMBLY



eye bolt



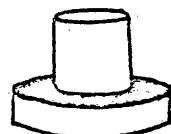
cap with thrust bolts



thrust ring



gland nut



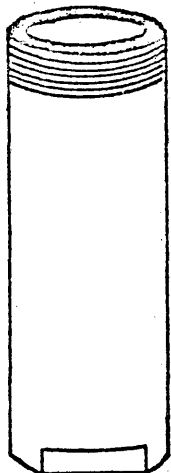
head



thermowell



gasket

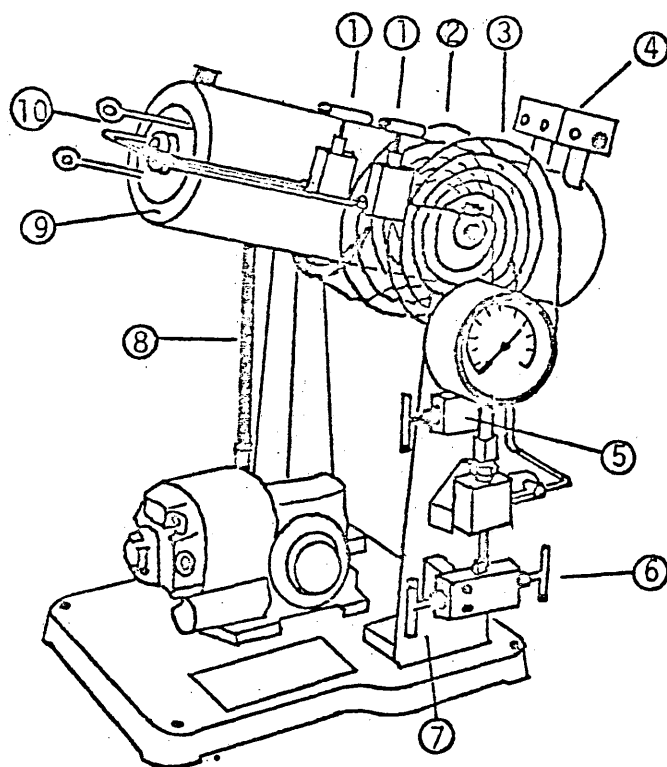


vessel body

consisted of a 6,000-watt, 208-volt heating jacket mounted on a rocker assembly. This system had a rapid heater and an on-off switch to control the rate of temperature rise. The heating jacket was rocked by means of a 1/3-hp, 220-volt electric motor actuating an eccentric lever drive connected to the heating jacket. The other two assemblies were standard Aminco 4-3/8-in. series and consisted of a 3,000-watt, 208-volt heating jacket mounted on a rocker assemblies. The rockers for the Aminco shaking assemblies were actuated by 1/3-hp, 110-volt motors driving eccentric levers connected to the heating jackets. Figure 3 shows the shaking mechanisms and the heater mounted on the rocker as used for this experimental work. The Aminco heating jackets had the capacity to heat from room temperature to 400°C in approximately 1 1/2 hr, while the HIP heating jacket could heat from room temperature to 400°C in about 2-1/4 hr. Aminco 30,000 psi valves and fittings were used to regulate the inlet and exit of the reaction gases from each reaction vessel. All reactor systems were equipped with 0 to 3000 pressure gauges. Tubing used on the shaking assemblies was 304 stainless steel, 1/4-in. o.d., and rated for operation at 100,000 psi at 100°F.

A Leeds and Northrup, Series 60 temperature controller, with a Model 11906 SCR final control element was used in the 6000-watt system. A Leeds and Northrup Speedomax H continuous

**FIGURE 3**  
**SHAKING ASSEMBLY**



- |                           |                                  |
|---------------------------|----------------------------------|
| 1. Valve, Shut-off        | 6. Valve, Exhaust                |
| 2. Spiral, Inlet          | 7. Valve, Inlet                  |
| 3. Spiral, Exhaust        | 8. Rod, Connecting               |
| 4. Switch, Heating Jacket | 9. Jacket, Heating               |
| 5. Valve, Discharge       | 10. Connections, Reaction Vessel |

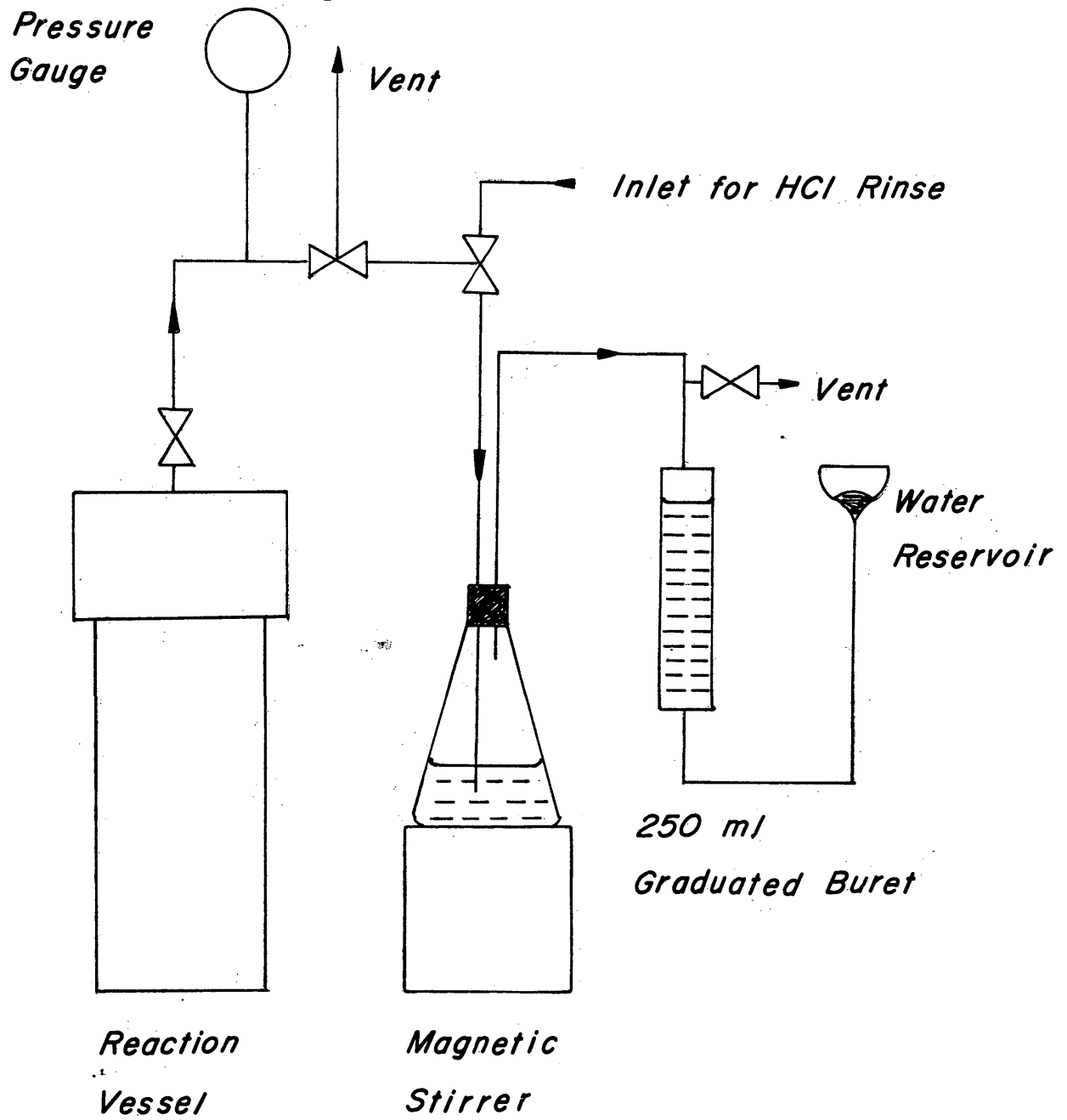
recorder monitored the temperature response of the reaction vessel. In the 3000-watt systems, Leeds and Northrup Electro-max III controllers, with Model 11906 SCR final control elements were used for temperature control. Temperatures were recorded on a Honeywell Elektronik III two-channel continuous recorder. The temperature sensors were chromel-alumel thermocouples.

All shaking assemblies were connected to purging-charging gas delivery systems. Each of these systems consisted of a nitrogen cylinder, a hydrogen gas cylinder, pressure regulators for each cylinder, and Aminco stainless steel tubing and fittings similar to those used on the shaking assemblies.

#### Off-Gas Scrubber System

A diagram of the off-gas scrubber system is shown in Figure 4. The tubing used was 304 stainless steel, 1/4-in. o.d., and rated for operation at 100,000 psi at 100°F. Residual pressure in the reaction vessel was measured by a 0-3000 psig Duragauge pressure gauge. A Foxboro Dynalog 6-point circular recorder with a range of 400°C and equipped with iron-constantan thermocouples was used to measure the reaction vessel temperature. The collection vessel was a 250-ml Erlenmeyer flask agitated with a magnetic stirrer for better absorption of the H<sub>2</sub>S. Gas volume was measured using water displacement in a 250-ml graduated buret.

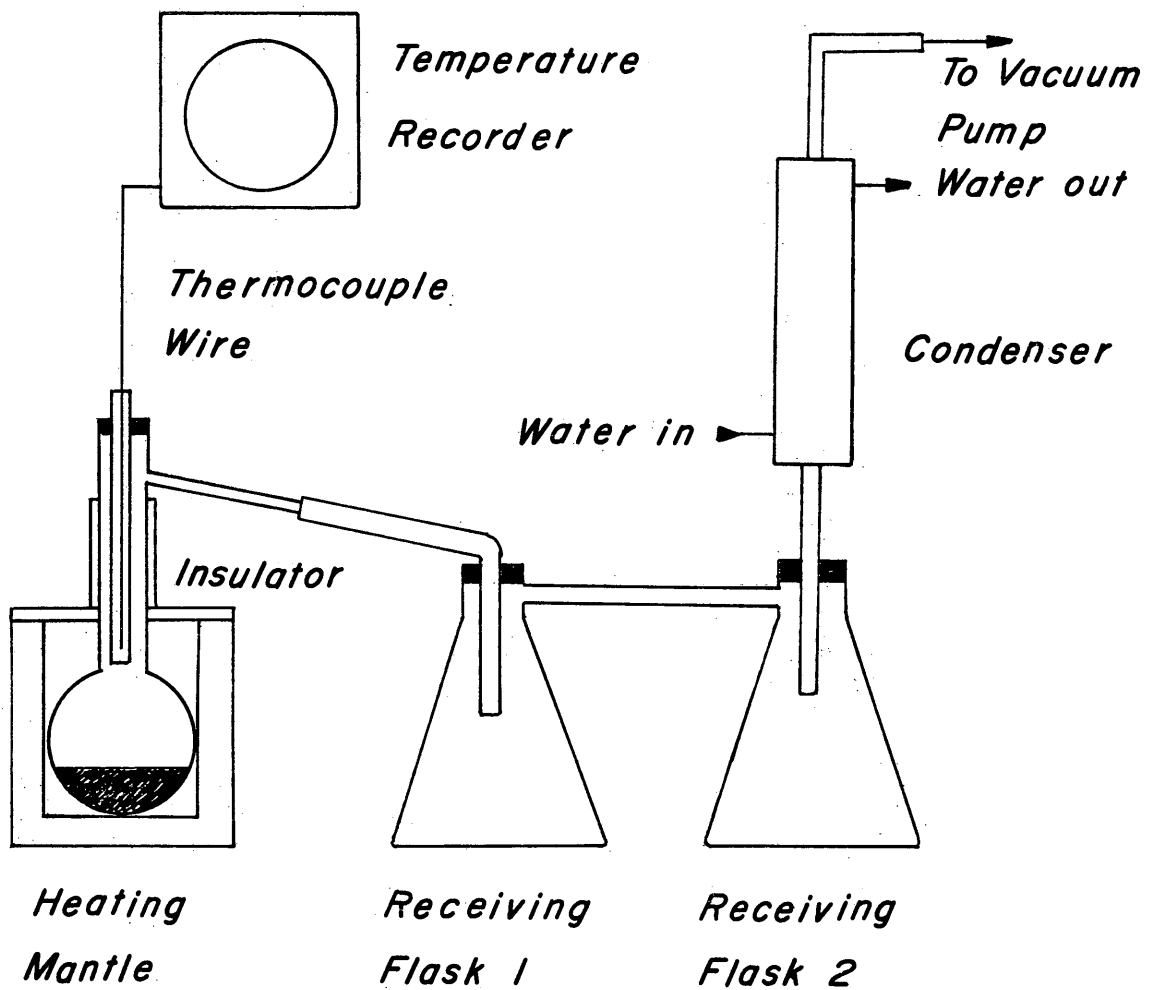
**FIGURE 4**  
**OFF-GAS SCRUBBER SYSTEM**



### Solvent Recovery System

The solvent recovery system used is shown in Figure 5. A 500-ml Hempel flask containing the treated char slurry was heated using a 330-watt, 115-volt heating mantle controlled with a Powerstat, a 110-volt and 7 1/2-amp variable transformer. The reclaimed solvent was trapped in two 1000-ml flasks along with condensed low-boiling solvent fractions. The vacuum for the system was supplied by a Cenco MegaVac pump driven by a 1/4-hp, 110-volt electric motor. The vacuum on the system was measured with a 0 to 30 in. Hg Duragauge vacuum gauge. A Foxboro Dynalog 6-point circular chart recorder continuously monitored the temperature of the distillation flask. Iron-constantan type thermocouples were used for the input to the recorder.

**FIGURE 5**  
**SOLVENT RECOVERY SYSTEM**



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## EXPERIMENTAL PROCEDURE

The experimental procedure may be divided into three major areas: preparation of char and char slurry, desulfurization and separation of treated products, and analysis of the treated char and solvent properties. A flowsheet indicating the treatment steps involved is given in Figure 6.

### Preparation of Char and Char Slurry

The coal char, as received from an Illinois No. 6-seam coal from the Peabody No. 10 mine and produced at a 1550°F temperature in FMC's Stage 4 pyrolyzer, R-240, was crushed and then screened to a size smaller than 28-mesh until all of the char passed through the sieve. Fifty grams of char and the appropriate amount of solvent (100 or 250 grams of anthracene oil or tetralin) were weighed, mixed, and placed in the reaction vessel.

### Desulfurization and Separation of Treated Products

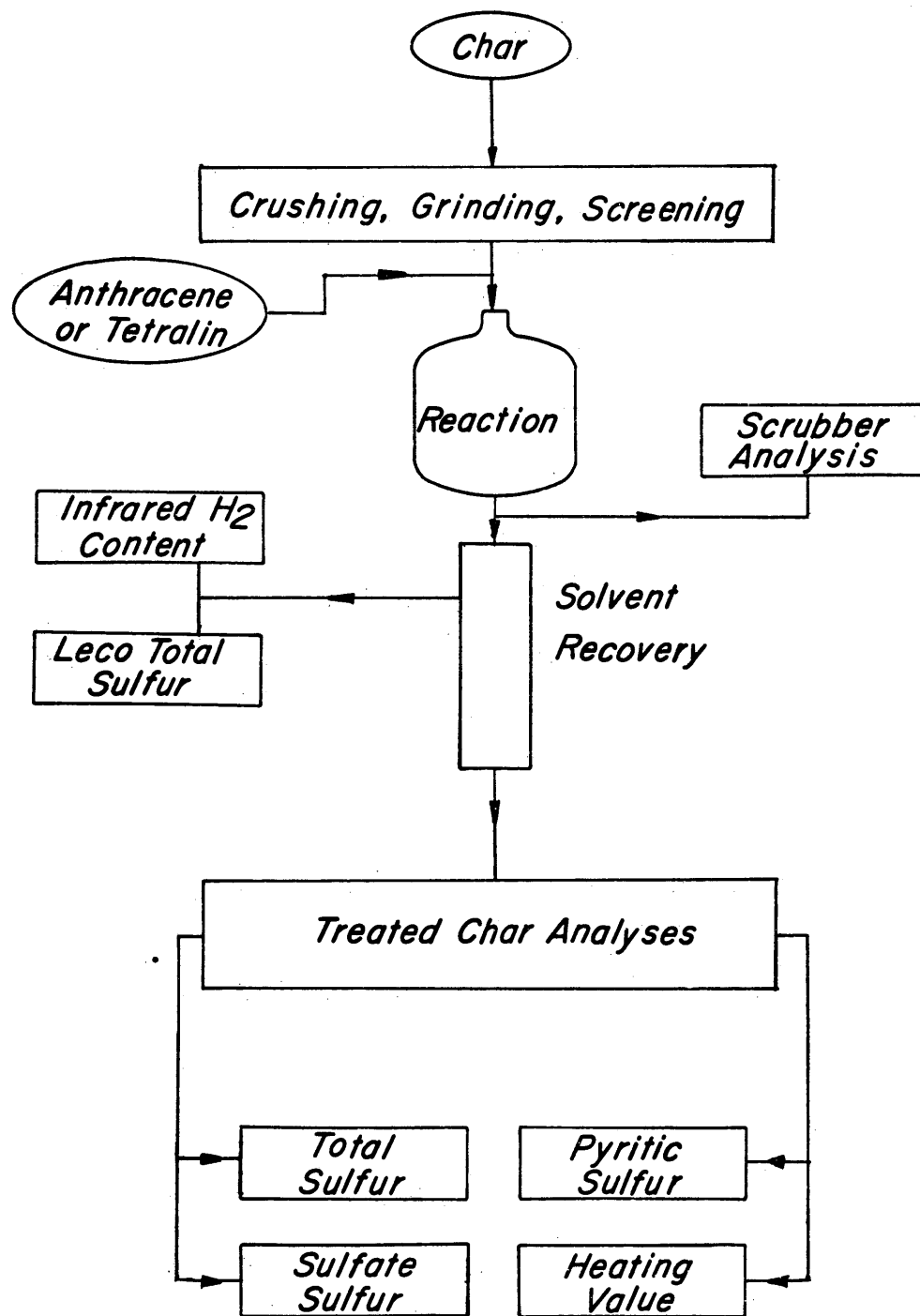
Desulfurization and separation of treated products can be discussed in three phases: the char processing reaction, the scrubber analysis, and the solvent recovery system.

#### Char Processing Reaction

The reaction vessel was closed by placing the head and thrust ring on top of the vessel, turning the vessel head until secure, and tightening the thrust bolts. With the eye-



**FIGURE 6**  
**SOLVENT REFINING OF CHAR PROCESS FLOWSHEET**



bolts and gas delivery connecting piece screwed into the cap couplings, the assembled reaction vessel was then inserted into the heating jacket of the shaker assembly, the gas connecting lines were securely tightened to the vessel, the thermocouple was placed in the thermowell, and the temperature recorder was turned on.

The assembled reaction vessel was then purged to 200 psig and vented to atmospheric pressure with nitrogen three times. The system was then purged to 200 psig and vented to atmospheric pressure one time with hydrogen before final pressure of hydrogen at room temperature was added according to Table 5. This pressure setting is a function of run temperature, run pressure, initial temperature, and H<sub>2</sub> compressibility factors. When the shut-off valves on the shaking assembly were closed and the system isolated, the system was checked with soap solution for leakage, and the initial temperature and pressure were recorded.

After assuring there were no leaks in the system, the temperature controller, heater, and rocker were switched on and heating began. The controller settings and the turn-off temperature for the rapid heater on the HIP assembly are shown in Table 6. The controller settings for the two Aminco assemblies were set approximately 20°C lower than the desired reaction temperature. When the reaction reached and leveled out at the desired maximum temperature, the shutoff valve on

Table 5

## Initial Pressure Settings for Reactor Systems

<u>Run Conditions</u>		<u>Initial Partial Hydrogen Pressure at Room Temperature, psig</u>		
<u>T, °C</u>	<u>P, psig</u>	<u>21°C</u>	<u>30°C</u>	<u>40°C</u>
325	1000	500	516	533
325	2000	1025	1054	1089
425	1000	427	440	455
425	2000	878	905	935
475	1000	398	410	424
475	2000	809	834	862

Table 6

## HIP Assembly Controller and Rapid Heater Settings

<u>Run Temperature</u>		<u>Controller Setting</u>	<u>Rapid Heater Off</u>
<u>°C</u>	<u>°F</u>	<u>°F</u>	<u>°F</u>
325	617	650	520
425	797	840	740
475	887	940	840

the shaking assembly was opened and the total pressure at reaction temperature (initial) was recorded. The reaction was held at the maximum temperature for 15 minutes and the system temperature and pressure (final) were again recorded. The reaction vessel, still pressurized, was then removed from the heating-rocking system and cooled by forced convection with a high speed fan.

### Scrubber Analysis

This method was developed by the Pittsburgh and Midway Coal Mining Company Research Department for their solvent refining of coal process (91) and is applicable in a concentration range of about 0.1 to 7 volume percent  $H_2S$ . As shown in Figure 5, the cooled reaction vessel was attached to the scrubber system. The residual reaction vessel temperature and pressure, ambient temperature, and barometric pressure were recorded. Thirty ml of ammoniacal zinc sulfate solution were diluted to 150 ml in four 250-ml Erlenmeyer flasks, and 200 ml of product gas was slowly injected and recorded by water displacement into each. The solution was magnetically stirred. Heavy turbidity formation was used as a guide to the volume of gas to use in the first test. The injection tube was washed with about 1 ml of 1:1 HCl and distilled water from a wash bottle.

The solution was transferred slowly while stirring magnetically to a 500-ml Erlenmeyer flask which contained 25 ml of 0.05 N iodine solution (measured by buret) and 40 ml of 1:1 HCl solution. The 250-ml flask was then rinsed with about 100 ml of water into a 500-ml flask. While continuously being stirred, the solution was immediately titrated with standardized 0.05 N sodium thiosulfate solution until the solution turned yellow. Two ml of 2 percent starch solution was then added, and the end point of the titration was

indicated by a permanent solution color change from blue to clear. The volume of sodium thiosulfate used was recorded. A blank test with three replicates was similarly run without a gas sample. Since the blank values do not change significantly, only a weekly check was necessary. If the sample titration volume was less than half of the reagent blank, the test was rerun using a smaller gas sample.

The mole percent of  $H_2S$  present in the reaction gas was calculated by the following formula:

$$H_2S \text{ mole } \% = \frac{(V_b - V_s) \times N_t \times F \times 100}{V_{\text{gas}}}$$

where:

- $V_b$  = volume (ml) of sodium thiosulfate used in blank
- $V_s$  = volume (ml) of sodium thiosulfate used in sample
- $N_t$  = normality of sodium thiosulfate
- $V_{\text{gas}}$  = volume (ml) of product gas used in test
- $F$  = factor in milliliters of hydrogen per milliequivalent of sodium thiosulfate. It is one-half of the reciprocal of the molar equivalent of one liter of gas (moles/liter) at the temperature and pressure of product gas at the time of testing.

#### Solvent Recovery

A diagram of the solvent recovery system is given in Figure 6. As soon as the off-gas had been vented, the reaction vessel was opened and the product was collected in a

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beaker for solvent recovery. After recording the weights of clean receiving flasks and the distillation flask, the product was transferred to the distillation flask, scraped with a spatula, and weighed. The distillation flask was placed in the heating mantle and the thermocouple, passed inside a glass tube connected to a rubber stopper, was placed in the flask's neck. The receiving apparatus was assembled and connected to the distillation flask and cooling water was passed through the condensers. After switching on the temperature recorder, the Variac controlling the heating mantle was adjusted to the 45 percent setting. The three-way valve was opened to the atmosphere so that any absorbed gas (hydrogen) could be driven from the reaction product. As soon as the solution temperature had reached 150°C, the vacuum pump was turned on. The vacuum was slowly increased until the solution temperature reached approximately 275°C, after which full vacuum of 24 in. Hg was applied. Additional heat was applied by increasing the Variac setting until the solvent appeared to be completely distilled. For anthracene solvent, this usually required a temperature in excess of 400°C, while no trace of tetralin appeared after about 325° to 350°C. The Variac was turned off along with the vacuum. Any solvent vapors remaining in the distillation flask were flashed into the receiving flasks.

The cooling water was shut off and the thermocouple was removed from the distillation flask. After being disconnected, the distillation flask and receivers were weighed and the weights of the char product and recovered solvent were determined by difference. A small quantity of the recovered solvent was stored in a sample vial for later sulfur content analysis. The solvent refined char, appearing similar to untreated char, easily poured from the distillation flask. This treated char was weighed and stored in small jars.

#### Analysis of Treated Char and Solvent Properties

The analysis of the char sulfur content was determined according to four sulfur types: total sulfur, sulfate sulfur, pyritic sulfur, and organic sulfur by weight percent. The analyses are outlined by ASTM standards for gaseous fuels, coals, and cokes (92).

##### Total Sulfur Content

Total sulfur content of the char was determined by the Eschka method as described by ASTM D271-68 (ASTM, 1970, pp. 23-25) with the following changes to Section 20(c):

- 1) Instead of digesting, heat gently with 100 ml of water for 1/2 hr.
- 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  $\text{BaSO}_4$  precipitate.
- 5) Smoke off the filter paper below  $500^\circ\text{C}$  for about 1 1/2 hr.

#### Sulfate Sulfur Content

The sulfate sulfur content of the char was determined by ASTM D2492-68 (ASTM, 1970, pp. 420-426) with the following changes:

- 1) Section 5.1.1 - Instead of using a cold finger condenser, let the coal-HCl mixture set in the Erlenmeyer flask overnight.
- 2) Section 5.1.2 - After adding  $\text{NH}_4\text{OH}$ , set the beaker aside for 15 minutes and allow the precipitate to coagulate.
- 3) Section 5.1.3 - Acidify the filtrate from 5.1.2 with concentrated HCl to a pH between one and three as measured by a pH meter.

#### Pyritic Sulfur Content

The pyritic sulfur content of the char was also determined by ASTM D2492-68 with Sections 5.15 and 5.2 replaced by the following:



- 1) Weigh out 2.0 grams of the char residue from the sulfate test (to 0.01 milligrams) Put the sample in a 250-ml Erlenmeyer flask and add 50 ml of 1:7 nitric acid solution. Stopper the flask and leave it for at least 12 hours.
- 2) Filter the mixture through a medium texture filter paper. Pour the filtrate back into the flask and refilter the solution removing additional coal residue. The flask is washed with 35 ml of 1:7 nitric acid solution. Discard the coal residue.
- 3) Add 2 ml of concentrated hydrogen peroxide to the filtrate. If there is coloration due to organic substances, add several milliliters of hydrogen peroxide in excess. Cover the beaker with a watch glass. Heat the solution to boiling and allow it to boil for at least 5 minutes. If some organic coloration remains, add more hydrogen peroxide (making sure that the solution boils for 5 min more before adding NaOH)
- 4) With constant stirring, slowly add concentrated NaOH until a red iron precipitate forms. Add 2 ml excess NaOH making sure that the stirring rod and sides of the beaker are washed. Set the beaker aside for 15 min to allow the iron precipitate to coagulate. (It may be necessary to reboil the solu-

- tion for 1 min to aid the coagulation of the iron precipitate.)
- 5) Filter the solution through medium texture, ashless filter paper. Carefully wash the beaker and filter paper with 75 ml of boiling water containing a trace of  $\text{NH}_4\text{Cl}$  and a trace of  $\text{NH}_4\text{OH}$ . At this point there should be no iron precipitate left in the beaker. Discard the filtrate.
  - 6) Place the filter paper containing the iron precipitate in a clean beaker. Add 25 to 50 ml of 2:3 hydrochloric acid to the beaker and dilute with water to 125 ml. Heat the solution to boiling. Allow it to boil until the filter paper is broken into very small pieces.
  - 7) While stirring, add dropwise  $\text{SnCl}_2$  solution until the mixture is milky white. Add 2 to 3 drops of  $\text{SnCl}_2$  in excess. Wash the sides of the beaker with water and allow the solution to cool to room temperature.
  - 8) While stirring, quickly add 10 ml of  $\text{HgCl}_2$ . Rewash the sides of the beaker with water. Let the solution set for 2 to 3 min (do not stir), then begin stirring. Add 20 ml of  $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  solution, 2 or 3 drops of diphenylamine sulfonate indicator, and water until there is 200 ml of solution.

- 9) Titrate the solution with 0.025 N  $K_2Cr_2O_7$ . The endpoint is indicated by a purple color that lasts for at least 20 seconds.

#### Organic Sulfur Content

The organic sulfur content was determined by difference, i.e. by subtracting the pyritic and sulfate sulfur weight percents from the total sulfur weight percent.

#### Sulfur Content of Solvent

To analyze for the total sulfur content of the solvent, the Leco induction furnace technique, ASTM D1552-64 (93) was used. A gas purification train, an induction furnace and a semi-automatic titrator unit were the three components of the analysis system. 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. As shown in Figure 7, the induction furnace was a Leco model 521, equipped with the "L" modification on the combustion chamber. A special feature of the "L" modification was the inclusion of a high temperature igniter in the combustion chamber, as shown in Figure 8. The exhaust gases from the induction furnace combustion chamber were sent through an electrically heated glass delivery tube and into the Leco semi-automatic titrator model 518. This piece of equipment is shown in Figure 9. The semi-automatic titrator used an idiometric reaction with a color change endpoint to analyze the combustion gases. The titrator proved to be a

*FIGURE 7*

LECO INDUCTION FURNACE

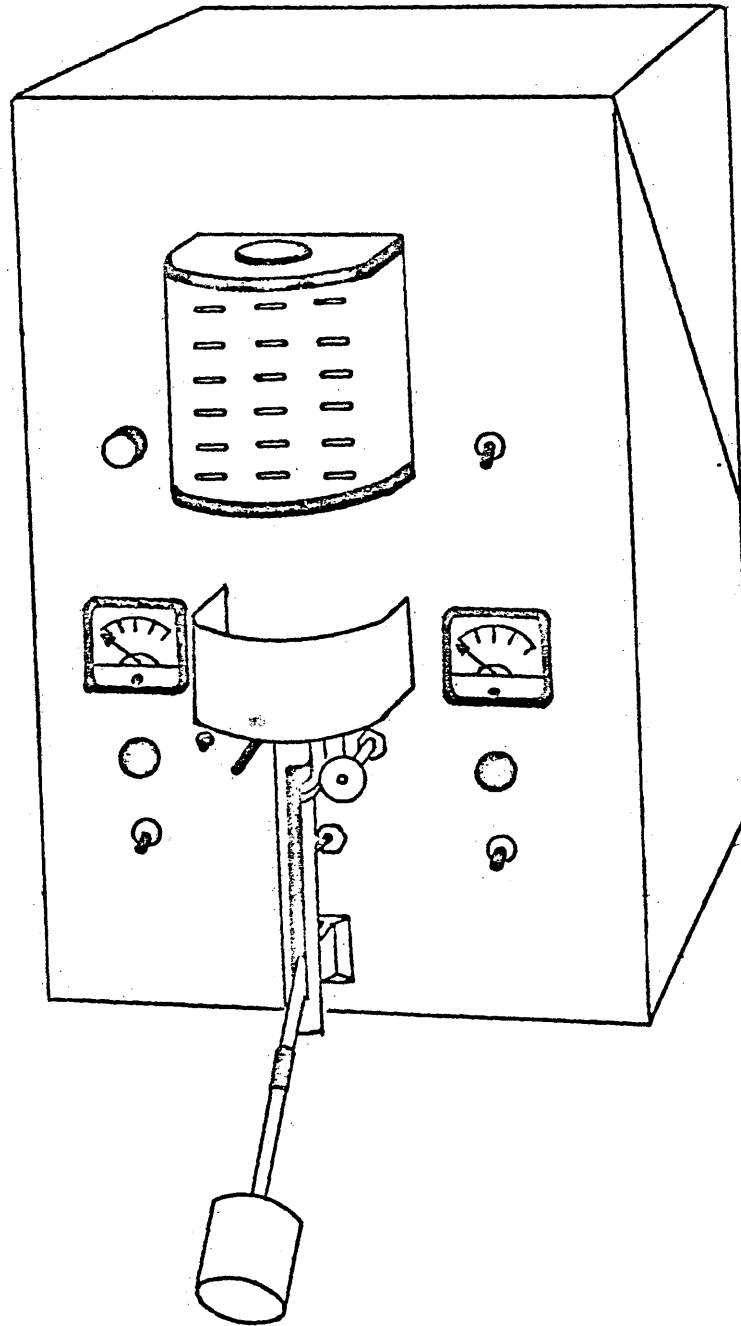
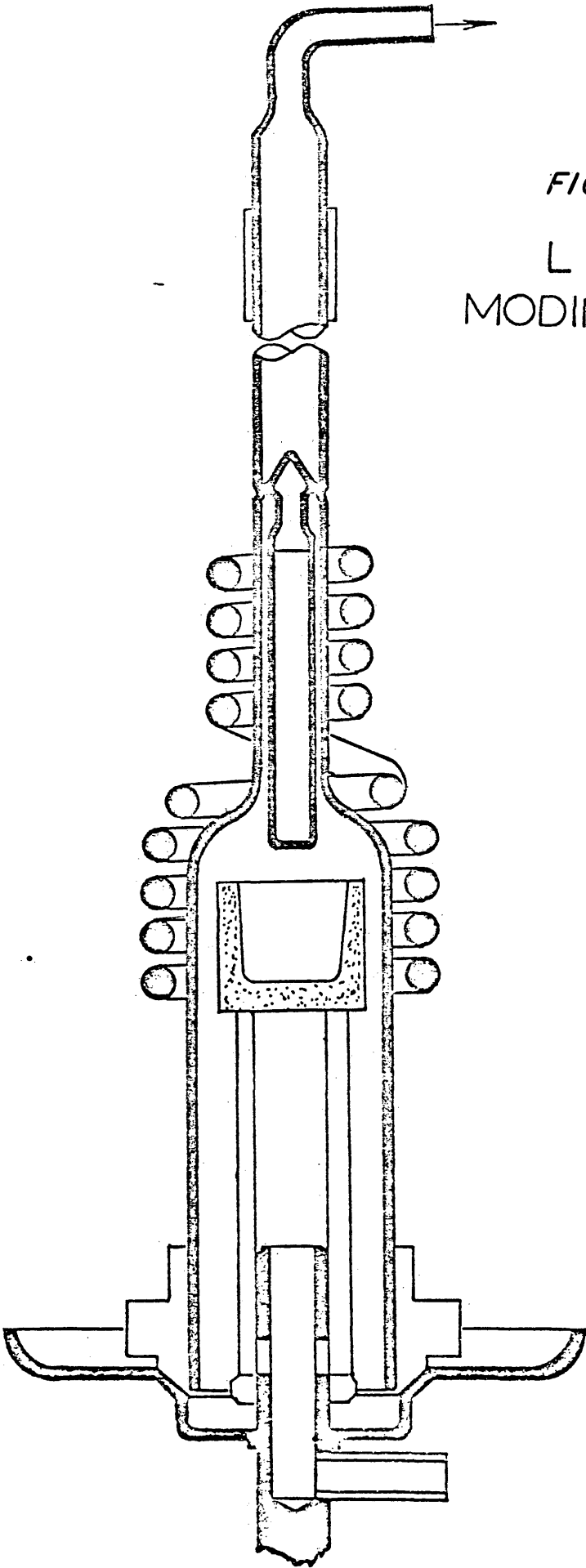
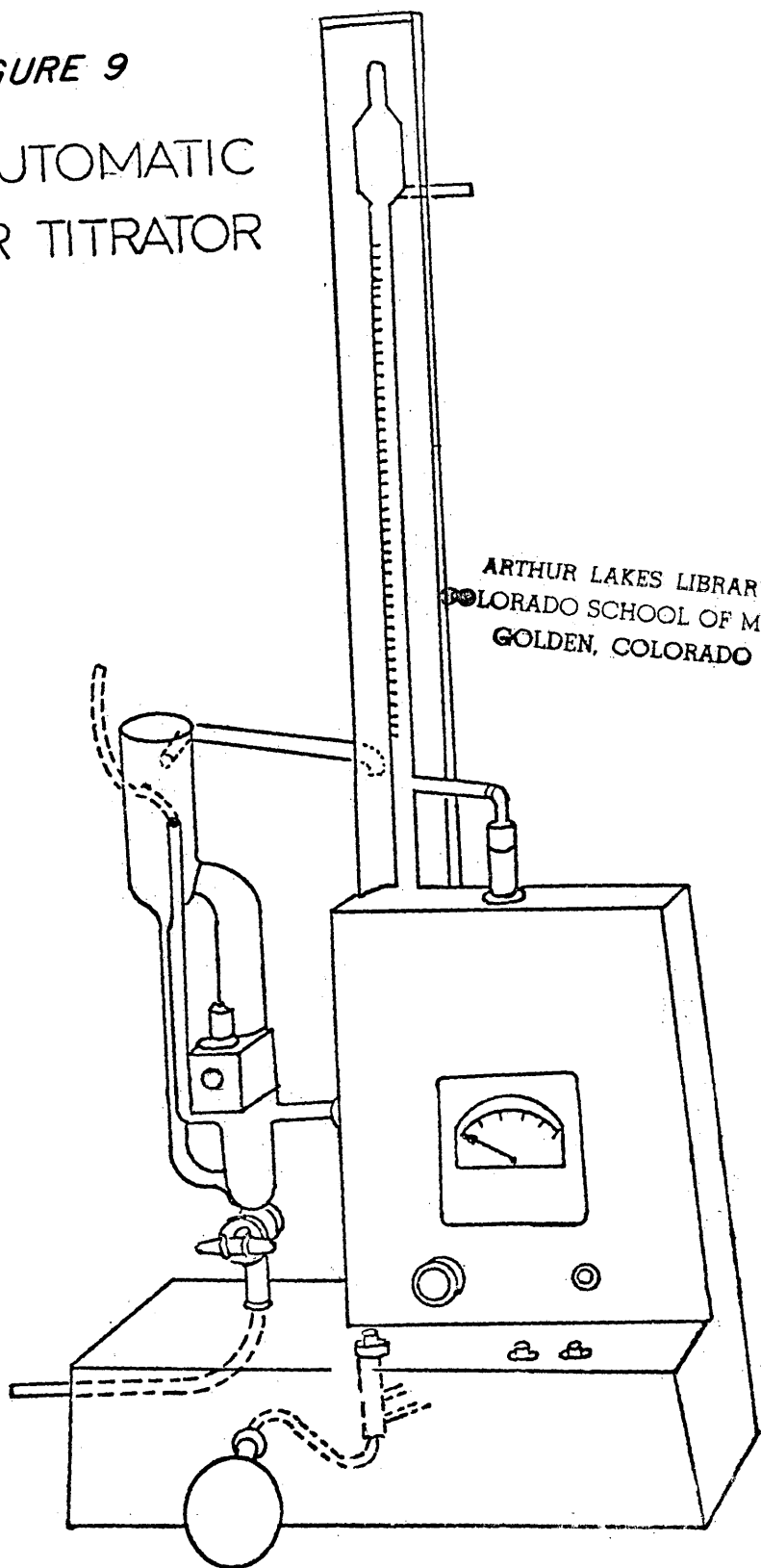


FIGURE 8  
L  
MODIFICATION



**FIGURE 9**  
SEMI-AUTOMATIC  
SULFUR TITRATOR



rapid and reliable method for analyzing the solvents for total sulfur. The reported accuracy of the test is  $\pm 0.01$  weight percent sulfur.

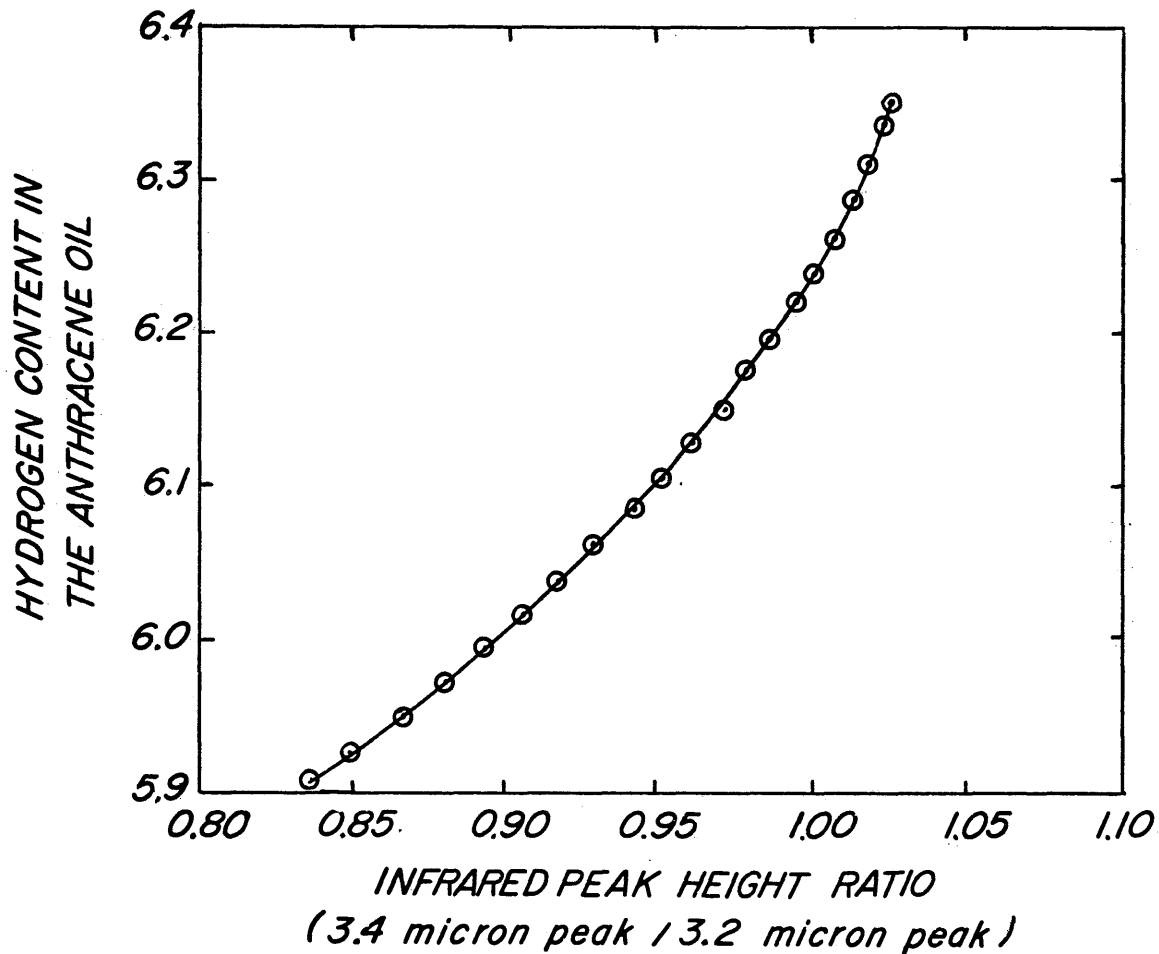
#### Infrared Spectrophotometric Analysis

The weight percent hydrogen contained by the anthracene oil was determined using an infrared spectrophotometric procedure provided by the Pittsburgh and Midway Coal Mining Company of Meriam, Kansas (94). A Perkin-Elmer Model 21 infrared spectrophotometer was used for this analysis. The test is based upon the carbon-hydrogen bond stretching when exposed to infrared energy. This stretching causes a pair of peaks at 3.2 and 3.4 microns to appear on the infrared chart. The ratio of the heights of the two peaks varies as does the percentage of hydrogen contained in the anthracene oil sample.

A standardization curve is determined by mixing varying amounts of raw anthracene oil with anthracene oil that was hydrogenated. Conventional carbon-hydrogen tests, performed by Huffman Laboratories, Inc. in Denver, Colorado, confirmed the I-R data. The reclaimed anthracene oil samples were tested and the ratio of the peak heights were compared to the calibration curve from which the weight percent hydrogen was directly read. This calibration curve is shown by Figure 10.

The tetralin samples were analyzed by Huffman Laboratories, Inc. for the weight percent hydrogen.

FIGURE 10  
INFRARED SPECTROPHOTOMETRIC  
ANALYSIS CALIBRATION CURVE



#### Heating Value Determination

The heating value of the char was determined using a standard bomb calorimetry technique (95), with the following modifications:

- 1) Determine the grams of total sulfur in the sample from the total sulfur data.
- 2) Determine the ml of  $\text{NH}_3$  solution titrated due to total sulfur content by dividing the total sulfur weight in the sample by 0.0061.



- 3) Determine the ml of  $\text{NH}_3$  solution titrated due to nitrogen by calculating the difference in ml of the reported titration and that due only to sulfur.
- 4) Determine the heat content due to sulfur, S, by multiplying the centigrams of sulfur with the sample by 23.3 Btu-g/lb-centigrams.
- 5) Determine the heat content due to nitrogen, N, by multiplying the ml required for nitrogen titration by 10 Btu-g/lb-ml.
- 6) Calculate the heating value of the sample char by the following formula:

$$\text{HV} = \frac{(\Delta T)(E) - \Delta F + S + N}{\text{sample wt in grams}}$$

where:

HV = heating value, Btu/lb

$\Delta T$  = corrected temperature change, °C

E = calorimeter water equivalent (Btu/lb)(g/°C)

$\Delta F$  = heat correction for nichrome wire fused during combustion, Btu-g/lb

S = correction for heat due to sulfur content, Btu-g/lb, and

N = correction for heat due to nitrogen content, Btu-g/lb.

The experimental tests were performed by the Colorado School of Mines Research Institute, Golden, Colorado.

## DISCUSSION OF RESULTS

### Material Balances and Sulfur Analyses

#### Experimental Run Mass Balances

After cooling and venting the reaction vessel, the reaction product was poured into the distillation flask and weighed. The nature of the char slurry was directly related to the solvent type and to the solvent-to-char ratio used for each run. The anthracene oil-char slurry varied in consistency from a thick, tar-like sludge at the 2/1 ratio to a viscous but easily-pourable liquid at the 5/1 ratio. Both the reaction feed and product slurries indicated a lower degree of dissolution of the char into the anthracene oil had taken place as compared to the previous coal desulfurization experiments at the Colorado School of Mines (1,2,3,4,5). The tetralin-char slurries were thin with the char easily identifiable and relatively unchanged in nature physically from the raw char in the feed. Losses due to solvent flashing and other gaseous products as well as transferred losses were calculated and the percent material accounted for before the vacuum distillation is shown in Table 7. These losses averaged about 10 percent of the total reaction mass charged to the reaction vessel.

Table 8 shows the mean material accountabilities before distillation as a function of the operating variables.

Table 7  
Material Accountability Before and During Vacuum Distillation

Run No.	Total Material Before (g)	Percent Material Accounted for Before Distillation	Total Material After (g)	Loss Due to Distillation (g)	Percent Material Lost During Vacuum Distillation
1A	267	89.0	267	0	0
1B	291	97.0	286	-5	1.7
2A	287	95.7	283	-4	1.4
2B	285	95.0	281	-4	1.4
3A	280	93.3	269	-11	3.9
3B	286	95.3	279	-7	2.4
4A	135	90.0	135	0	0
4B	128	85.3	126	-2	1.6
5A	116	77.3	116	0	0
5B	132	88.0	124	-8	6.1
6A	127	84.7	122	-5	3.9
6B	137	91.3	134	-3	2.2
7A	271	90.3	253	-18	6.6
7B	280	93.3	278	-2	0.7
8A	129	84.0	120	-9	7.0
8B	138	92.0	126	-12	8.7
9A	284	94.7	284	0	0
9B	283	94.3	279	-4	1.4

Table 7 (Cont.)

Run No.	Total Material Before (g)	Percent Material Accounted for Before Distillation	Total Material After (g)	Loss Due to Distillation (g)	Percent Material Lost During Vacuum Distillation
10A	140	93.3	135	-5	3.6
10B	123	82.0	119	-4	3.3
11A	128	85.3	125	-3	2.3
11B	131	87.3	126	-5	3.8
12A	132	88.0	127	-5	3.8
12B	136	90.7	131	-5	3.7
13A	288	96.0	275	-13	4.5
13B	281	93.7	279	-2	0.7
14A	276	92.0	272	-4	1.4
14B	279	93.0	273	-6	2.2
15A	274	91.3	271	-3	1.1
15B	287	95.7	283	-4	1.4
16A	123	82.0	119	-4	3.3
16B	130	86.7	126	-4	3.1
17A	263	87.7	259	-4	1.5
18A	121	80.7	121	0	0
19A	274	91.3	274	0	0
20A	119	79.3	115	-4	3.4

Table 8  
 Mean Material Accountabilities Before Distillation as  
 a Function of Operating Variables

<u>Solvent Type</u>	<u>% Accounted For</u>	<u>Solvent-to-Char Ratio</u>	<u>% Accounted For</u>
Tetralin	90.0	2/1	86.0
Anthracene Oil	89.4	5/1	93.3

<u>Temperature</u>	<u>% Accounted For</u>	<u>Hydrogen Partial Pressure</u>	<u>% Accounted For</u>
325°C	90.5	1000 psig	89.1
425°C	89.9	2000 psig	90.2
475°C	84.8		

Solvent type, pressure, and lower temperature showed no trends on material losses, but losses were significantly higher at the 2/1 solvent-to-char ratio and at the highest temperature studied, 475°C. Assuming that actual transfer losses in grams were about equal at both solvent-to-char ratios, the loss at the lower (2/1) ratio would be a greater percentage of the total mass than at the higher ratio. More loss at the higher temperature (475°C) indicates more flashing of solvent and formation of more gases than at lower temperatures (325°C, 425°C)

The distillation flasks were sealed and the vacuum distillation proceeded until no more solvent could be recovered from the treated char, usually about 325°C for tetralin and 400°C for anthracene oil. Recovered solvent and char

product weights were determined by difference measurements made on the distillation vessels before and after the vacuum distillation operation, and overall mass balances are given in Table 9. Since the losses during the distillation operation were small, averaging about 2-3 percent as shown in Table 7, and since the char yield was essentially 100 percent, most of the solvent losses were probably due to transferring of fluids from the various vessels, beakers, and flasks used.

The separation of solvents from the treated char was relatively easy as compared to the previous coal experiments (1,2,3,4,5), indicating little or no depolymerization of the char and only partial dissolution of the char had occurred as compared to the high degree of dissolution of coal in anthracene oil. The solvent refined char product was still in granular form and could be poured from the distillation flask in all of the runs, again indicating little interaction between the solvent and the char. However, anthracene oil was found to be a better solvent than tetralin, due to the slight degree of dissolution of char in the anthracene oil as compared to no association of the tetralin and char. This is also supported by the tendency of slightly higher than 100 percent char yields in the anthracene oil runs and slightly lower than 100 percent char yields with tetralin as a solvent.

Table 9  
Overall Mass Balance on Char and Solvent

Run No.	Solvent Refined Char (g)	Solvent (g)	% Char Yield	% Solvent Recovered
1A	49	218	98.0	87.2
1B	50	236	100.0	94.4
2A	61	222	122.0	88.8
2B	51	230	102.0	92.0
3A	52	217	104.0	86.8
3B	51	228	102.0	91.2
4A	51	83	102.0	83.0
4B	47	79	94.0	79.0
5A	47	69	94.0	69.0
5B	52	72	104.0	72.0
6A	43	79	86.0	79.0
6B	53	81	106.0	81.0
7A	33	220	66.0	88.0
7B	56	222	112.0	88.8
8A	39	81	78.0	81.0
8B	50	76	100.0	76.0
9A	53	231	106.0	92.4
9B	57	222	114.0	88.8
10A	49	86	98.0	86.0
10B	44	75	88.0	75.0
11A	45	80	90.0	80.0
11B	42	84	84.0	84.0
12A	50	77	100.0	77.0
12B	47	84	94.0	84.0
13A	51	224	102.0	89.6
13B	50	229	100.0	91.6
14A	49	223	98.0	89.2
14B	53	220	106.0	88.0
15A	49	222	98.0	88.8
15B	54	229	108.0	91.6
16A	45	74	90.0	74.0
16B	47	79	94.0	79.0
17A	60	199	120.0	79.6
18A	55	66	110.0	66.0
19A	53	221	106.0	88.4
20A	67	48	134.0	48.0

### Sulfur Content of the Solvent Refined Char

The sulfur content of the raw and treated char samples is listed in Table 10. The inorganic sulfur content is the sum of pyritic and sulfate sulfur content, while the organic sulfur content is the difference between total and inorganic sulfur contents.

Note that in Table 10 the absolute pyritic and sulfate sulfur contents are very small compared to the organic and total sulfur contents. This is due to the fact that most of the inorganic sulfur containing compounds were removed during the formation of char, and that the organic sulfur remaining is more tightly bonded than was the released inorganic sulfur. Since the ASTM techniques have accuracies of  $\pm 0.02$  weight percent for sulfate sulfur content and  $\pm 0.05$  weight percent for pyritic sulfur content, and since the measured pyritic and sulfur contents are no larger than these tolerances in most cases, wide variations in replicate runs, such as those observed, can be expected. Thus, the importance of the sulfur removal results rests in the total sulfur analysis, where the data better agrees with the reported accuracy of the test at  $\pm 0.05$  weight percent.

Although the uncertainty in the analytical procedure for the detection of the insoluble inorganic sulfur form, FeS, is noted (4,5), the magnitude of the FeS in char should not be significant in respect to total sulfur content.



Table 10  
Sulfur Content of Solvent Refined Char

<u>Run No.</u>	<u>Weight Percent Sulfur</u>				<u>Total</u>
	<u>Sulfate</u>	<u>Pyritic</u>	<u>Inorganic</u>	<u>Organic</u>	
Char Head	0.02	0.09	0.11	3.63	3.74
1A	0.03	0.41	0.44	2.04	2.48
1B	0.02	0.04	0.06	2.44	2.50
2A	0.04	0.21	0.25	2.39	2.64
2B	0.01	0.13	0.14	2.62	2.76
3A	0.04	0.10	0.14	2.45	2.59
3B	0.02	0.18	0.20	2.36	2.56
4A	0.03	0.06	0.09	2.61	2.70
4B	0.01	0.04	0.05	2.73	2.78
5A	0.03	0.19	0.22	3.26	3.48
5B	0.02	0.14	0.16	3.29	3.45
6A	0.02	0.08	0.10	2.94	3.04
6B	0.02	0.04	0.06	3.16	3.22
7A	0.02	0.09	0.11	3.04	3.15
7B	0.01	0.07	0.08	2.85	2.93
8A	0.02	0.06	0.08	3.31	3.39
8B	0.01	0.06	0.07	3.12	3.19
9A	0.02	0.06	0.08	2.47	2.55
9B	0.01	0.27	0.28	2.39	2.67
10A	0.02	0.05	0.07	3.00	3.07
10B	0.01	0.07	0.08	2.94	3.02
11A	0.02	0.22	0.24	2.80	3.04
11B	0.01	0.17	0.18	3.12	3.30
12A	0.02	0.16	0.18	2.99	3.15
12B	0.02	0.23	0.25	3.04	3.29
13A	0.02	0.15	0.17	2.74	2.91
13B	0.01	0.22	0.23	2.61	2.84
14A	0.02	0.13	0.15	2.60	2.75
14B	0.01	0.16	0.17	2.69	2.86
15A	0.01	0.06	0.07	3.27	3.34
15B	0.02	0.08	0.10	3.20	3.30
16A	0.01	0.22	0.23	2.62	2.85
16B	0.02	0.24	0.26	2.49	2.75
17A	0.00	0.18	0.18	2.51	2.69
18A	0.00	0.09	0.09	2.78	2.87
19A	0.00	0.16	0.16	2.27	2.43
20A	0.01	0.45	0.46	1.84	2.30

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Percent Sulfur Removal

Table 11 presents the percentage values for the inorganic sulfur, organic sulfur, and total sulfur removal from the solvent refined chars, with an asterisk (\*) indicating a gain in sulfur type upon treatment. As was previously mentioned, the inorganic sulfur content is relatively small and is composed of uncertain values for pyritic and sulfate sulfur contents. The more reliable total sulfur percent removal ranges from 7.0 to 38.5 percent.

The mean average percent removal of total residual sulfur content for each of the operating variables is given in Table 12. Examination of these values shows clearly the importance of temperature in the reaction as better desulfurization of the char was achieved at 475°C than at 425°C or at 325°C. It is also evident that the higher hydrogen partial pressure, 2000 psig, allowed more desulfurization than the runs at 1000 psig. The data do not support such an absolute judgement for solvent-to-char ratio or solvent type, where general trends are not as easily identified. Statistical analysis will support these trends and detect the significance of solvent type and solvent-to-char ratios.

Sulfur Content of Recovered Solvents

After recovering the anthracene oil and tetralin solvents from the treated char by vacuum distillation, the solvent's total sulfur content was measured by the Leco induction

Table 11

## Percent Sulfur Removal of Solvent Refined Char

<u>Run No.</u>	<u>Inorganic Sulfur</u>	<u>Organic Sulfur</u>	<u>Total Sulfur</u>
1A	*300.0	43.8	33.7
1B	45.5	32.8	33.2
2A	*127.3	34.2	29.4
2B	* 27.3	27.8	26.2
3A	* 27.3	32.5	30.7
3B	* 81.8	35.0	31.6
4A	18.2	28.1	27.8
4B	54.5	24.8	25.7
5A	*100.0	10.2	7.0
5B	* 45.5	9.4	7.8
6A	9.1	19.0	18.7
6B	45.5	12.9	13.9
7A	0.0	16.3	15.8
7B	27.3	21.5	21.7
8A	27.3	8.8	9.4
8B	36.4	14.0	14.7
9A	27.3	32.0	31.8
9B	*154.5	34.1	28.6
10A	36.4	17.4	17.9
10B	27.3	19.0	19.3
11A	*118.2	22.9	18.7
11B	* 63.6	14.0	11.8
12A	* 63.6	17.6	15.8
12B	*127.3	16.3	12.0
13A	* 54.5	24.5	22.2
13B	*109.1	28.1	24.1
14A	* 36.4	28.4	26.5
14B	* 54.5	25.9	23.5
15A	36.4	9.9	10.7
15B	9.1	11.8	11.8
16A	*109.1	27.8	23.8
16B	*136.4	31.4	26.5
17A	* 63.6	30.9	28.1
18A	18.2	23.4	23.3
19A	45.5	37.5	35.0
20A	*318.2	49.3	38.5

\*Indicates percentage gained by treatment, i.e. Run 1A increased its inorganic sulfur content by 300.0 percent upon treatment.

Table 12

Mean Percent Total Residual Sulfur Removal  
as a Function of Operating Variables

<u>Solvent Type</u>	<u>% Total Residual Sulfur Removal</u>	<u>Solvent-to-Char Ratio</u>	<u>% Total Residual Sulfur Removal</u>
Tetralin	20.9	2/1	20.0
Anthracene Oil	23.1	5/1	25.8
<u>Temperature</u>	<u>% Total Residual Sulfur Removal</u>	<u>Hydrogen Partial Pressure</u>	<u>% Total Residual Sulfur Removal</u>
325°C	18.5		
425°C	23.6	1000 psig	17.2
475°C	31.2	2000 psig	27.1

furnace technique. These values are shown in Table 13. The tetralin solvent showed no measureable sulfur content either initially or after recovery. However, the anthracene oil lost up to 90 percent of its initial sulfur content upon treatment with the char. Again, higher temperatures and pressures decreased the percent sulfur remaining in the recovered anthracene oil.

#### Sulfur Balances

An effort was made to close the sulfur balance for the experimental runs. The grams of sulfur lost by the reaction feeds and products were compared to the grams of sulfur, as H<sub>2</sub>S, detected by the scrubber analysis. These results are given in Table 14. The wide range of sulfur accountability

Table 13

## Sulfur Content of Recovered Solvents

Run No.	Wt % Sulfur	Total Sulfur Mass (g)	% Change in Sulfur Content	Run No.	Wt % Sulfur	Total Sulfur Mass (g)	% Change in Sulfur Content
1A	-	-	-	10A	-	-	-
1B	-	-	-	10B	-	-	-
2A	0.39	0.87	0.0	11A	0.22	0.18	-43.6
2B	0.38	0.87	-2.6	11B	0.36	0.31	-7.7
3A	0.27	0.59	-30.8	12A	0.27	0.21	-30.8
3B	0.37	0.84	-5.1	12B	0.27	0.22	-30.8
4A	-	-	-	13A	0.25	0.56	-35.9
4B	-	-	-	13B	0.24	0.56	-38.5
5A	0.29	0.20	-25.6	14A	0.23	0.50	-41.0
5B	0.66	0.48	+69.2	14B	0.21	0.48	-46.2
6A	-	-	-	15A	-	-	-
6B	-	-	-	15B	-	-	-
7A	-	-	-	16A	0.11	0.08	-71.8
7B	-	-	-	16B	0.09	0.07	-76.9
8A	-	-	-	17A	0.11	0.22	-71.8
8B	-	-	-	18A	0.16	0.11	-59.0
9A	-	-	-	19A	0.11	0.25	-71.8
9B	-	-	-	20A	0.04	0.02	-89.7

Sulfur content of raw anthracene oil = 0.39 wt %

Raw anthracene oil sulfur content at 5/1 solvent/char ratio  
(250 g total mass) = 0.98 g

Raw anthracene oil sulfur content at 2/1 solvent/char ratio  
(100 g total mass) = 0.39 g

Sulfur content of raw tetralin = 0.00 wt %

Table 14  
Sulfur Balances

Run No.	Reaction (Char+Solvent)		Off-Gas		Moles H <sub>2</sub> S	Wt Sulfur (g)	% Sulfur Accounted
	In (g)	Out (g)	Δ (g)	Liter H <sub>2</sub> S at STP			
1A	1.87	1.22	0.65	0.071	0.003	0.10	15.4
1B	1.87	1.25	0.62	0.276	0.012	0.39	62.9
2A	2.84	2.47	0.37	0.105	0.005	0.15	40.5
2B	2.84	2.26	0.58	0.371	0.017	0.53	91.4
3A	2.84	1.93	0.91	0.372	0.017	0.53	58.2
3B	2.84	2.14	0.70	0.271	0.012	0.39	55.7
4A	1.87	1.38	0.49	0.102	0.005	0.15	30.6
4B	1.87	1.31	0.56	0.250	0.011	0.36	64.3
5A	2.26	1.84	0.42	0.413	0.018	0.59	*140.5
5B	2.26	2.27	*0.01	0.394	0.018	0.56	*5600.0
6A	1.87	1.31	0.56	0.081	0.004	0.12	21.4
6B	1.87	1.71	0.16	0.151	0.007	0.21	*131.3
7A	1.87	1.02	0.85	0.130	0.006	0.19	22.4
7B	1.87	1.64	0.23	0.041	0.002	0.06	26.1
8A	1.87	1.32	0.55	0.118	0.005	0.17	30.9
8B	1.87	1.60	0.27	0.083	0.004	0.12	44.4
9A	1.87	1.35	0.52	0.125	0.006	0.18	34.6
9B	1.87	1.52	0.35	0.030	0.001	0.04	11.4

\*Indicates more sulfur in off-gas than lost in reaction, probably due to poor off-gas analysis.

Table 14 (Cont.)

Run No.	Reaction (Char+Solvent)		Off-Gas			Wt Sulfur (g)	% Sulfur Accounted
	In (g)	Out (g)	$\Delta$ (g)	Liter H <sub>2</sub> S at STP	Moles H <sub>2</sub> S		
10A	1.87	1.50	0.37	0.308	0.014	0.44	*118.9
10B	1.87	1.33	0.54	0.112	0.005	0.16	29.6
11A	2.26	1.54	0.72	0.446	0.020	0.64	88.9
11B	2.26	1.69	0.57	0.002	0.000	0.00	0.0
12A	2.26	1.78	0.48	0.317	0.014	0.45	93.8
12B	2.26	1.77	0.49	0.317	0.014	0.45	91.8
13A	2.84	2.04	0.80	0.171	0.008	0.24	30.0
13B	2.84	1.98	0.86	0.087	0.004	0.13	15.1
14A	2.84	1.85	0.99	0.385	0.017	0.55	55.5
14B	2.84	1.99	0.85	0.054	0.002	0.08	9.4
15A	1.87	1.62	0.25	0.130	0.006	0.19	76.0
15B	1.87	1.78	0.09	0.033	0.002	0.05	55.5
16A	2.26	1.36	0.90	0.216	0.010	0.31	34.4
16B	2.26	1.37	0.89	0.144	0.006	0.21	23.6
17A	2.84	1.84	1.00	0.247	0.011	0.35	35.0
18A	2.26	1.69	0.57	0.274	0.012	0.39	68.4
19A	2.84	1.54	1.30	0.383	0.017	0.55	42.3
20A	2.26	1.56	0.70	0.349	0.016	0.50	71.4

\*Indicates more sulfur in off-gas than lost in reaction, probably due to poor off-gas analysis.

may be explained by handling losses or may be an indication of poor reliability of the scrubber technique. Similar results and uncertainties were obtained by Bao (4)

#### Effect on Hydrogen Content of the Solvents

In addition to total sulfur analysis, the hydrogen content of the solvents were measured. This effect is important if the process is to be tested on a continuous basis, since recycling of the solvent will be an economic necessity. Table 15 lists the weight percent hydrogen contents and corresponding percent deficiencies or gains for the tetralin and anthracene oil experimental runs. The data shows slight hydrogen deficiencies for the 2/1 tetralin-to-char ratio runs with corresponding hydrogen gains at the 5/1 tetralin-to-char ratio. All of the anthracene oil runs show a gain in weight percent hydrogen, but no obvious trend can be made with respect to the operating variables. Statistical analysis will add more insight to these results.

#### Effect on Heating Value of the Char

The heating value, or the Btu content, of the chars was measured by bomb calorimetry techniques and the data with corresponding percentage gains is given in Table 16. Although all runs show an improvement in heating value, experimental runs 2A and 3A, using an anthracene oil-to-char ratio of 5/1 and reactor conditions at 2000 psig, gave the

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Table 15

## Weight Percent Hydrogen Content of Solvents

<u>Tetralin Runs</u>			<u>Anthracene Runs</u>		
<u>Run No.</u>	<u>Wt % Hydrogen</u>	<u>% Change</u>	<u>Run No.</u>	<u>Wt % Hydrogen</u>	<u>% Change</u>
Raw	9.16		Raw	5.93	
1A	9.24	0.87	2A	5.95	0.34
1B	9.23	0.76	2B	5.95	0.34
4A	9.14	-0.22*	3A	6.08	2.53
4B	9.04	-1.31*	5A	6.00	1.18
6A	9.00	-1.75*	5B	6.07	2.36
6B	9.09	-0.76*	11A	6.19	4.38
7A	9.30	1.53	11B	6.11	3.04
7B	9.23	0.76	12A	6.12	3.20
8A	9.37	2.29*	12B	6.05	2.02
8B	9.15	-0.11*	13A	5.96	0.51
9A	9.23	0.76	14A	6.06	2.19
9B	9.20	0.44	14B	6.04	1.85
10A	9.10	-0.66*	16A	6.27	5.73
10B	9.15	-0.11*	16B	6.29	6.07
15A	9.23	0.76	17A	6.03	1.69
15B	9.18	0.22	18A	5.99	1.01
			19A	6.15	3.71
			20A	6.09	2.70

Note: negative sign denotes hydrogen deficiency after treatment.

\* Denotes 2/1 solvent-to-char ratio.

Table 16  
Heating Values of Solvent Refined Char

<u>Run No.</u>	<u>Heating Value Btu/lb</u>	<u>Percent Gain</u>
1B	12800	5.9
2A	13470	11.4
3A	13350	10.4
4A	12560	3.9
5A	12180	0.7
6A	12180	0.7
7A	12100	0.1
8B	12440	2.9
9B	12500	3.4
10A	12960	7.2
11A	12330	2.0
12A	12680	4.9
13A	12530	3.6
14A	12980	7.4
15A	12460	3.1
16A	13100	8.4

most improvement. Effects of the process variables are shown by Figures 11 to 14. The tetralin and anthracene oil isobars indicate a greater improvement at 2000 psig for both solvent-to-char ratios, while heating values at the 2/1 SCR for the tetralin and the 5/1 SCR for anthracene oil are greater at each pressure level. Isotherms in Figures 13 and 14 show the importance of increasing pressure, while the effect of temperature is obvious for tetralin but not for anthracene oil.

#### Statistical Analysis

The experimental data were statistically studied by means of an analysis of variance technique. Also, a hypothesis testing method was used to validate the plots of the isobars

FIGURE 11  
HEATING VALUE ISOBARS  
TETRALIN SOLVENT

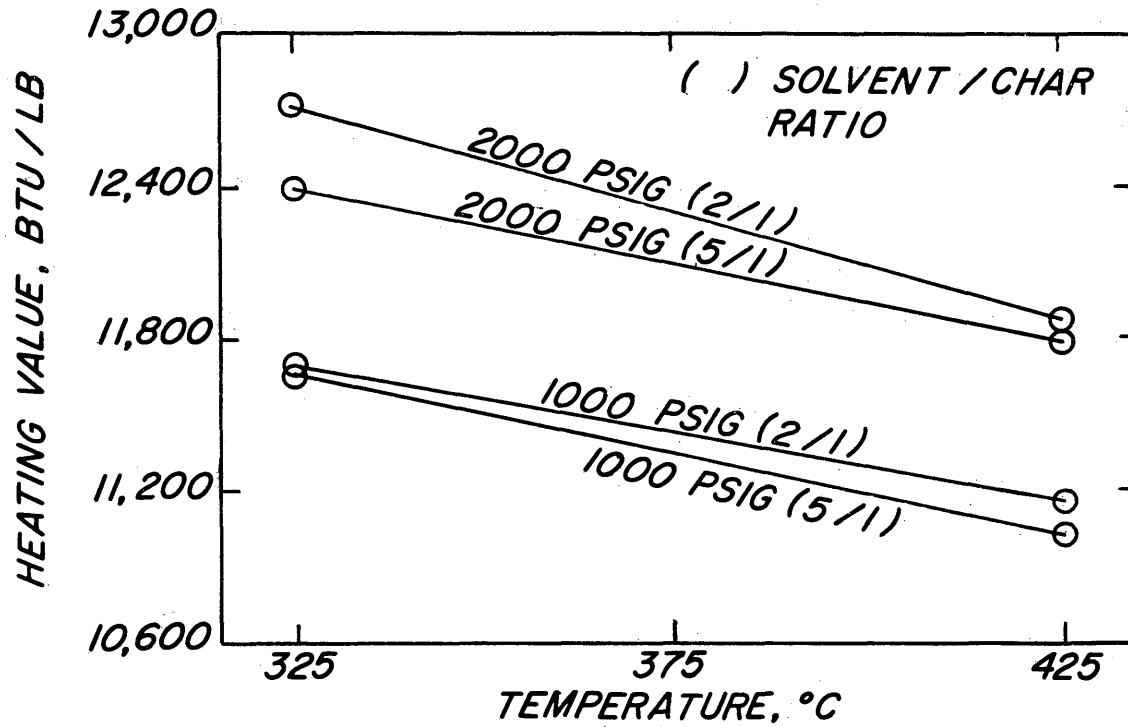


FIGURE 12  
HEATING VALUE ISOBARS  
ANTHRACENE OIL SOLVENT

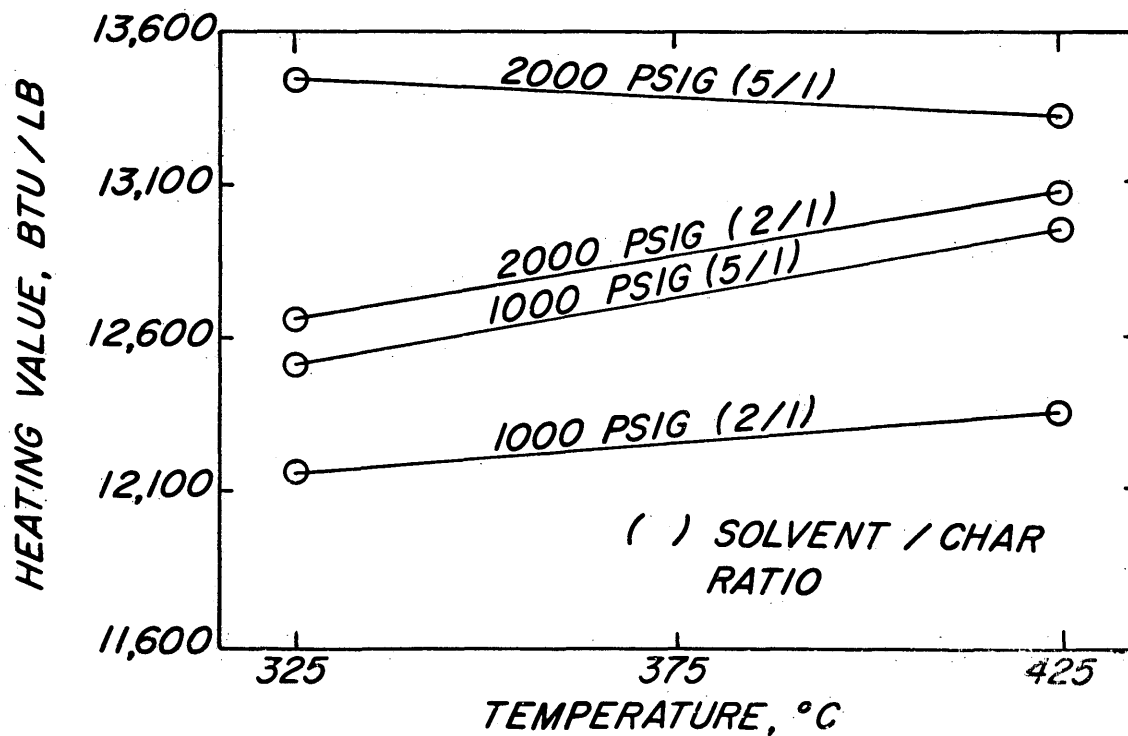


FIGURE 13  
HEATING VALUE ISOTHERMS  
TETRALIN SOLVENT

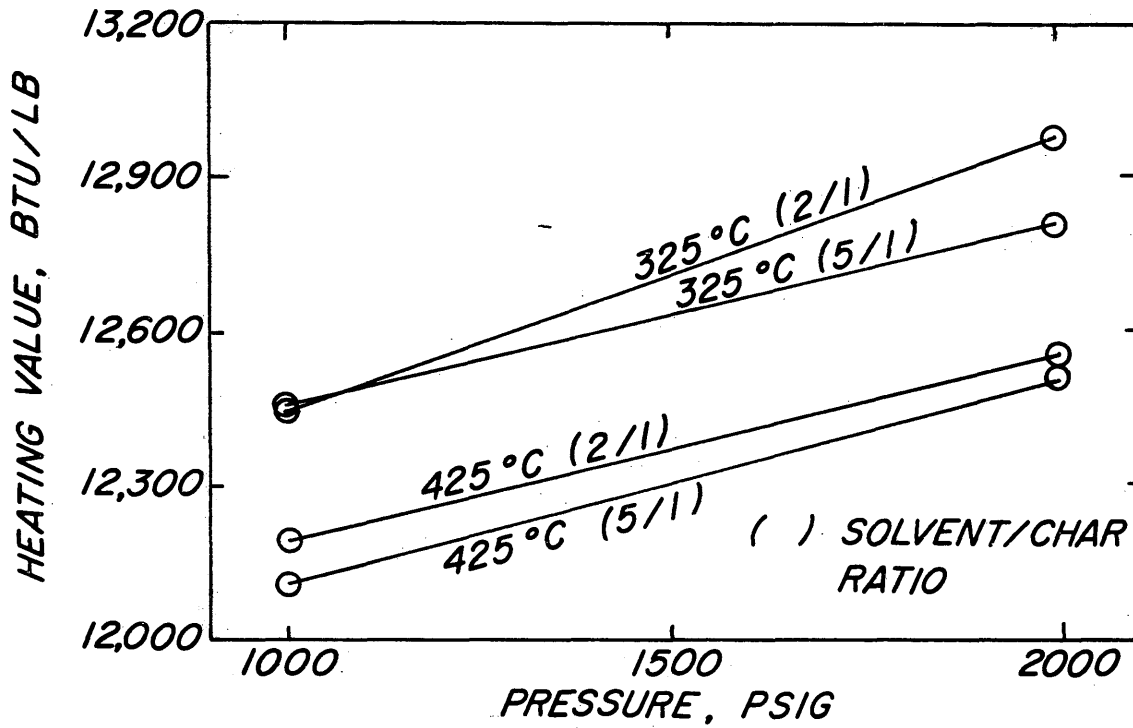
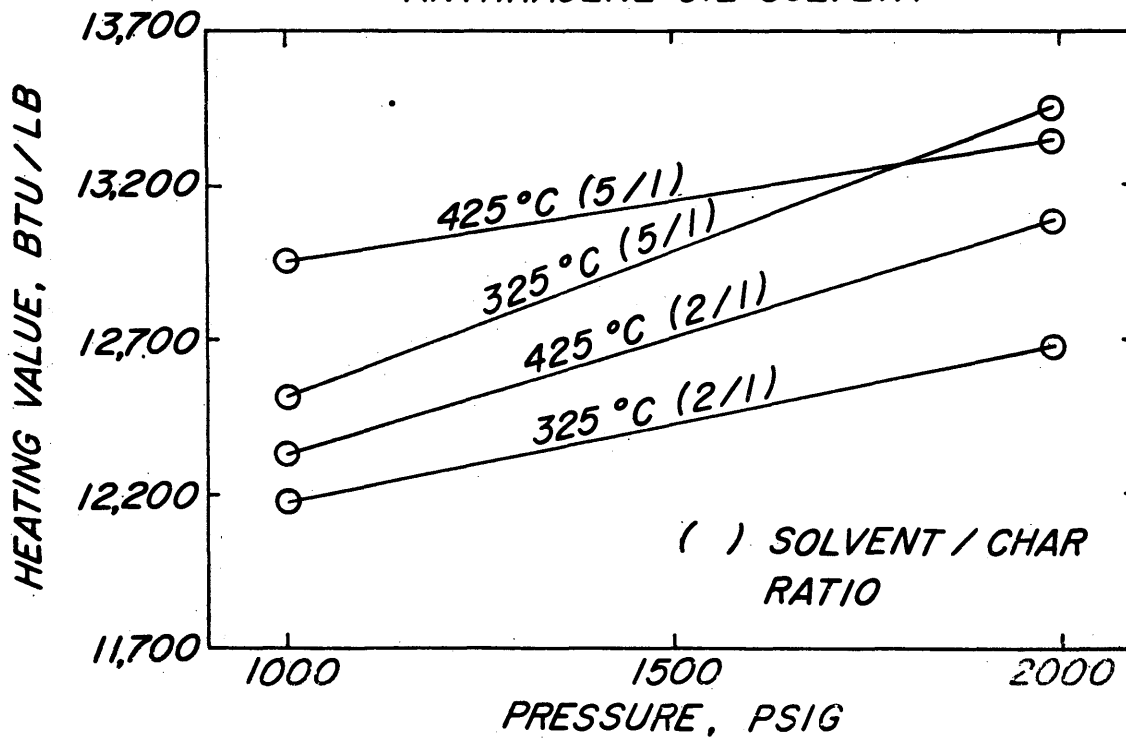


FIGURE 14  
HEATING VALUE ISOTHERMS  
ANTHRACENE OIL SOLVENT



and isotherms for the average values of total residual sulfur contents.

#### Analysis of Variance Technique

The importance of the main effects and interactions of the 4 process variables used in this investigation was studied and analyzed in a statistical manner. The "F" statistic was employed as a measure of the relative significance of the variables, with the comparative "F" values at varying confidence levels given in Table 17.

Table 17

#### "F" Values at Varying Confidence Levels

<u>Confidence Level</u>	<u>"F" Statistic (16,1)</u>	<u>Confidence Level</u>	<u>"F" Statistic (1,1)</u>
95	4.49	75	5.83
99	8.53	90	39.86
99.9	16.12	95	161.4

The significance of the process variables were analyzed for each of the following sets of data: total residual sulfur content, organic residual sulfur content, inorganic residual sulfur content (pyritic + sulfate), percent change in hydrogen content of the recovered solvent, and heating value of the treated char. Two computer programs, listed in Appendix 2, were written to use Yates' technique to compute the ANOVA tables for this data, and these ANOVA tables are given in Tables 18 to 22.

Table 18

## ANALYSIS FOR TOTAL SULFUR

## NOMENCLATURE:

A = TEMPERATURE  
 B = PRESSURE  
 C = SOLVENT/CHAR RATIO  
 D = SOLVENT TYPE

EXP.	EXP. DATA					
	REP 1	REP 2	EXP	REP 1	REP 2	
(1)	3.39	3.19	D	3.48	3.45	
A	3.04	3.22	AD	3.04	3.30	
B	3.07	3.02	BD	3.15	3.29	
AB	2.70	2.78	ABD	2.85	2.75	
C	3.34	3.30	CD	2.91	2.84	
AC	3.15	2.93	ACD	2.75	2.86	
BC	2.48	2.50	BCD	2.64	2.76	
ABC	2.55	2.67	ABCD	2.59	2.56	

## ANOVA TABLE

EFFECT	COLUMN OPERATIONS					S.S.	MSR	
(1)	6.58	12.84	24.41	47.33	94.55			
A	6.26	11.57	22.92	47.22	-3.07	-0.19	0.29	34.09
B	6.09	12.72	25.31	-1.25	-5.83	-0.36	1.06	122.93
AB	5.48	10.20	21.91	-1.82	0.15	0.01	0.00	0.08
C	6.64	13.27	-0.93	-3.79	-4.89	-0.31	0.75	86.49
AC	6.08	12.04	-0.32	-2.04	1.65	0.10	0.09	9.85
BC	4.98	11.36	-1.43	0.51	-0.83	-0.05	0.02	2.49
ABC	5.22	10.55	-0.39	-0.36	1.23	0.08	0.05	5.47
D	6.93	-0.32	-1.27	-1.49	-0.11	-0.01	0.00	0.04
AD	6.34	-0.61	-2.52	-3.40	-0.57	-0.04	0.01	1.18
BD	6.44	-0.56	-1.23	0.61	1.75	0.11	0.10	11.08
ABD	5.60	0.24	-0.81	1.04	-0.87	-0.05	0.02	2.74
CD	5.75	-0.59	-0.29	-1.25	-1.91	-0.12	0.11	13.19
ACD	5.61	-0.84	0.80	0.42	0.43	0.03	0.01	0.67
BCD	5.40	-0.14	-0.25	1.09	1.67	0.10	0.09	10.09
ABCD	5.15	-0.25	-0.11	0.14	-0.95	-0.06	0.03	3.26

TOTAL SUM OF SQUARES 2,7617874  
 TREATMENT SUM OF SQUARES 2,6235469  
 RESIDUAL SUM OF SQUARES 0,1382405  
 MEAN RESIDUAL SUM OF SQUARES 0,0086400

Table 19

## ANALYSIS FOR ORGANIC SULFUR

## NOMENCLATURE:

A = TEMPERATURE  
 B = PRESSURE  
 C = SOLVENT/CHAR RATIO  
 D = SOLVENT TYPE

EXP.	EXP. DATA:		EXP	REP 1	REP 2
	REP 1	REP 2			
(1)	3.31	3.12	D	3.27	3.29
A	2.93	3.17	AD	2.81	3.12
B	3.01	2.94	BD	2.97	3.04
AB	2.61	2.72	ABD	2.63	2.49
C	3.26	3.20	CD	2.75	2.61
AC	3.04	2.85	ACD	2.60	2.70
BC	2.04	2.45	BCD	2.39	2.62
ABC	2.47	2.39	ABCD	2.45	2.36

## ANOVA TABLE

EFFECT	COLUMN OPERATIONS					S.S.	MSR	
(1)	6.43	12.53	23.81	45.51	89.61			
A	6.10	11.28	21.70	44.10	-2.93	-0.18	0.27	16.00
B	5.95	12.35	23.62	-1.15	-6.45	-0.40	1.30	77.54
AB	5.33	9.35	20.48	-1.78	0.25	0.02	0.00	0.12
C	6.46	12.49	-0.95	-4.25	-5.25	-0.33	0.86	51.37
AC	5.89	11.13	-0.20	-2.20	2.01	0.13	0.13	7.53
BC	4.49	10.66	-1.52	0.65	-1.23	-0.08	0.05	2.82
ABC	4.86	9.82	-0.26	-0.40	1.35	0.08	0.06	3.40
D	6.56	-0.33	-1.25	-2.11	-1.41	-0.09	0.06	3.71
AD	5.93	-0.62	-3.00	-3.14	-0.63	-0.04	0.01	0.74
BD	6.01	-0.57	-1.36	0.75	2.05	0.13	0.13	7.83
ABD	5.12	0.37	-0.84	1.26	-1.05	-0.07	0.03	2.05
CD	5.36	-0.63	-0.29	-1.75	-1.03	-0.06	0.03	1.98
ACD	5.30	-0.89	0.94	0.52	0.51	0.03	0.01	0.48
BCD	5.01	-0.06	-0.26	1.23	2.27	0.14	0.16	9.60
ABCD	4.81	-0.20	-0.14	0.12	-1.11	-0.07	0.04	2.30

TOTAL SUM OF SQUARES 3,4115047  
 TREATMENT SUM OF SQUARES 3,1432469  
 RESIDUAL SUM OF SQUARES 0,2682579  
 MEAN RESIDUAL SUM OF SQUARES 0,0167661

Table 20

## ANALYSIS FOR INORG, SULFUR

## NOMENCLATURE:

A = TEMPERATURE  
 B = PRESSURE  
 C = SOLVENT/CHAR RATIO  
 D = SOLVENT TYPE

EXP.	EXP. DATA:		EXP	EXP. DATA:	
	REP 1	REP 2		REP 1	REP 2
(1)	0.08	0.07	D	0.21	0.16
A	0.10	0.06	AD	0.24	0.18
B	0.06	0.08	BD	0.18	0.24
AB	0.09	0.05	ABD	0.22	0.26
C	0.07	0.09	CD	0.17	0.23
AC	0.11	0.08	ACD	0.15	0.17
BC	0.44	0.06	BCD	0.24	0.14
ABC	0.08	0.28	ABCD	0.14	0.20

## ANOVA TABLE

EFFECT	COLUMN OPERATIONS					S.S.	MSR	
(1)	0.15	0.31	0.59	1.80	4.93			
A	0.16	0.28	1.21	3.13	-0.11	-0.01	0.00	0.06
B	0.14	0.35	1.69	-0.10	0.59	0.04	0.01	1.59
AB	0.14	0.86	1.44	-0.01	-0.13	-0.01	0.00	0.08
C	0.16	0.79	0.01	0.48	0.37	0.02	0.00	0.63
AC	0.19	0.90	-0.11	0.11	-0.35	-0.02	0.00	0.56
BC	0.50	0.72	0.11	-0.18	0.43	0.03	0.01	0.85
ABC	0.36	0.72	-0.12	0.05	-0.13	-0.01	0.00	0.08
D	0.37	0.01	-0.03	0.62	1.33	0.08	0.06	8.10
AD	0.42	0.00	0.51	-0.25	0.09	0.01	0.00	0.04
BD	0.42	0.03	0.11	-0.12	-0.37	-0.02	0.00	0.63
ABD	0.48	-0.14	0.00	-0.23	0.23	0.01	0.00	0.24
CD	0.40	0.05	-0.01	0.54	-0.87	-0.05	0.02	3.47
ACD	0.32	0.06	-0.17	-0.11	-0.11	-0.01	0.00	0.06
BCD	0.38	-0.08	0.01	-0.16	-0.65	-0.04	0.01	1.94
ABCD	0.34	-0.04	0.04	0.03	0.19	0.01	0.00	0.17

TOTAL SUM OF SQUARES                   0,2351719  
 TREATMENT SUM OF SQUARES           0,1260219  
 RESIDUAL SUM OF SQUARES            0,1091500  
 MEAN RESIDUAL SUM OF SQUARES      0,0068219



Table 21

## ANALYSIS FOR % CHANGE H2

## NOMENCLATURE:

A = TEMPERATURE  
 B = PRESSURE  
 C = SOLVENT/CHAR RATIO  
 D = SOLVENT TYPE

EXP.	EXP. DATA:		EXP	REP	
	REP 1	REP 2		REP 1	REP 2
(1)	2.29	-0.11	D	1.18	2.36
A	-1.75	-0.76	AD	4.38	3.04
B	-0.66	-0.11	BD	3.20	2.02
AB	-0.22	-1.31	ABD	5.73	6.07
C	0.76	0.22	CD	0.51	0.51
AC	1.53	0.76	ACD	2.19	1.85
BC	0.87	0.76	BCD	0.34	0.34
ABC	0.76	0.44	ABCD	2.53	2.53

## ANOVA TABLE

EFFECT	COLUMN OPERATIONS					S.S.	MSR
(1)	2.18	-0.33	-2.63	3.47	42.25		
A	-2.51	-2.30	6.10	38.78	13.29	0.83	5.52
B	-0.77	3.27	27.98	-4.57	4.33	0.27	0.59
AB	-1.53	2.83	10.80	17.86	6.25	0.39	1.22
C	0.98	10.96	-5.45	-2.41	-8.45	-0.53	2.23
AC	2.29	17.02	0.88	6.74	3.27	0.20	0.33
BC	1.63	5.06	10.46	2.19	-3.85	-0.24	0.46
ABC	1.20	5.74	7.40	4.06	-7.01	-0.44	1.54
D	3.54	-4.69	-1.97	8.73	35.31	2.21	38.96
AD	7.42	-0.76	-0.44	-17.18	22.43	1.40	15.72
BD	5.22	1.31	6.06	6.33	9.15	0.57	2.62
ABD	11.80	-0.43	0.68	-3.06	1.87	0.12	0.11
CD	1.02	3.88	3.93	1.53	-25.91	-1.62	20.98
ACD	4.04	6.58	-1.74	-5.38	-9.39	-0.59	2.76
BCD	0.68	3.02	2.70	-5.67	-6.91	-0.43	1.49
ABCD	5.06	4.38	1.36	-1.34	4.33	0.27	0.59

TOTAL SUM OF SQUARES 102,1335000  
 TREATMENT SUM OF SQUARES 95,1128490  
 RESIDUAL SUM OF SQUARES 7,0206490  
 MEAN RESIDUAL SUM OF SQUARES 0,4387906

Table 22

## ANALYSIS FOR HEATING VALUE

## NOMENCLATURE:

A = TEMPERATURE  
 B = PRESSURE  
 C = SOLVENT/CHAR RATIO  
 D = SOLVENT TYPE

		EXP. DATA:	
EXP.	REP 1	EXP	REP 1
(1)	12,440	D	12,180
A	12,180	AD	12,330
B	12,960	BD	12,680
AB	12,560	ABD	13,100
C	12,460	CD	12,530
AC	12,100	ACD	12,980
BC	12,800	BCD	13,470
ABC	12,500	ABCD	13,350

## ANOVA TABLE

EFFECT	COLUMN OPERATIONS						S.S.	MSR
(1)	12,440	24,620	50,140	100,000	202,620			
A	12,180	25,520	49,860	102,620	-0,420	=0,052	0,011	0,163
B	12,960	24,560	50,290	-1,320	4,220	0,527	1,113	16,465
AB	12,560	25,300	52,330	0,900	-0,380	=0,047	0,009	0,134
C	12,460	24,510	-0,660	1,640	1,760	0,220	0,194	2,864
AC	12,100	25,780	-0,660	2,580	-0,240	=0,030	0,004	0,053
BC	12,800	25,510	0,570	-0,080	-0,120	=0,015	0,001	0,013
ABC	12,500	26,820	0,330	-0,300	-0,640	=0,080	0,026	0,379
D	12,180	-0,260	0,900	-0,280	2,620	0,327	0,429	6,347
AD	12,330	-0,400	0,740	2,040	2,220	0,278	0,308	4,557
BD	12,680	-0,360	1,270	0,000	0,940	0,118	0,055	0,817
ABD	13,100	-0,300	1,310	-0,240	-0,220	=0,028	0,003	0,045
CD	12,530	0,150	-0,140	-0,160	2,320	0,290	0,336	4,976
ACD	12,980	0,420	0,060	0,040	-0,240	=0,030	0,004	0,053
BCD	13,470	0,450	0,270	0,200	0,200	0,025	0,003	0,037
ABCD	13,350	-0,120	-0,570	-0,840	-1,040	=0,130	0,068	1,000
TOTAL SUM OF SQUARES							2,5621338	
TREATMENT SUM OF SQUARES							2,5621753	
RESIDUAL SUM OF SQUARES							0,0676000	
MEAN RESIDUAL SUM OF SQUARES							0,0676000	

In general, the statistical results reinforce the general trends noted above. For the total residual sulfur data, temperature, pressure, and the solvent-to-char ratio were all shown to be very highly significant (99.9 percent confidence level). The T-SCR interaction, P-ST interaction, SCR-ST interaction, and the P-SCR-ST interaction were all significant at the 99 percent confidence level. The T-P-SCR interaction was significant at the 95 percent confidence level.

As the partial pressure of hydrogen is increased, the donor characteristics of the solvent increases, thus supporting a higher degree of desulfurization. More association of the char in higher solvent to char ratios, as supported by the high degree of significance of the solvent-to-char ratio, tends to uphold the theory that hydrogen is donated from the liquid solvent to the dissolved, or partially dissolved, solid char. The importance of higher temperatures supports the activation energy theory which states that more heat is needed to release the tightly bonded organic sulfur not freed during the devolatilization of the original coal. The significance of the many interactions may complicate the reaction mechanism but does indicate the importance in achieving optimum operating variable settings for maximum desulfurization.

The organic sulfur content showed pressure and solvent-

to-char ratio to be very highly significant at the 99.9 percent confidence level, and temperature to be highly significant at the 99 percent confidence level. The inorganic sulfur content analysis showed significance at the 95 percent confidence level to the solvent type effects. Since the absolute values of the pyritic and sulfate sulfur contents are questionable, the significance derived from the inorganic data, and thus the organic data, which is dependent on the inorganic data, may not show the total significance of the effects studied. Although the significance of pressure was very high for the organic sulfur content (99.9 percent), the effect of pressure was not noticeable from the inorganic sulfur data. This may be due to the need for more intimate hydrogen contact during organic sulfur removal than for inorganic sulfur removal, or just due to the fact that the inorganic sulfur content was reduced to a level from which increasing the partial pressure of hydrogen had no effect.

The analysis of the percent change in hydrogen content of the solvent showed that solvent type, T-ST interaction, and the SCR-ST interaction were very highly significant at the 99.9 percent confidence level. Temperature was significant at the 99 percent level, and the T-SCR-ST interaction, the P-ST interaction, and the solvent-to-char ratio were all significant at the 95 percent level. The significance of the solvent type effect on this response is critical to

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the economic success of the process. Since the anthracene oil solvent showed a tendency to increase its hydrogen content during the process, it should be suitable for recycling. The tetralin solvent either lost hydrogen or showed little change in hydrogen content, making it less desirable as a solvent. Significance of the T-ST interaction may indicate a degree of solvent degradation at higher temperatures, while the significance of the SCR-ST interaction may indicate the need to vary the ratio of solvent-to-char as the hydrogen content of the original solvent varies.

The modified statistical analysis of the heating value of the treated char showed a rather low degree of significance (75.0% confidence level) for pressure and solvent type, while the other effects were not even apparent. Although the heating value increase is noted, the variables cannot be statistically linked as to their significance. The increase in heating value of the char may be due to the formation of polyaromatic compounds in the char structure or may be linked to the removal of sulfur and other compounds which may tend to reduce the overall heating value of the char.

Hypothesis Testing of Plots of Isotherms and Isobars

In order to plot values of total residual sulfur content as a function of temperature (isobars) and pressure (isotherms) for the 2 solvents at 2 solvent-to-char ratios, a hypothesis test using a t-distribution was performed on the original analytical data from which the previously

discussed data was derived. This test confirmed the uniqueness of the various sets of data points in relation to each other so that the average of the populations could be plotted. If the hypothesis that the means of 2 data sets (2 levels of an effect) were from the same population could not be rejected at the 90 percent or greater confidence level, then the two levels have the same mean. Table 23 presents the results of the hypothesis test. All but one of the hypotheses were rejected, thus confirming the uniqueness of the average values and also the character of the data. Plots of anthracene oil isobars and isotherms are given in Figures 15 to 18 and tetralin isobars and isotherms are given in Figures 19 to 22.

#### Mathematical Modelling

A multiple linear regression technique was used to formulate a mathematical model relating the total residual sulfur content,  $S_{TOT}$ , to the operating variables studied. The generalized model can be stated as follows:

$$S_{TOT} = a_0 + a_1T + a_2P + a_3SCR$$

where  $T$  = temperature, °C

$P$  = hydrogen partial pressure, psig

$SCR$  = solvent-to-char ratio

$a_i$  = coefficients to be determined.

A computer program, listed in Appendix 2, solved the input matrix and the solution equation with corresponding error

Table 23

## Hypothesis Testing of Population Means

Data Set A	Data Set B	t-Distribution Value	Degrees of Freedom	Reject $\bar{X}_A \neq \bar{X}_B$	Confidence Level
13	2	3.721	10	yes	99%
14	3	5.339	10	yes	99%
17	19	4.218	4	yes	95%
13	14	1.434	10	no	
13	17	15.811	7	yes	99%
14	17	2.495	7	yes	95%
2	3	2.931	10	yes	95%
2	19	5.196	7	yes	99%
3	19	3.008	7	yes	95%
15	1	13.486	10	yes	99%
7	9	7.119	10	yes	99%
8	10	4.759	10	yes	99%
6	4	4.881	9	yes	99%
8	6	2.495	10	yes	95%
10	4	4.504	9	yes	99%
15	7	5.155	10	yes	99%
9	1	1.831	10	yes	90%
5	12	2.557	9	yes	95%
11	16	4.338	10	yes	99%
18	20	10.142	4	yes	99%
5	11	2.507	9	yes	95%
5	18	4.785	6	yes	99%
11	18	2.686	7	yes	95%
12	16	6.747	10	yes	99%
12	20	13.209	7	yes	99%
16	20	7.624	7	yes	99%

FIGURE 15  
DESULFURIZATION ISOBARS  
2/1 ANTHRACENE OIL / CHAR RATIO

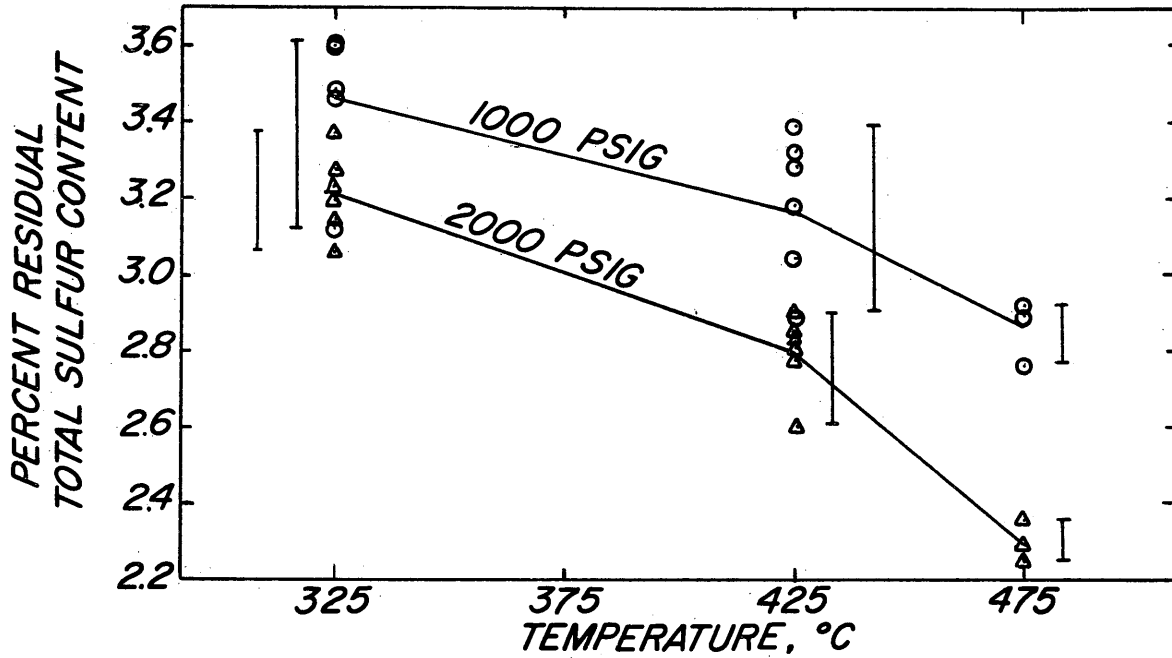


FIGURE 16  
DESULFURIZATION ISOBARS  
5/1 ANTHRACENE OIL / CHAR RATIO

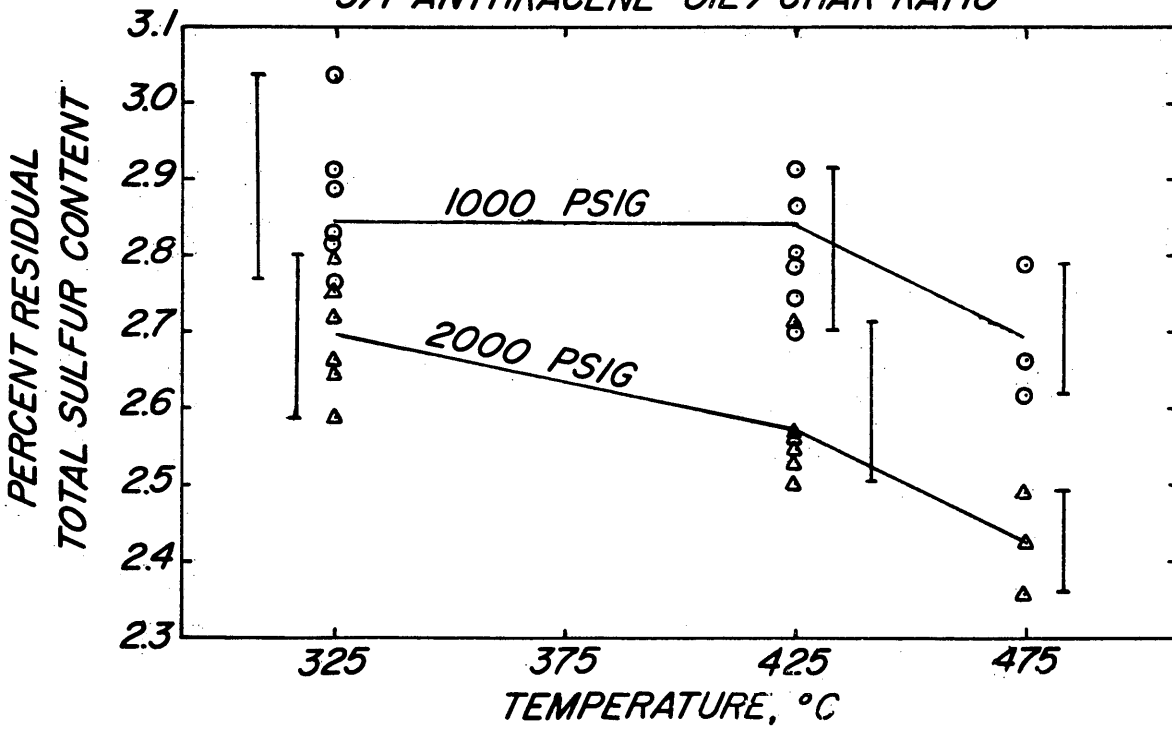




FIGURE 17  
DESULFURIZATION ISOTHERMS  
2/1 ANTHRACENE OIL / CHAR RATIO

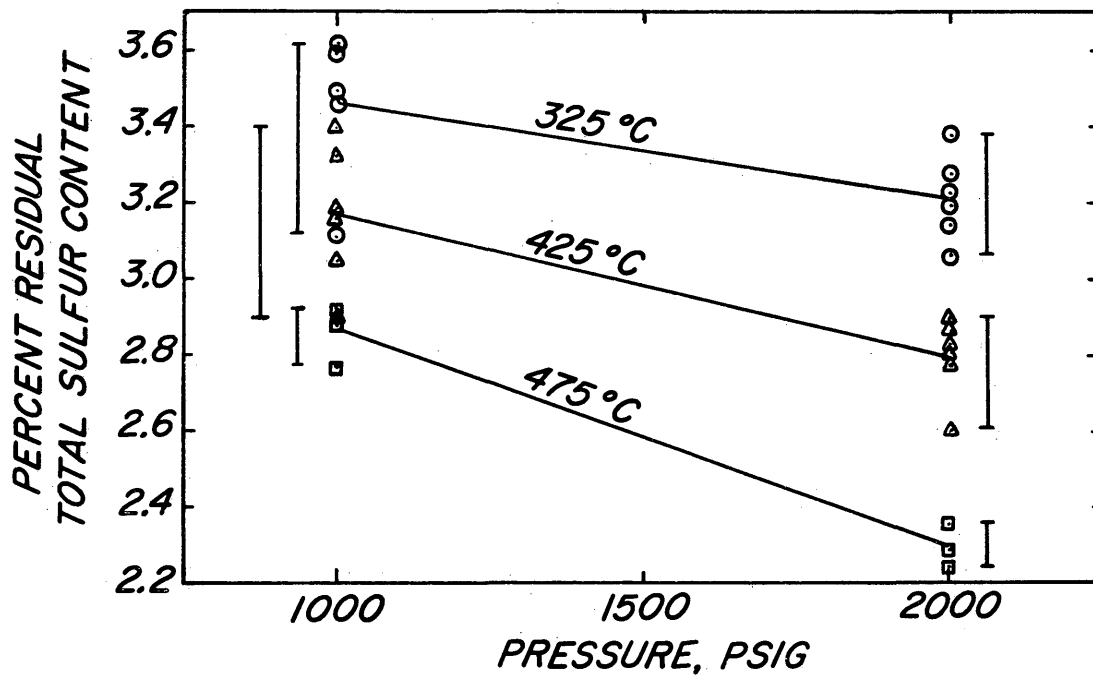


FIGURE 18  
DESULFURIZATION ISOTHERMS  
5/1 ANTHRACENE OIL / CHAR RATIO

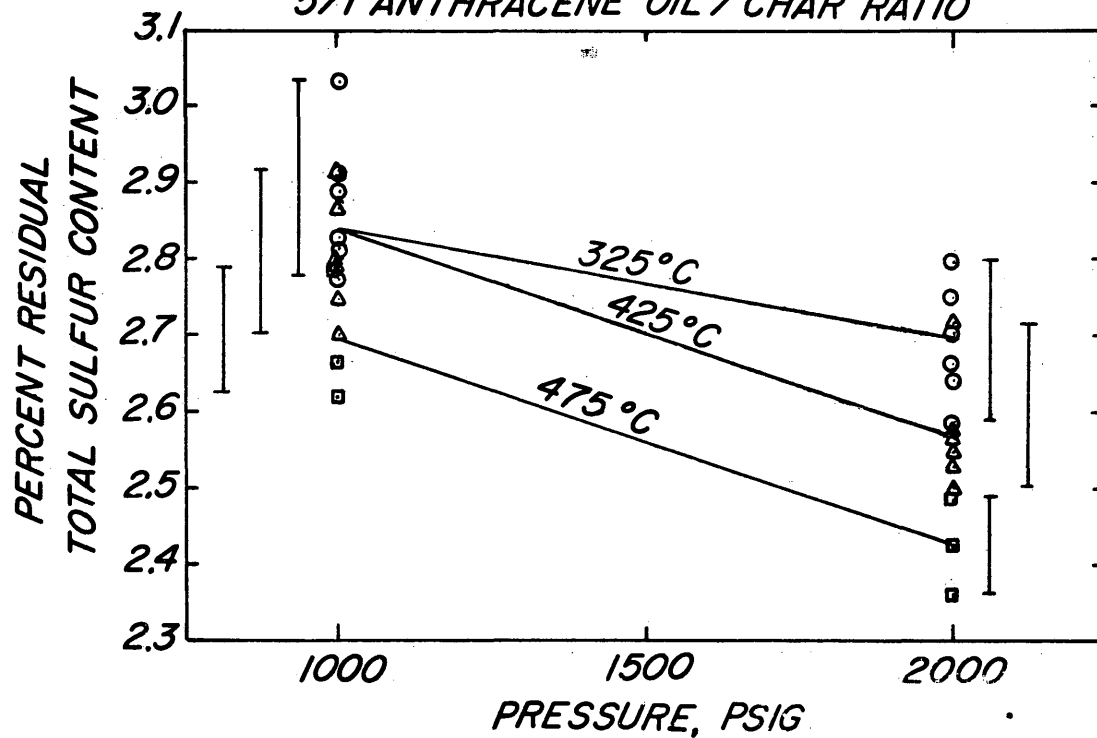


FIGURE 19  
DESULFURIZATION ISOBARS  
2/1 TETRALIN / CHAR RATIO

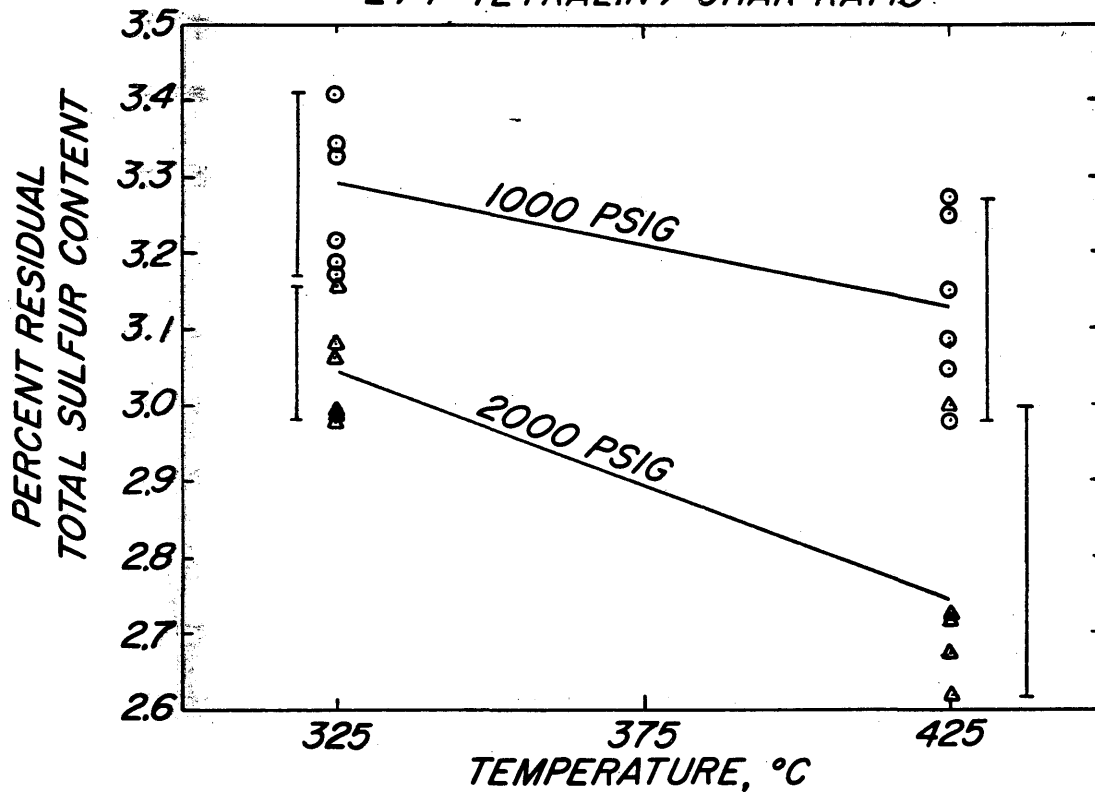


FIGURE 20  
DESULFURIZATION ISOBARS  
5/1 TETRALIN / CHAR RATIO

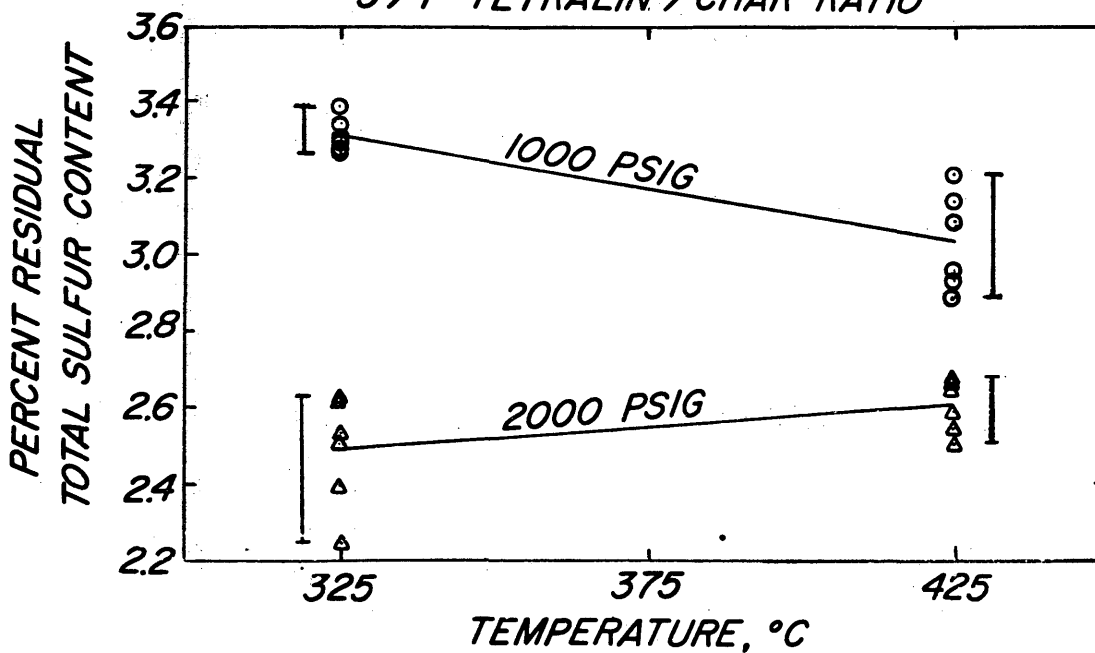


FIGURE 21  
DESULFURIZATION ISOTHERMS  
2/1 TETRALIN / CHAR RATIO

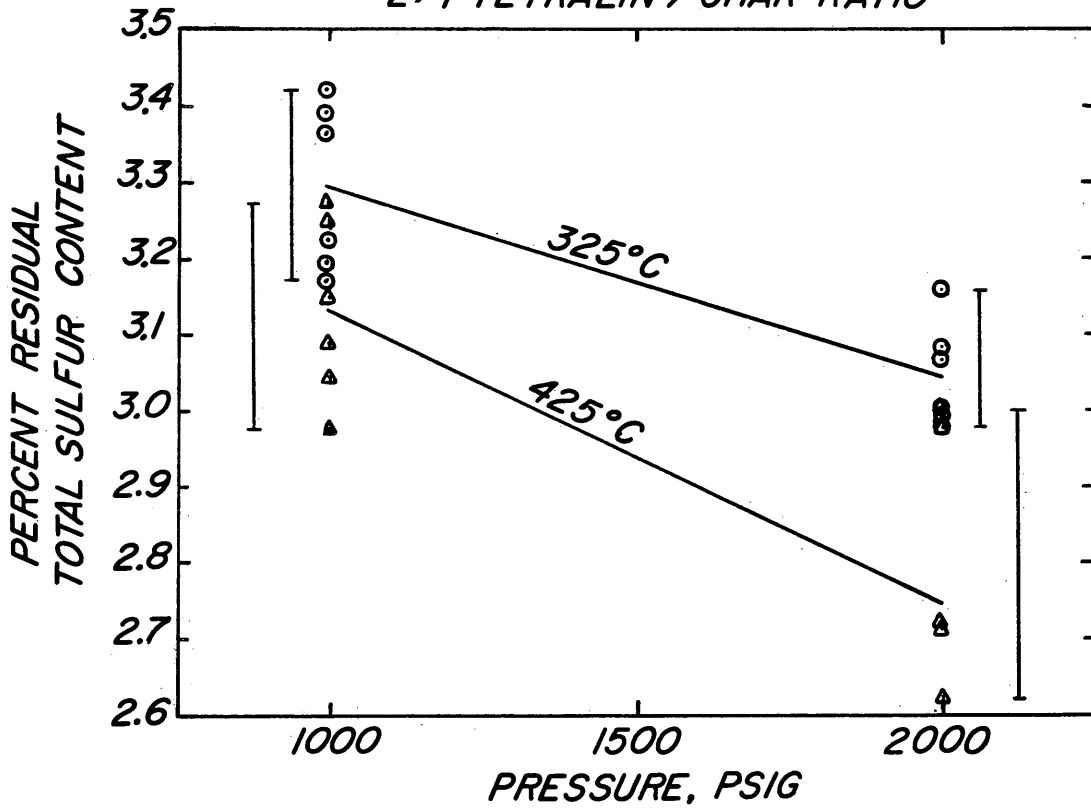
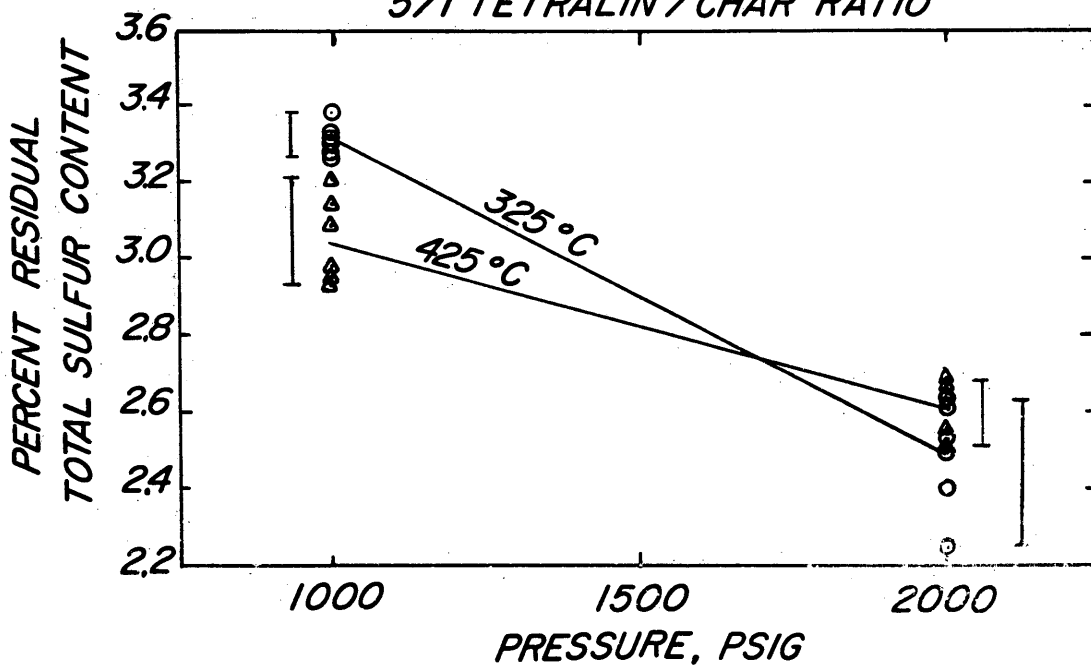


FIGURE 22  
DESULFURIZATION ISOTHERMS  
5/1 TETRALIN / CHAR RATIO



analysis is listed as follows:

$$S_{TOT} = 4.901 - 0.003 T - 0.0003 P \\ - 0.097 SCR$$

Total Sum of Squares = 96.97

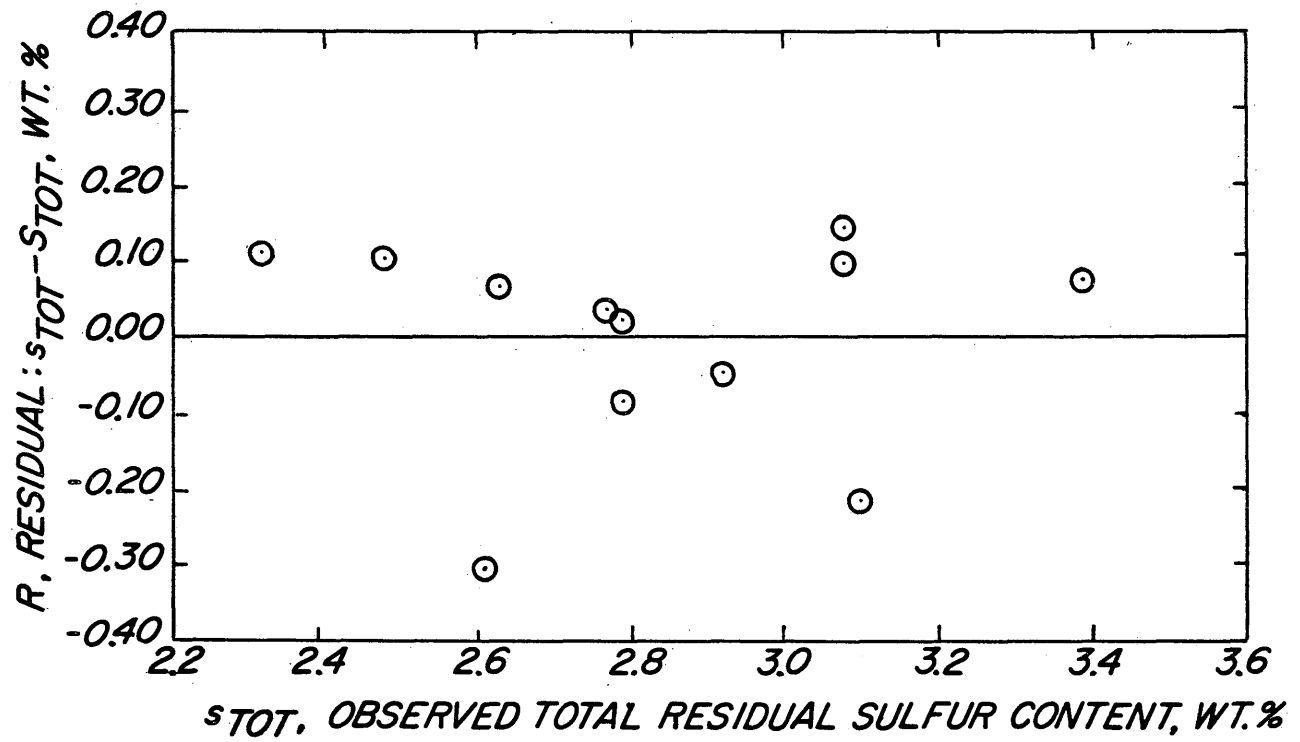
Sum of Squares Due to Regression = 96.76

Sum of Squares of Residuals = 0.21

In making a regression analysis, the assumptions that must be made on the data are that the errors are independent, that they have zero mean and a constant variance, and that they follow a normal distribution. If the fitted model is correct, residuals should exhibit tendencies that tend to confirm these assumptions, or at least, should not exhibit a denial of the assumptions. A plot of the observed total residual sulfur content,  $s_{TOT}$ , as a function of the residual  $R$ , the difference between  $s_{TOT}$  and  $S_{TOT}$ , the total residual sulfur content calculated from the regression equation, is shown in Figure 19. Since a symmetric, regular trend in the pattern is not found, the data is so irregularly scattered that the correctness of the regression equation may be accepted.

The mathematical model is good only for the range of variables tested, and does not represent maximum desulfurization, since the batch reactor was equilibrium limited.

FIGURE 23  
REGRESSION ANALYSIS RESIDUAL PLOT



CONCLUSIONS

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Based on the results of this investigation, the following conclusions are presented:

- 1) Approximately one-third of the total sulfur content in coal char may be removed by the solvent refining process using the batch autoclave experimental technique of this study.
- 2) Pressure, temperature, and solvent-to-char ratio are very highly significant variables (99.9% confidence level) in the solvent refining process for the desulfurization of char.
- 3) A combination of anthracene oil, high pressure, high temperature, and high solvent-to-char ratio increased desulfurization of char for the variable ranges studied.
- 4) Anthracene oil is a better solvent for use in the solvent refining process since the char is partially soluble in the anthracene oil while not at all soluble in the tetralin.
- 5) The hydrogen content of the anthracene oil is improved during the process, thus increasing its hydrogen donor characteristics. Solvent type and temperature are highly significant (99 percent or greater confidence level) variables for the change in hydrogen content of the solvent.
- 6) Since the inorganic sulfur content of the char is less than 0.3 weight percent, no reliable effect of the

process variables could be determined as to their effect on inorganic sulfur removal

7) Char is essentially 100 percent recoverable from the solvent in original granular form, and little depolymerization of the char was observed.

8) The total sulfur content of anthracene oil is reduced up to 90 percent by the solvent refining process.

9) The heating value of the treated char is up to 10 percent greater than the original char. Pressure is only significant at the 75.0 percent confidence level for this response.

10) An empirical model of total residual sulfur content of solvent refined char is presented as follows:

$$S_{TOT} = 4.901 - 0.003 T - 0.0003 P \\ - 0.097 SCR$$

where  $S_{TOT}$  = total residual sulfur content

T = temperature, °C

P = hydrogen partial pressure, psig

SCR = anthracene-to-char ratio.

11) The mathematical model is good only for the range of variables tested, and does not represent maximum desulfurization, since the batch reaction was equilibrium limited.

### RECOMMENDATIONS

Improvements on the analysis of the products from the solvent refining process are necessary to better understand the effects of the process. Chromatographic techniques should be used to analyze the gaseous products rather than the titration techniques used in this study. More difficulties in the analysis for forms of sulfur were found with char than with coal. More care should be taken in the analytical procedures to secure better data, with the possible use of the Leco induction furnace technique being used for total sulfur content of the coal. Direct analysis of organic sulfur content would eliminate the dependence of detecting the char's small inorganic contents for difference calculation of organic sulfur content.

Further study of the effects of solvent refining process for char will supplement these initial findings. A specific boiling fraction of anthracene oil, such as 200° to 350°C, should be used, along with the study of the process effects on recycling of the solvent. This will be necessary for a realistic economic evaluation of this process in a commercial plant. Further investigation of the reaction mechanism may provide kinetic data necessary to evaluate the reactor specifications. The change in the char's ash content should be evaluated along with desulfuriza-



tion. Finally, more economic sources of hydrogen, such as a carbon monoxide-steam mixture with the char feed, will greatly improve the chances for economic success of the process.

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APPENDIX 1

EXPERIMENTAL DATA

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Run and Analysis Data, Coal Char Desulfurization

Run Number Date	1A 8/23/73	1B 8/29/73	2A 8/24/73	2B 8/29/73	3A 8/24/73	3B 8/30/73	4A 8/27/73
Run System	Aminco	Aminco	HIP	Aminco	Aminco	Aminco	Aminco
Run Temp., °C	325	325	325	325	425	425	425
Run Pressure, psig	2000	2000	2000	2000	2000	2000	2000
SCR	5/1	5/1	5/1	5/1	5/1	5/1	2/1
ST	T	T	A	A	A	A	T
Initial T/P	56/1060	30/1050	24/1030	48/1120	31/890	30/890	55/955
Run Start T/P	325/1970	325/2070	327/1985	325/2070	425/1955	422/1960	425/2115
Run Finish T/P	330/1975	326/2060	338/1990	332/2040	433/1900	425/1880	423/2120
Run Residual, T/P	41/1070	38/1010	42/1000	40/1040	53/815	53/790	38/850
Dist. Vac., in Hg	24	24	24	24	24	24	24
Dist. Temp., °C	225	270	325	400	325	400	310
Mole % H <sub>2</sub> S, avg.	0.075	0.309	0.114	0.388	0.513	0.387	0.115
Total Sulfur, wt %							
1)	2.397	2.249	2.668	2.724	2.550	2.568	2.672
2)	2.530	2.626	2.647	2.798	2.507	2.532	2.720
3)	2.501	2.627	2.589	2.753	2.715	2.572	-
Pyritic Sulfur, wt %							
1)	0.547	0.045	0.137	0.124	0.135	0.187	0.058
2)	0.339	0.036	0.242	0.138	0.084	0.179	0.058
3)	0.354	0.040	0.248	0.123	0.087	0.177	0.058
Sulfate Sulfur, wt %							
1)	0.028	0.018	0.031	0.017	0.039	0.016	0.025
2)	0.030	0.014	0.034	0.014	0.035	0.020	0.031
3)	0.024	0.012	0.039	0.004	0.038	0.015	0.023
Soivent Sulfur, wt %							
1)	-	-	0.389	0.429	0.318	0.364	-
2)	-	-	0.476	0.322	0.257	0.367	-
3)	-	-	0.311	0.390	0.235	0.367	-
Bomb Calorimetry Data							
ΔT, °C	-	2.716	2.978	-	2.8361	-	2.717
Fuse Wire, Btu-g/lb	-	23	20	-	39	-	16
Acid Titration	-	49	45	-	56	-	43
Weight, g	-	0.9984	1.0344	-	1.0018	-	1.0135

Run Number	4B	5A	5B	6A	6B	7A	7B
Date	8/30/73	8/24/73	8/30/73	8/27/73	8/30/73	8/27/73	8/30/73
Run System	Aminco	Aminco	HIP	Aminco	Aminco	Aminco	Aminco
Run Temp., °C	425	325	325	425	425	425	425
Run Pressure, psig	2000	1000	1000	1000	1000	1000	1000
SCR	2/1	2/1	2/1	2/1	2/1	5/1	5/1
ST	T	A	A	T	T	T	T
Initial T/P	30/900	50/545	43/540	29/405	47/470	30/410	43/440
Run Start T/P	422/2170	325/980	321/970	424/1170	425/1160	422/1260	425/1370
Run Finish T/P	417/2200	330/980	327/970	429/1210	422/1170	426/1290	421/1370
Run Residual, T/P	48/890	42/525	42/500	44/460	45/455	59/450	55/480
Dist. Vac., in Hg	24	24	24	24	24	24	24
Dist. Temp., °C	305	400	400	400	350	310	275
Mole % H <sub>2</sub> S, avg.	0.282	0.780	0.780	0.171	0.323	0.342	0.100
Total Sulfur, wt %	2.998	3.465	3.613	3.042	3.149	3.209	2.937
1)	2.713	3.496	3.601	2.979	3.272	3.095	2.962
2)	2.619	-	3.125	3.088	3.250	3.144	2.887
Pyritic Sulfur, wt %	0.042	0.174	0.156	0.084	0.046	0.082	0.070
1)	0.036	0.188	0.130	0.085	0.048	0.087	0.073
2)	0.048	0.199	0.144	0.084	0.036	0.086	0.059
Sulfate Sulfur, wt %	0.014	0.030	0.012	0.023	0.014	0.027	0.006
1)	0.009	0.024	0.016	0.021	0.016	0.022	0.009
2)	0.010	0.022	0.017	0.010	0.018	0.020	0.012
Solvent Sulfur, wt %	-	0.294	0.685	-	-	-	-
1)	-	0.293	0.508	-	-	-	-
2)	-	0.293	0.792	-	-	-	-
Bomb Calorimetry Data	-	2.719	-	2.689	-	2.670	-
ΔT, °C	-	30	-	23	-	36	-
Fuse Wire, Btu-g/lb	-	47	-	55	-	51	-
Acid Titration	-	1.0487	-	1.0445	-	1.0396	-
Weight, g	-	-	-	-	-	-	-

Run Number Date	8A 8/27/73	8B 8/31/73	9A 8/27/73	9B 8/31/73	10A 8/27/73	10B 8/31/73	11A 8/28/73
Run System	HIP	HIP	Aminco	Aminco	Aminco	Aminco	Aminco
Run Temp., °C	325	325	425	425	325	325	425
Run Pressure, psig	1000	1000	2000	2000	2000	2000	1000
SCR	2/1	2/1	5/1	5/1	2/1	2/1	2/1
ST	T	T	T	T	T	T	A
Initial T/P	32/520	18/495	48/960	30/890	50/1090	30/1050	45/465
Run Start T/P	321/1020	321/1100	420/2250	425/2390	325/1925	325/2080	425/1000
Run Finish T/P	327/1030	327/1120	435/2360	420/2340	330/1910	327/2080	426/960
Run Residual, T/P	43/475	45/570	48/750	50/920	43/975	30/1025	49/425
Dist. Vac., in Hg	24	24	24	24	24	24	24
Dist. Temp., °C	300	340	340	215	300	335	400
Mole % H <sub>2</sub> S, avg.	0.239	0.163	0.192	0.038	0.309	0.104	1.068
Total Sulfur, wt %							
1)	3.420	3.172	2.513	2.651	3.081	3.064	2.898
2)	3.358	3.220	2.551	2.685	2.980	2.993	3.151
3)	3.388	3.190	2.587	2.679	3.156	2.989	3.049
Pyritic Sulfur, wt %							
1)	0.058	0.043	0.065	0.245	0.047	0.061	0.240
2)	0.057	0.064	0.065	0.269	0.042	0.072	0.218
3)	0.054	0.065	0.058	0.300	0.046	0.062	0.201
Sulfate Sulfur, wt %							
1)	0.020	0.016	0.017	0.010	0.017	0.016	0.013
2)	0.023	0.019	0.022	0.013	0.017	0.014	0.035
3)	0.019	0.006	0.023	0.010	0.017	0.014	0.008
Solvent Sulfur, wt %							
1)	-	-	-	-	-	-	0.215
2)	-	-	-	-	-	-	0.223
3)	-	-	-	-	-	-	-
Bomb Calorimetry Data							
ΔT, °C	-	2.694	-	2.609	2.821	-	2.422
Fuse Wire, Btu-g/lb	-	18	-	20	32	-	36
Acid Titration	-	49	-	57	54	-	50
Weight, g	-	1.0198	-	0.9903	1.0263	-	0.9278

Run Number	11B	12A	12B	13A	13B	14A	14B
Date	8/31/73	8/28/73	8/31/73	8/28/73	8/31/73	8/28/73	9/4/73
Run System	Aminco	Aminco	HIP	Aminco	Aminco	Aminco	Aminco
Run Temp., °C	425	325	325	325	325	425	425
Run Pressure, psig	1000	2000	2000	1000	1000	1000	1000
SCR	2/1	2/1	2/1	5/1	5/1	5/1	5/1
ST	A	A	A	A	A	A	A
Initial T/P	45/450	31/1040	41/1100	30/515	40/535	50/450	24/430
Run Start T/P	425/980	325/2000	321/1950	425/1030	325/1025	430/1000	425/965
Run Finish T/P	420/960	327/1980	327/1945	434/1010	334/1000	432/980	422/920
Run Residual, T/P	40/400	45/1065	35/955	40/510	40/500	44/410	37/360
Dist. Vac., in Hg	24	24	24	24	24	24	24
Dist. Temp., °C	400	410	400	410	400	400	400
Mole % H <sub>2</sub> S, avg.	0.006	0.304	0.328	0.359	0.188	0.014	0.160
Total Sulfur, wt %							
1)	3.171	3.234	3.381	3.035	2.916	2.749	2.870
2)	3.395	3.145	3.281	2.816	2.831	2.803	2.917
3)	3.332	3.066	3.201	2.890	2.772	2.702	2.793
Pyritic Sulfur, wt %							
1)	0.163	0.155	0.212	0.161	0.200	0.148	0.131
2)	0.156	0.173	0.264	0.142	0.229	0.166	0.132
3)	0.203	0.151	0.207	0.148	0.238	0.159	0.130
Sulfate Sulfur, wt %							
1)	0.009	0.017	0.025	0.013	0.009	0.018	0.005
2)	0.007	0.018	0.006	0.021	0.021	0.019	0.011
3)	0.015	0.020	0.013	0.014	0.005	0.011	0.008
Solvent Sulfur, wt %							
1)	0.375	0.274	0.258	0.249	0.246	0.214	0.200
2)	0.353	0.258	0.271	0.246	0.239	0.237	0.216
3)	-	-	-	-	-	-	-
Bomb Calorimetry Data							
ΔT, °C	-	2.883	-	2.912	-	2.736	-
Fuse Wire, Btu-g/lb	-	23	-	18	-	16	-
Acid Titration	-	58	-	56	-	63	-
Weight, g	-	1.0744	-	1.0969	-	1.0030	-

Run Number	15A	15B	16A	16B	17A	18A	19A
Date	8/29/73	9/4/73	9/5/73	9/4/73	9/6/73	9/6/73	9/12/73
Run System	Aminco	HIP	Aminco	Aminco	Aminco	Aminco	Aminco
Run Temp., °C	325	325	425	425	475	475	475
Run Pressure, psig	1000	1000	2000	2000	1000	1000	2000
SCR	5/1	5/1	2/1	2/1	5/1	2/1	5/1
ST	T	T	A	A	A	A	A
Initial T/P	30/500	16/490	25/890	25/870	30/395	45/425	27/825
Run Start T/P	325/970	321/1100	425/1950	425/1930	475/1000	475/1005	475/1900
Run Finish T/P	324/1005	327/1125	428/1900	426/1880	480/975	480/1010	480/1810
Run Residual, T/P	45/555	34/400	42/800	41/800	35/330	40/385	30/605
Dist. Vac., in Hg	24	24	24	24	24	24	24
Dist. Temp., °C	370	310	400	400	400	400	400
Mole % H <sub>2</sub> S, avg.	0.268	0.092	0.278	0.185	0.786	0.709	0.661
Total Sulfur, wt %							
1)	3.385	3.304	2.837	2.783	2.668	2.921	2.363
2)	3.338	3.273	2.902	2.866	2.790	2.908	2.492
3)	3.282	3.313	2.812	2.607	2.624	2.777	2.430
Pyritic Sulfur, wt %							
1)	0.058	0.080	0.232	0.250	0.177	0.091	0.168
2)	0.061	0.078	0.227	0.224	0.186	0.091	0.174
3)	0.058	0.074	0.190	-	0.172	0.090	0.150
Sulfate Sulfur, wt %							
1)	0.013	0.018	0.004	0.024	0.001	0.001	0.001
2)	0.013	0.019	0.011	0.027	0.002	0.004	0.001
3)	0.016	0.013	0.003	0.012	0.003	0.002	0.002
Solvent Sulfur, wt %							
1)	-	-	0.108	0.071	0.112	0.145	0.108
2)	-	-	0.112	0.114	0.112	0.182	0.115
3)	-	-	-	-	-	-	-
Bomb Calorimetry Data							
ΔT, °C	2.610	-	2.817	-	-	-	-
Fuse Wire, Btu-g/lb	20	-	32	-	-	-	-
Acid Titration	56	-	64	-	-	-	-
Weight, g	0.9937	-	1.0703	-	-	-	-



Run Number	20A	Char Head
Date	9/11/73	
Run System	Aminco	
Run Temp., °C	475	
Run Pressure, psig	2000	
SCR	2/1	
ST	A	
Initial T/P	32/825	
Run Start T/P	475/1935	
Run Finish T/P	470/1860	
Run Residual, T/P	40/680	
Dist. Vac., in Hg	24	
Dist. Temp., °C	400	
Mole % H <sub>2</sub> S, avg.	0.521	
Total Sulfur, wt %		
1)	2.298	3.712
2)	2.250	3.786
3)	2.364	3.720
Pyritic Sulfur, wt %		
1)	0.459	0.109
2)	0.499	0.101
3)	0.378	0.048
Sulfate Sulfur, wt %		
1)	0.013	0.023
2)	0.012	0.017
3)	0.005	0.021
Solvent Sulfur, wt %		
1)	0.037	-
2)	0.038	-
3)	-	-
Bomb Calorimetry Data		
ΔT, °C	-	2.578
Fuse Wire, Btu-g/lb	-	27
Acid Titration	-	57
Weight, g	-	1.0120

APPENDIX 2

COMPUTER PROGRAMS

```

C      PROGRAM --- STAT,F4
C
C      THIS PROGRAM SOLVES A 2 TO THE 4TH, DOUBLY REPLICATED,
C      FULL FACTORIAL EXPERIMENTAL DESIGN BY YATES' TECHNIQUE
C
C      WRITTEN BY:
C      RICHARD J, LONG
C      CPR DEPT
C      COLORADO SCHOOL OF MINES
C      GOLDEN, COLORADO
C
C      WRITTEN IN FORTRAN-IV FOR DEC, MODEL PDP-10 DIGITAL COMPUTER
C      TIMESHARING MONITOR VERSION 506A.73(25)
C      REFERENCE:
C      'STATISTICS AND EXPERIMENTAL DESIGN IN ENGINEERING AND
C      THE PHYSICAL SCIENCES, VOL II' BY N.L. JOHNSON AND
C      F.C. LEONE
C
C      DIMENSION A(20,8),B(40),C(16),AP(20)
1      FORMAT (1A4)
2      FORMAT ((F))
3      FORMAT (4A5)
201    FORMAT(' WHAT IS INPUT FILENAME ?','/, ' EXIT STOPS EXECUTION'//)
202    FORMAT (A5)
203    FORMAT (21X,A4,8F8.2)
204    FORMAT (/,20X,' TOTAL SUM OF SQUARES ',9X,F,/,20X,' TREATMENT'
1      ' SUM OF SQUARES ',5X,F,/,20X,' RESIDUAL SUM OF SQUARES ',6X,F
2      ',/,20X,' MEAN RESIDUAL SUM OF SQUARES ',F)
205    FORMAT (21X,A4,5F8.2)
206    FORMAT (20X,' EFFECT'12X,' COLUMN OPERATIONS ',17X,' S.S.  MSR
1      '//)
207    FORMAT (/,40X,'NOMENCLATURE:',/,45X,'A = ',4A5,/,45X,'B = ',4A5,
1      ',/,45X,'C = ',4A5,/,45X,'D = ',4A5,/)
208    FORMAT (1H1,/////////,40X,'ANALYSIS FOR '3A5,/)
209    FORMAT (3A5)
210    FORMAT (31X,1A4,2X,2F8.2,6X,1A4,2X,2F8.2)
211    FORMAT (50X,'EXP, DATA:',/,31X,'EXP,',5X,'REP 1  REP 2',
1      ' 7X,'EXP',5X,'REP 1  REP 2'//)
212    FORMAT (//,50X,'ANOVA TABLE'//)
      DATA C/' (1)', ' A', ' B', ' AB', ' C', ' AC', ' BC',
1      ' ABC', ' D', ' AD', ' BD', ' ABD', ' CD', ' ACD', ' BCD', 'ABCD'//
1000  WRITE (4,201)
      READ (4,202) FILEI
      IF (FILEI.EQ.4HEXIT) GO TO 500
      CALL IFILE (2,FILEI)
      READ (2,3) (AP(I),I=1,16)
      READ (2,209) D1,D2,D3
10    READ (2,2) (B(I),I=1,32)
      WRITE (6,208) D1,D2,D3
      WRITE (6,207) (AP(I),I=1,16)
      WRITE (6,211)

```

```

DO 50 I=1,8
J=2*I-1
K=2*I
II=8+I
L=16+J
M=16+K
50 WRITE (6,210) C(I),B(J),B(K),C(II),B(L),B(M)
DO 11 I=1,16
J=2*I
11 A(I,1)=B(J-1)+B(J)
DO 12 M=2,5
DO 12 I=1,8
J=2*I-1
K=2*I
LK=I+8
A(I,M)=A(J,M-1)+A(K,M-1)
12 A(LK,M)=A(K,M-1)-A(J,M-1)
SUM=0.0
DO 20 J=2,16
A(J,6)=A(J,5)/16.0
A(J,7)=A(J,5)*A(J,5)/32.0
20 SUM=SUM+A(J,7)
S1=0.0
S2=0.0
DO 22 I=1,32
S1=S1+B(I)*B(I)
22 S2=S2+B(I)
SST=S1-S2+S2/32.0
SSR=SSS-SUM
SSRM=SSR/16.0
DO 25 J=1,16
25 A(J,8)=A(J,7)/SSRM
WRITE (6,212)
WRITE (6,206)
WRITE (6,205) C(1),(A(1,J),J=1,5)
WRITE (6,203) (C(I),(A(I,J),J=1,8),I=2,16)
WRITE (6,204) SST,SUM,SSR,SSRM
GO TO 1000
500 STOP
END

```

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```

C      PROGRAM --- STAT2.F4
C
C      THIS PROGRAM SOLVES A 2 TO THE 4TH, SINGLY REPLICATED,
C      FULL FACTORIAL EXPERIMENTAL DESIGN BY YATES' TECHNIQUE
C
C      WRITTEN BY:
C          RICHARD J. LONG
C          CPR DEPT
C          COLORADO SCHOOL OF MINES
C          GOLDEN, COLORADO
C
C      WRITTEN IN FORTRAN-IV FOR DEC, MODEL PDP-10 DIGITAL COMPUTER
C      TIMESHARING MONITOR VERSION 506A.73(25)
C      REFERENCE:
C          'STATISTICS AND EXPERIMENTAL DESIGN IN ENGINEERING AND
C          THE PHYSICAL SCIENCES, VOL II' BY M.L. JOHNSON AND
C          F.C. LEONE
C
C      DIMENSION A(20,8),B(40),C(16),AP(20)
1      FORMAT (1A4)
2      FORMAT ((F))
3      FORMAT (4A5)
201    FORMAT(' WHAT IS INPUT FILENAME ?','/, ' EXIT STOPS EXECUTION'/)
202    FORMAT (A5)
203    FORMAT (21X,A4,8F8,3)
204    FORMAT (/,20X,' TOTAL SUM OF SQUARES ',9X,F,/,20X,' TREATMENT'
1      ' SUM OF SQUARES ',5X,F,/,20X,' RESIDUAL SUM OF SQUARES ',6X,F
2      ',/,20X,' MEAN RESIDUAL SUM OF SQUARES ',F)
205    FORMAT (21X,A4,5F8,3)
206    FORMAT (20X,' EFFECT'12X,' COLUMN OPERATIONS ',17X,' S,S. MSR
1      '/')
207    FORMAT (/,40X,'NOMENCLATURE:',/,45X,'A = ',4A5,/,45X,'B = ',4A5,
1      ',/,45X,'C = ',4A5,/,45X,'D = ',4A5,/)
208    FORMAT (1H1,/////////,40X,'ANALYSIS FOR '3A5,/)
209    FORMAT (3A5)
210    FORMAT (31X,1A4,2X,F8,3,11X,1A4,2X,F8,3)
211    FORMAT (50X,'EXP. DATA:',/,31X,'EXP.',5X,'REP 1',7X,
1      7X,'EXP',5X,'REP 1',7X/)
212    FORMAT (//,50X,'ANOVA TABLE'//)
      DATA C/' (1)', ' A', ' B', ' AB', ' C', ' AC', ' BC',
1      ' ABC', ' D', ' AD', ' BD', ' ABD', ' CD', ' ACD', ' BCD', 'ABCD'//
1000  WRITE (4,201)
      READ (4,202) FILEI
      IF (FILEI.EQ.4HEXIT) GO TO 500
      CALL IFILE (2,FILEI)
      READ (2,3) (AP(I),I=1,16)
      READ (2,209) D1,D2,D3
10    READ (2,2) (B(I),I=1,16)
      WRITE (6,208) D1,D2,D3
      WRITE (6,207) (AP(I),I=1,16)
      WRITE (6,211)

```

```

DO 50 I=1,8
  II=8+I
50  WRITE (6,210) C(I),B(I),C(II),B(II)
DO 11 I=1,16
11  A(I,1)=B(I)
DO 12 M=2,5
DO 12 I=1,8
  J=2*I-1
  K=2*I
  LK=I+8
  A(I,M)=A(J,M-1)+A(K,M-1)
12  A(LK,M)=A(K,M-1)-A(J,M-1)
  SUM=0.0
DO 20 J=2,16
  A(J,6)=A(J,5)/8.0
  A(J,7)=A(J,5)*A(J,5)/16.0
20  SUM=SUM+A(J,7)
  S1=0.0
  S2=0.0
DO 22 I=1,16
  S1=S1+B(I)*B(I)
22  S2=S2+B(I)
  SST=S1-S2*S2/16.0
  SSR=A(16,7)
  SSRM=SSR
DO 25 J=1,16
25  A(J,8)=A(J,7)/SSRM
  WRITE (6,212)
  WRITE (6,206)
  WRITE (6,205) C(1),(A(1,J),J=1,5)
  WRITE (6,203) (C(I),(A(I,J),J=1,8),I=2,16)
  WRITE (6,204) SST,SUM,SSR,SSRM
GO TO 1000
500 STOP
END

```

```
C PROGRAM ZAP.F4
C THIS PROGRAM SOLVES FOR THE COEFFICIENTS FOR A REGRESSION
C ANALYSIS MATHEMATICAL MODEL OF RESIDUAL TOTAL SULFUR CONTENT
C IN COAL CHAR PROCESSED VIA THE SOLVENT REFINING TECHNIQUE,
C A GAUSSIAN ELIMINATION WITH PARTIAL PIVOTING MATRIX INVERSION
C TECHNIQUE IS UTILIZED.
C WRITTEN BY:
C RICHARD J. LONG
C CPR. DEPT
C COLORADO SCHOOL OF MINES
C GOLDEN, COLORADO
C
C WRITTEN IN FORTRAN-IV FOR DEC. MODEL PDP-10 DIGITAL COMPUTER
C TIMESHARING MONITOR VERSION 506A,73(25)
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```
SUBROUTINE DROG(N,NP,X,Y,BETA,YHAT,RES,A,B,AA,AINV)
  IMPLICIT DOUBLE PRECISION(A-H,O-Z)
  DIMENSION X(12,4),Y(12),BETA(4),YHAT(12),RES(12)
  DIMENSION XT(4,12),A(4,4),B(4),AINV(4,4)
  DO 2 I=1,NP
  DO 2 J=1,N
2  XT(I,J)=X(J,I)
  DO 3 I=1,NP
  DO 3 J=1,NP
  SUM=0.
  DO 4 L=1,N
4  SUM=SUM+XT(I,L)*X(L,J)
3  A(I,J)=SUM
  DO 5 I=1,NP
  SUM=0.
  DO 6 L=1,N
6  SUM=SUM+XT(I,L)*Y(L)
5  R(I)=SUM
  CALL INVERT (4,A,AINV)
  DO 8 I=1,NP
  SUM=0.
  DO 9 L=1,NP
9  SUM=SUM+AINV(I,L)*B(L)
8  BETA(I)=SUM
  DO 10 I=1,N
  SUM=0.
  DO 11 L=1,NP
11  SUM=SUM+X(I,L)*BETA(L)
10  YHAT(I)=SUM
  DO 12 I=1,N
12  RES(I)=Y(I)-YHAT(I)
  RETURN
  END
```



```
      SUBROUTINE INVERT(N,A,AINV)
      IMPLICIT DOUBLE PRECISION(A-H,O-Z)
      DIMENSION A(4,4),UL(4,4),AINV(4,4),B(10),X(10),IPS(10)
      CALL DECOMP (N,A,UL,IPS)
      DO 100 J=1,N
      DO 104 I=1,N
      IF(I-J)102,103,102
102  B(I)=0.
      GOTO 104
103  B(I)=1.
104  CONTINUE
      CALL SOLVE(N,UL,B,X,IPS)
      DO 105 I=1,N
105  AINV(I,J)=X(I)
106  CONTINUE
      RETURN
      END
```

```

SUBROUTINE DECOMP(NN,A,UL,IPS)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION A(4,4),UL(4,4),SCALES(10), IPS(10)
111 FORMAT(54HOMATRIX WITH ZERO ROW IN DECOMPOSE. )
112 FORMAT(54HOSINGULAR MATRIX IN DECOMPOSE. ZERO DIVIDE IN SOLVE. )
N = NN
C
C   INITIALIZE IPS, UL AND SCALES
DO 5 I = 1,N
  IPS(I) = I
  ROWNRM = 0.0
  DO 2 J = 1,N
    UL(I,J) = A(I,J)
    IF(ROWNRM-DABS(UL(I,J))) 1,2,2
1    ROWNRM =DABS(UL(I,J))
2    CONTINUE
3    SCALES(I) = 1.0/ROWNRM
    GO TO 5
4    WRITE(4,111)
    SCALES(I) = 0.0
5    CONTINUE
C
C   GAUSSIAN ELIMINATION WITH PARTIAL PIVOTING
NM1 = N-1
DO 17 K = 1,NM1
  BIG = 0.0
  DO 11 I = K,N
    IP = IPS(I)
    SIZE =DABS(UL(IP,K))*SCALES(IP)
    IF (SIZE-BIG) 11,11,10
10    BIG = SIZE
    IDXPIV = I
11    CONTINUE
    IF (BIG) 13,12,13
12    WRITE(4,112)
    GO TO 17
13    IF (IDXPIV-K) 14,15,14
14    J = IPS(K)
    IPS(K) = IPS(IDXPIV)
    IPS(IDXPIV) = J
15    KP = IPS(K)
    PIVOT = UL(KP,K)
    KP1 = K+1
    DO 16 I = KP1,N
      IP = IPS(I)
      EM = -UL(IP,K)/PIVOT
      UL(IP,K) = -EM
      DO 16 J = KP1,N
        UL(IP,J) = UL(IP,J) + EM*UL(KP,J)
C      INNER LOOP. USE MACHINE LANGUAGE CODING IF COMPILER

```

```
C          DOES NOT PRODUCE EFFICIENT CODE.  
  16      CONTINUE  
  17      CONTINUE  
          KP = IPS(N)  
          IF (UL(KP,N)) 19,18,19  
  18      WRITE(4,112)  
  19      RETURN  
          END
```

```

SUBROUTINE SOLVE(NN,UL,B,X,IPS)
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION UL(4,4),X(10),B(10),IPS(10)
  N=NN
  NP1=N+1
C
  IP = IPS(1)
  X(1) = B(IP)
  DO 21 I = 2,N
    IP = IPS(I)
    IM1 = I-1
    SUM = 0.0
    DO 51 J = 1,IM1
      51 SUM = SUM + UL(IP,J)*X(J)
  21 X(I) = B(IP) - SUM
C
  IP = IPS(N)
  X(N) = X(N)/UL(IP,N)
  DO 41 IBACK = 2,N
  C
    I = NP1-IBACK
    I GOES (N-1),...,1
    IP = IPS(I)
    IP1 = I+1
    SUM = 0.0
    DO 31 J = IP1,N
      31 SUM = SUM + UL(IP,J)*X(J)
  41 X(I) = (X(I)-SUM)/UL(IP,I)
  RETURN
  END
IMPLICIT DOUBLE PRECISION(A-H,O-Z)
DIMENSION NRUN(81),T(81),P(81),SCR(81),Y(81)
DIMENSION X(12,4),B(4),AINV(4,4),YHAT(81)
DIMENSION YBAR(81),DIFF(81)
DIMENSION BETA(4),A(4,4),AA(16),RES(81)
EQUIVALENCE(AA,AINV)
READ(12,10)(NRUN(I),Y(I),T(I),P(I),SCR(I),I=1,12)
10 FORMAT(I,4F)
DO 3 I=1,12
  X(I,1)=1.0
  X(I,2)=T(I)
  X(I,3)=P(I)
  X(I,4)=SCR(I)
  3 CONTINUE
CALL DROG(12,4,X,Y,BETA,YHAT,RES,A,B,AA,AINV)
SRES=0.00
DO 16 I=1,12
  16 SRES=SRES+(RES(I)*RES(I))
DO 30 I=1,12
  TOT=Y(I)**2
  30 SSTOT=SSTOT+TOT
SSREG=SSTOT-SRES

```

```
XMSSRG=SSREG/4.0
WRITE(4,900)(BETA(I),I=1,4)
900  FORMAT( ' REGRESSION PARAMETERS ',/,4F)
WRITE(4,902)SSTOT
WRITE(4,903)SSREG
WRITE(4,904)SRES
902  FORMAT( ' TOTAL SUM OF SQUARES = ',F)
903  FORMAT( ' SUM OF SQUARES DUE TO REGRESSION = ',F)
904  FORMAT( ' SUM OF SQUARES OF RESIDUALS = ',F)
STOP
END
```

APPENDIX 3

SAMPLE CALCULATIONS

SAMPLE CALCULATIONSScrubber Analysis

$$\text{Mole \% H}_2\text{S} = \frac{(V_b - V_s) \times N_t \times F \times 100}{V_{\text{gas}}}$$

where

- $V_b$  = volume (ml) of sodium thiosulfate used in blank  
 $V_s$  = volume (ml) of sodium thiosulfate used in sample  
 $N_t$  = normality of sodium thiosulfate  
 $V_{\text{gas}}$  = volume (ml) of product gas used in test, and  
 $F$  = factor in ml of  $\text{H}_2\text{S}$  per milliequivalent of sodium thiosulfate.

For this study,

$$N_t = 0.05$$

$$F = 0.5/\text{ME}$$

where

$$\text{ME} = \frac{P}{760} \times \frac{273.2}{T} \times \frac{1}{22.4}$$

with P and T the atmospheric pressure (psia) and temperature ( $^{\circ}\text{K}$ ).

For sample 7A, 3 sets of raw data were taken as follows:

<u>Run</u>	<u>P</u> <u>mm Hg</u>	<u>T</u> <u><math>^{\circ}\text{K}</math></u>	<u><math>V_s</math></u> <u>ml</u>	<u><math>V_b</math></u> <u>ml</u>	<u><math>V_{\text{gas}}</math></u> <u>ml</u>
1	621.4	303.2	23.3	24.2	200.0
2	621.4	303.2	23.3	24.2	200.0
3	621.4	303.2	23.3	24.2	201.0

$$ME = \frac{621.4}{760.0} \times \frac{273.2}{303.2} \times \frac{1}{22.4} = 0.0329$$

$$F = 0.5/0.0329 = 15.20$$

$$\% \text{H}_2\text{S}(1) = \frac{(24.2 - 23.3)(0.05)(15.20)(100)}{200.0}$$

$$\% \text{H}_2\text{S}(1) = 0.342$$

$$\% \text{H}_2\text{S}(2) = 0.342$$

$$\% \text{H}_2\text{S}(3) = 0.340$$

$$\% \text{H}_2\text{S Avg.} = \frac{0.342 + 0.342 + 0.340}{3} = 0.341$$

#### Heating Value of Solvent Refined Char

$$\text{Heating value, Btu/lb} = \left( \frac{[(\Delta T)(E)] - \Delta F + S + N}{\text{wt of sample}} \right)$$

where

$\Delta T$  = corrected temperature change,  $^{\circ}\text{C}$

$E$  = calorimeter water equivalent (Btu/lb)(g/ $^{\circ}\text{C}$ )

$\Delta F$  = heat released by fuse wire, Btu-g/lb

$S$  = heat due to sulfur content, Btu-g/lb

$N$  = heat due to nitrogen content, Btu-g/lb

Sample 1B, the raw data is:

$$\Delta T = 2.716^{\circ}\text{C}$$

$$E = 4525(\text{Btu/lb})(\text{g}/^{\circ}\text{C})$$

$$\Delta F = 23 \text{ Btu-g/lb}$$

$$\text{Total Acid Titration} = 49 \text{ ml}$$

$$\text{Wt of Sample} = 0.9984$$

From the total sulfur analysis, the treated char contained 2.50 wt % sulfur. Therefore, the grams of sulfur in the



sample were:

$$\frac{2.50(0.9984)}{100} = 0.025 \text{ g sulfur}$$

Since the value of 1 ml of ammonia solution in grams of sulfur equals 0.0061, the grams of sulfur in the sample divided by 0.0061 will give the ml of titration due to sulfur:

$$\frac{0.025 \text{ g sulfur}}{0.0061 \text{ g sulfur/ml titration}} = 4.0 \text{ ml titration due to sulfur}$$

The reported total acid titration minus the titration due to sulfur yields the titration due to nitrogen:

$$49 \text{ ml} - 4 \text{ ml} = 45 \text{ ml of titration due to nitrogen.}$$

The ml of titration due to nitrogen multiplied by 10 Btu, the factor for nitric acid, gives the heat due to nitrogen:

$$N = 45 \text{ ml} \left( \frac{10 \text{ Btu-g/lb}}{\text{ml}} \right) = 450 \text{ Btu-g/lb}$$

The centigrams of sulfur multiplied by 23.3 Btu, the factor for sulfuric acid, gives the heat due to sulfur:

$$S = 2.5 \text{ centigrams S} \left( \frac{23.3 \text{ Btu-g/lb}}{\text{centigrams S}} \right) = 58 \text{ Btu-g/lb}$$

Therefore

Heating Value, Btu/lb =

$$\frac{(2.716)(4525) - 23 + 58 + 450}{0.9984} = 12800 \text{ Btu/lb.}$$

### Sulfur Balances

To calculate the amount of sulfur in the off gas, the mole percent  $\text{H}_2\text{S}$  from the scrubber analysis is used. Since the volume of the reaction bomb is approximately 1.410 liters,

the volume occupied by the reaction gas is obtained from the known volume of char slurry used for the sample. By using the ideal gas law equation, the volume of gas at reaction residual conditions (after cooling) may be calculated as follows:

$$V_2 = V_1 \frac{P_1}{P_2} \frac{T_2}{T_1}$$

where

$V_2$  = volume (ℓ) at atmospheric conditions

$V_1$  = free space in bomb, ℓ

$P_1$  = residual pressure, atm

$P_2$  = atmospheric pressure, atm

$T_2$  = atmospheric temperature, °K

$T_1$  = residual temperature, °K

The volume,  $V_2$ , at atmospheric conditions multiplied by the mole percent  $H_2S$  from the scrubber analysis gives the liters of  $H_2S$ . The liters of  $H_2S$  divided by 22.4 gives the moles  $H_2S$ , and the weight of sulfur with off-gas is obtained from the multiplication of the moles  $H_2S$  by 32/34.

For sample 7A,

$P_1 = 31.61$  atm

$V_1 = (1410 \text{ ml} - \frac{300 \text{ g slurry}}{.935 \text{ ml/g slurry}}) = 1.079$  ℓ

$P_2 = 0.818$  atm

$T_2 = 303.2$ °K

$T_1 = 328$ °K

$$V_2 = (1079) \frac{(31.61)}{(0.818)} \frac{(303.2)}{(328)} = 38 \text{ l}$$

$$\text{Liters H}_2\text{S at Standard T \& P} = 38 \text{ liters} \frac{(0.341)}{100} = .13 \text{ l}$$

$$0.13 \text{ l} \left( \frac{\text{mole H}_2\text{S}}{22.4 \text{ l}} \right) = 0.0058 \text{ moles H}_2\text{S}$$

$$0.006 \text{ moles H}_2\text{S} \left( \frac{32 \text{ g sulfur}}{34 \text{ g H}_2\text{S}} \right) = 0.186 \text{ g sulfur.}$$

### Hypothesis Testing t-Distribution Values

To test the independence of the population sets, a t-distribution value was calculated and compared against tabular values for the confidence levels. If the calculated t-value was larger than the tabular t-value at a preset confidence level, then the hypothesis that the population had the same means was rejected, thus confirming their independence. A minimum of 90% level of confidence was necessary to reject the hypothesis of equality of means.

For comparison of samples 17 and 19 on Figure 16, the following calculations were made:

$$\begin{array}{ll} N_{17} = 3 & N_{19} = 3 \\ \bar{X}_{17} = 2.69 & \bar{X}_{19} = 2.43 \\ S_{17}^2 = 0.0075 & S_{19}^2 = 0.0044 \end{array}$$

where N = no. of data points

$\bar{X}$  = population mean

$S^2$  = population variance

Hypothesis:  $\bar{X}_{17} = \bar{X}_{19}$

$$t_{\text{calc}} = \frac{\bar{X}_{17} - \bar{X}_{19} \sqrt{\frac{N_1 N_2 (N_1 + N_2 - 2)}{N_1 + N_2}}}{\sqrt{(N_1 - 1)S_1^2 + (N_2 - 1)S_2^2}}$$

$$t_{\text{calc}} = \frac{2.69 - 2.43 \sqrt{3(3)(4)/6}}{\sqrt{2(0.0075) + 2(0.0044)}}$$

$$t_{\text{calc}} = 4.22$$

Tabular value of  $t$  at 95% confidence level and 4 degrees of freedom is 2.78. Therefore, since  $t_{\text{calc}}$  is greater than  $t_{\text{tabular}}$ , reject  $H_0$  at 95% confidence level, and

$$\bar{X}_{17} \neq \bar{X}_{19}$$