THE EFFECTS OF TEMPERATURE AND PRESSURE ON COAL DESULFURIZATION BY HYDROGEN TREATMENT

by

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ABSTRACT

The purpose of this research study was to determine if temperature and/or pressure significantly affects the desulfurization of coal by solvent treatment under a hydrogen blanket. A 3^2 cross doubly-replicated factorial design was used to study the following two coals:

Coal	Source	Rank	Total Sulfur Content
CK	Cherokee Seam Lovilla Mine #4, Iowa	Subbituminous	3.50%
IM	Pittsburgh No. 8 Seam Ireland Mine, W. Virg.	Bituminous	4.42%

The operating variables examined in this study were:

Temperature: 325, 360, 400°C

Pressure: 600, 1200, 1800 psig.

For each experimental run, 50 gm of coal was mixed with 250 gm of anthracene oil and then charged to an autoclave rocking bomb reactor. After completion of the reaction, vacuum distillation was used to recover the coal product. Using an analysis of variance test at a 90% confidence level, pressure (linear) and temperature-pressure interaction were significant for subbituminous coal while temperature (linear and quadratic) was significant for bituminous coal. Solvent recovery of the process ranged from 76 to 94% while the yield of the solvent refined coal was higher than 90%. Loss of

vapor due to vacuum distillation was well below 3%.

The maximum percent sulfur removal for each coal was as follows:

Coal	Rank	% Sulfur Removal
CK	Subbituminous	51.14
IM	Bituminous	48.72

A multiple linear regression technique was used to formulate an empirical mathematical model of percent of sulfur removal in this process. The models for bituminous and subbituminous coals on total sulfur removal were:

Bituminous coal: $y = 578.19 + 0.0048\ T^2 - 3.27\ T$

Subbituminous coal: $y = -37.04 + 0.21\ T + 0.061\ P - 0.00016\ (TP)$

where y = percent of total sulfur removal

T = temperature, °C (325-400°C)

P = pressure, psia. (600-1800 psi)

A response surface study indicated that a combination of low pressure and high temperature improved desulfurization on both of the coals. An attempt was made to obtain the activation energy of the proposed (assumed) pseudo-first order reaction model, but no reliable result was obtained due to the complexity of the coal reactions and the inherent limitations in the original experimental design.

DEDICATION

With affection

to

my mother, Lam Sau-ying

and

my wife, Nina Ngau-ming

for

their faith and encouragement

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INTRODUCTION

Previous Work

The solvent refining technique for coal processing can be traced back to 1937 when the first commercial application of the Pott-Broche Coal-Extraction Process (1) was used for the extraction of coal with solvents at elevated temperatures in Germany. Recently, Spencer Chemical Division of Gulf Oil Corporation (2) has been investigating the technical and commercial feasibility of this process. The Australian Coal Industry Research Laboratories Ltd. (3) has been studying this process for demineralizing and deashing coal for metallurgical applications. More recently, the Colorado School of Mines (4,5) with support from the Office of Coal Research of the Department of the Interior, and the State of Colorado, has been studying the optimum process conditions for desulfurization of coal.

Statement of the Problem

This research was designed to determine if reaction temperature and initial hydrogen pressure significantly affect the desulfurization of coal by the solvent refining process. The study of two variables at three levels was approached as a 3^2 completely crossed, doubly-replicated, factorial experimental design. For two coal samples, 36 experimental runs were required. The coal samples used were:

I. Bituminous Coal: Pittsburgh #8 seam, Ireland Mine, West Virginia, total sulfur content: 4.42%.

II. Subbituminous Coal: Cherokee seam, Lovilla Mine #4, Iowa, total sulfur content: 3.50%.

The variables found to be important by statistical analysis were also analyzed for linearity. An empirical mathematical model based on multiple linear regression was established.

LITERATURE SURVEY

Solvent Refining Process

The Pott–Broche Process (1) was developed in Germany and was intended for use in obtaining an ash-free mixture that could be hydrogenated readily to liquid hydrocarbons. In this process, ground coal was mixed in a 1:2 ratio with a middle oil and heated to 400°-420°C under a pressure of 100 atmospheres. The solution was filtered to remove the ash and undissolved coal, and the solvent was then removed by vacuum distillation.

Kloepper et al (2) carried out extensive research on the solvent refining process which was carried under a hydrogen blanket. A raw coal having ash content of 12% was reduced to 0.2% with a concurrent reduction in total sulfur content from 1.4% to 0.5%.

The Pittsburgh & Midway Coal Mining Company (6-9) developed a solvent refining process using an internally generated solvent and hydrogen to dissolve the raw coal to produce low ash and low sulfur coal.

Cudmore and Guyot (3) studied the solvent extraction of coal using anthracene oil as a solvent under a hydrogen blanket in a batch autoclave which produced coal with 0.4% total sulfur from a raw coal of 1.1% total sulfur.

Kirchner (5) studied solvent type, solvent-to-coal ratio and coal rank in a statistically designed set of experiments to determine the effects of these three variables on the removal of total sulfur, organic sulfur, and inorganic sulfur (sulfate and pyritic) from four raw coals. His findings show a maximum removal of total, organic and inorganic sulfur of 74.0, 70.2, and 98.6 percent, respectively. The analysis of the data showed both solvent type and coal rank to be statistically significant at the 0.95 confidence level for the removal of sulfur from coal.

Ferrall (10) also studied the desulfurization of coal in anthracene under a hydrogen blanket and showed that pressure and temperature were significant variables in the process, but that reaction times in excess of 15 minutes were not statistically significant.

Desulfurization by Other Methods

Atlantic Richfield Company (11) was granted a patent for a process which could simultaneously desulfurize and deash coal. Total sulfur content was reduced by 54% and ash content reduced by 27% by simply treating the coal in a batch reactor with water at 650°F and a pressure of 2350 psig of nitrogen for one hour.

Flotation methods have been examined and developed by Miller and Baker (12), Galiguzov (13), Leonard and Cockrell (14) and Terchik (15). Deurbrouck (16) has an extensive computer study of the removal of pyritic sulfur by flotation.

A carbonization process was used by Van Hoessle and Quadri (17) to produce a smokeless fuel from subbituminous coal and resulted in a 95% reduction of pyritic sulfur and 60-70% reduction on both organic and sulfate sulfur.

Alkali metal hydroxides have been used by Murphy and Messman (18) in a patented process that reduces the total sulfur content of coal by 35-50%. A process has been patented by Lefrancois, Barclay and Van Hook (19), in which coal is mixed with a sodium carbonate melt. Sulfur is then leached from the coal by the sodium carbonate melt.

Pyritic Sulfur Removal

Given and Jones (20) have found that some of the pyritic sulfur released is fixed in the organic matter of coal and contributes to the higher organic sulfur content of the treated coal. Although several reactions are capable in principle of removing sulfur from pyrite in volatile or soluble form, the rate of reaction is too slow for practical use, because the pyrite is finely dispersed and embedded in the coal matrix with little surface exposure. This observation agreed with results reported by Smith (21).

Hydrogen contacting was first used by McKinley and Henke (22) in a patented process achieving a removal of 53% sulfur removal on a coal with high pyritic sulfur content.

Blum and Cindea (23) optimized an air-steam fluidized process and reported 90-95% of the pyritic sulfur could be removed under optimum conditions. Abel et al (24) used a centrifugal-electrostatic method and removed 50-70% of pyritic sulfur and 30-40% total sulfur with stage grinding. Nearly 90% of the pyritic sulfur was removed from a Pittsburgh seam roof coal with this technique.

Meyers et al (25) achieved a 40-70% sulfur reduction on coal by treatment with a ferric ion solution. The pyritic sulfur in the coal matrix was oxidized and elemental sulfur and iron sulfate were recovered. A subsequent patent was issued to Meyers (26).

Organic Sulfur Removal

A U.S. patent was granted to Mayland (27) for a pebble heated gasification unit. Mayland observed that a major portion of the organic sulfur in the coal was converted to H_2S during the process. Mukai et al (28) reported that they removed 100 percent of the organic sulfur from a bituminous coal by a room temperature treatment to the coal with a 3 percent solution of hydrogen peroxide. Apparently they were able to oxidize all the organic sulfur in the coal without changing the properties of the coal's coking ability. Meyers, Laud, and Flegal (29) investigated several coals, and found that a leaching process using a weak organic acid would remove 45-80 percent of the organic sulfur. They reported that phenyl-nitrate was the most efficient solvent for organic sulfur removal and a patent was later issued to Meyers (30).

Background Information

This section investigates the parameters which relate directly or indirectly to coal desulfurization. Topics covered here are: Catalyst, thermodynamic aspects, kinetic considerations, effect of hydrogen on dissolution of coal, choice of organic solvent, and forms of sulfur.

1. Catalyst

Winkler (31) found that activated iron powder on finely ground bituminous coal in a highly aromatic oil under heat can reduce the coal's total sulfur content by 56%. A French patent was granted to Fohlen (32), who lists catalysts capable of splitting organic sulfur linkages prior to desulfurization. These catalysts include the oxides and salts of calcium, magnesium, lead, copper, zinc, and molybdenum. Manmohan and Goswami (33) found that sodium chloride gave 80% total sulfur removal during carbonizing.

2. Thermodynamic Aspects

Cudmore and Guyot (3) in their study of the dissolution of coal in anthracene oil, noted that the overall heat of combustion of the products exceeds the heat of combustion of the reactants. Kloepper et al (2) also indicated an overall improvement in the heating value of a product with the solvent refined coal exhibiting a heating value 20% higher than that of the parent coal. Kloepper et al (2) 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. This conclusion is supported by Cudmore and Guyot (3), who observed an enrichment in polycyclic aromatic compounds in their solvent refined product and a corresponding increase in the heating value of the treated coal.

3. Kinetic Considerations

The kinetic studies of the dissolution of bituminous coal in tetralin by Hill (34) have shown that the ΔH (heat of activation) and ΔS (entropy of activation) can be determined from the temperature dependence of the rate. By applying the Eyring Absolute Reaction Rate Theory, Hill reported at temperatures below 350°C, the low activation energy suggests the dissolution of interstitial material in the coal, the process being under diffusion control. At temperatures above 350°C, thermal decomposition reactions as well as simple dissolution occurs. Kloepper (2) reached the same conclusion in his study. He concluded that the transfer of hydrogen from the solvent phase was the most important mechanism of free radical termination for the dissolved coal. Formation of low molecular weight compounds during the dissolution of coal at high temperatures was favored by using a solvent which can transfer hydrogen or by having available a highly active hydrogen atmosphere during the reaction. He found a marked increase on the amount of coal in solution as the partial pressure of hydrogen was increased in a batch autoclave system.

Charlot (35) has observed the dissolution process had an average activation energy of 7 kcal/mole. Above 250°C, the average activation energy for the initial process was 19 kcal/mole.

Hill proposed a model for the dissolution process and suggested that the reaction rate is first order with respect to solvent and first order with respect to coal.

$$\text{tetralin} + \text{coal} \xrightarrow{K_o'} R_o + L_o + G_o$$

$$\text{tetralin} + R_o \xrightarrow{K_1'} R_1 + L_1 + G_1$$

$$\vdots \qquad\qquad \vdots$$

$$\text{tetralin} + R_{n-1} \xrightarrow{K_n'} R_n + L_n + G_n$$

where R_i = solid coal residue

L_i = extract in solution

G_i = gaseous products.

This model indicates that the overall rate constant for dissolution process would be an average of each of the individual rate constants. Hill concludes that the model assumes that the dissolution process involves thermal decomposition with chemical bonds of increasing strength being broken at progressively higher temperatures. An increase in the fraction of sites available for reaction accounts for the apparent entropy increase.

4. Effect of Hydrogen on Dissolution of Coal

Blackwood and McCarthy (36) considered the reaction of coal and hydrogen to be a two-stage process, with the first step being very rapid hydrogenation of the oxygen containing functional groups of the coal, followed by a slow reaction between the hydrogen and residual char. The hydrogen in the process serves two purposes: to saturate the solvent used and to form H_2S with sulfur compounds present. Curran et al (37) have found that very little hydrogen transfer was necessary to dissolve the first 50% of the coal but the amount of hydrogen required increased seven times for the next 40% of the coal. He proposed that the dissolution is a pseudo-first order reaction.

5. Choice of Organic Solvent

Orechkin (38) 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 is high due to the fact that hydrogen required to reduce the coal to low molecular weight compounds is supplied entirely by the solvent, and this quantity is limited by the solvent characteristics and degree of unsaturation.

6. Forms of Sulfur

Sulfur found in coal can be classified as organic and inorganic. The most common sulfate in coal is gypsum ($CaSO_4 \cdot 2H_2O$). Sulfates of iron, copper and magnesium may also occur as a result of the action of sulfuric acid on carbonates or by the oxidation of sulfides. The sulfuric acid may result from the oxidation of iron pyrite as suggested by Burke and Downs (39):

$$FeS_2 + 3O_2 = FeSO_4 + SO_2$$

$$2SO_2 + O_2 + 2H_2O = 2H_2SO_4$$

The organic sulfur content of the coal ranges from 0.5%-2%. Thiessen points out that there is sulfur in proteins of practically all plants and in addition to the protein sulfur there is some non-protein sulfur in most plants.

Jolly and Wheeler (40) have shown that organic sulfur compounds exist in coal in two forms, differing in stability. These originate in the plant tissues, but change in varying degrees during coalification. The proportions of sulfur extracted from coal by different chemical treatments will therefore depend upon the proportions of the more stable and less stable compounds present.

Wnekowska suggested in the 3rd International Conference on Coal Science at Vālkenburg, 1959, that the ratio of thiophenic to thioether groups increases with the rank of coal. Robertson and Steedman (41) found that sulfur in coal in thiophenic and thioether structures will be largely removed in the volatiles or converted to more stable structures in the course of carbonization. Relatively speaking the thiophenic group is more readily desulfurized than the phenolic group. This finding suggests that thiophenic structures are unlikely to be important in coal structures. The thioether links show some degree of stability and seem more favored than disulfide bridge. It is suggested that as rank increases, sulfur is more likely to occur in stable heterocyclic rings than in simple thioether structures.

Aitken, Heep, and Steedman (42) found that cyclic aromatic thioether structures would degrade during pyrolysis of coal. Sulfur is lost only in part from cyclic thioether structures in coal during pyrolysis.

EXPERIMENTAL DESIGN AND ANALYSIS

Two operating variables, temperature and initial hydrogen pressure, were studied at the following levels:

Temperature: 325°C, 360°C, 400°C

Pressure: 600 psig, 1200 psig, 1800 psig

The two coals used for this study were:

1) Pittsburgh #8 seam bituminous coal from Ireland Mines in West Virginia (designated IM), total sulfur 4.42%.
2) Cherokee seam subbituminous coal from Lovilla Mines #4 in Iowa (designated CK), total sulfur 3.50%.

The desulfurized coal products were analyzed for total, organic, pyritic, and sulfate forms of sulfur.

Throughout the experiments, a coal to anthracene oil weight ratio of 1:5 was used. The choices of coal to solvent weight ratio and the type of solvent used was projected from Kirchner's (5) study on coal desulfurization.

The study of 2 variables at 3 levels was approached as a 3^2 completely crossed, doubly-replicated factorial experimental design. For 2 types of coal, this design requires 36 experimental runs. The experimental design is illustrated in Table 1.

In all runs, the amount of coal and anthracene oil used were 50 and 250 grams, respectively. The bomb was rocked throughout the heating period. When the reaction temperature

Table 1

3^2 Crossed, Doubly-replicated Factorial Design

			Temperature					
			325°C		360°C		400°C	
Pressure	CK Coal	600 psig	1A	1B	4A	4B	7A	7B
		1200 psig	2A	2B	5A	5B	8A	8B
		1800 psig	3A	3B	6A	6B	9A	9B
	IM Coal	600 psig	10A	10B	13A	13B	16A	16B
		1200 psig	11A	11B	14A	14B	17A	17B
		1800 psig	12A	12B	15A	15B	18A	18B

was reached, it was maintained for 15 minutes. The bomb was cooled under forced convection by a fan.

A standard statistical method of analyzing the data sets resulting from the 36 experimental runs is presented by Johnson and Leone (43). The method uses an analysis of variance table and F statistic to determine which, if any, of the factors or interactions show a significant effect on the outcome of the experiment. A statistical analysis was conducted for each of the data sets; percent of total sulfur removed, percent of organic sulfur removed, and percent of inorganic sulfur removed. A Fortran-IV computer program to be run on DEC, Model PDP-10 digital computer constructed the necessary analysis of variance tables. The program is presented in the appendix.

An empirical mathematical model for desulfurization was established by means of multiple linear regression techniques. The statistical manipulations of the multiple linear regression analysis were performed by a computer program which was developed by Mr. Keith Linck, a graduate student of the Chemical and Petroleum-Refining Engineering Department, Colorado School of Mines.

A pseudo-first order reaction model was assumed for the reaction, thus the rate constant and the activation energy were found by conforming the corresponding coefficients to the coefficients of the empirical model.

EQUIPMENT

Three major equipment systems were employed in the study: 1) Reactor system, 2) Scrubber system, and 3) Solvent recovery system.

Reactor System

The reactor used was of the batch autoclave generic type. A gas delivery system, a reaction vessel, and a shaking assembly existed as functional parts of the reactor system.

The reaction vessel, as shown in Figure 1, was manufactured by the American Instrument Company of Silver Spring, Maryland, and was from the 4-3/8 inch series. The vessel had an inside depth of 10 inches and inside diameter of 3-5/16 inches with an approximate weight of 50 pounds. The working pressure of the vessel was rated 5050 psi at 100^{o}F and its effective volume was approximately 1.4 liters.

The shaking assembly consisted of a 6-kw, 220-volt heating jacket mounted on a rocker assembly and was manufactured by the High Pressure Equipment Company Inc. 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 shaking mechanism and the heater mounted on the rocker is shown in Figure 2.

FIGURE 1

REACTION VESSEL ASSEMBLY

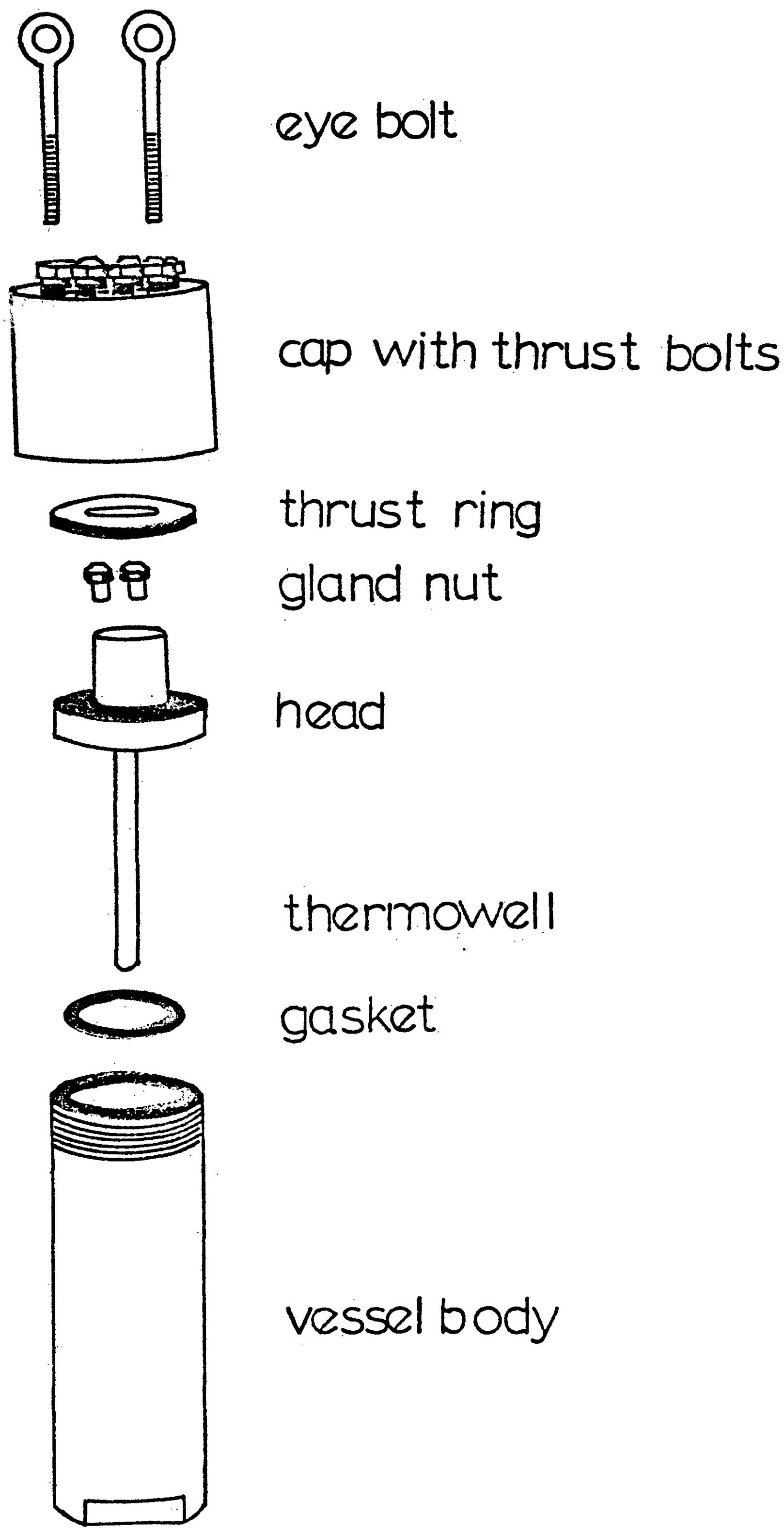
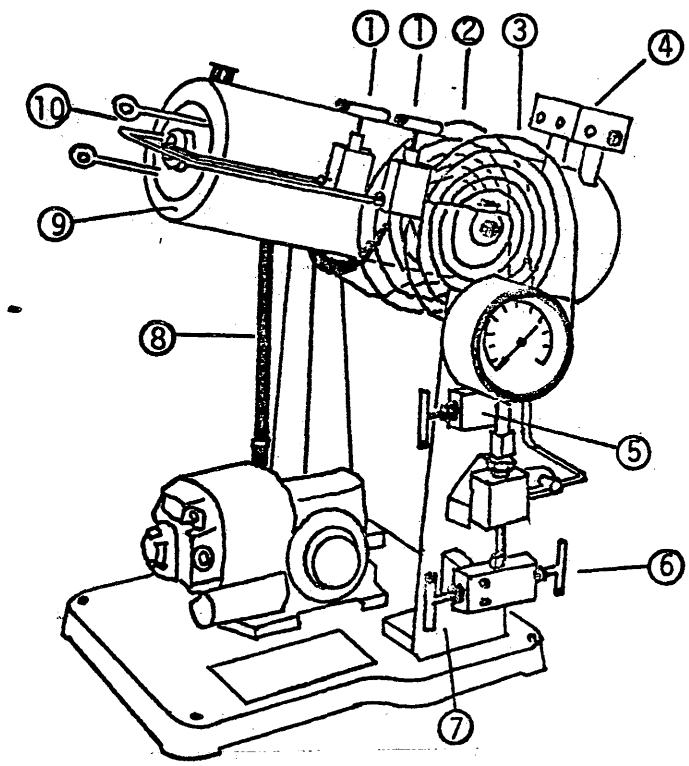


FIGURE 2

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

The shaking assembly was equipped with 30,000 psi Aminco valves and fittings. These were used to regulate the inlet and exit of the reaction gases from the reaction vessel.

The tubing used was 304 stainless steel, 1/4 inch outside diameter, and rated for operation at 100,000 psi at 100°F.

The automatic temperature controller used was a series 60 Leeds and Northrup current adjusting type controller, 0-5 ma output, with proportional, integral and derivative control action. The recorder used was Speedomax H, with a 0-2000°F calibrated range. The temperature sensor used was a chromel-alumel thermocouple.

The final control element used was a Leeds and Northrup model 11906 zero-voltage firing package. The input was 0-5 ma and the output was 0-208 AC volts, single phase.

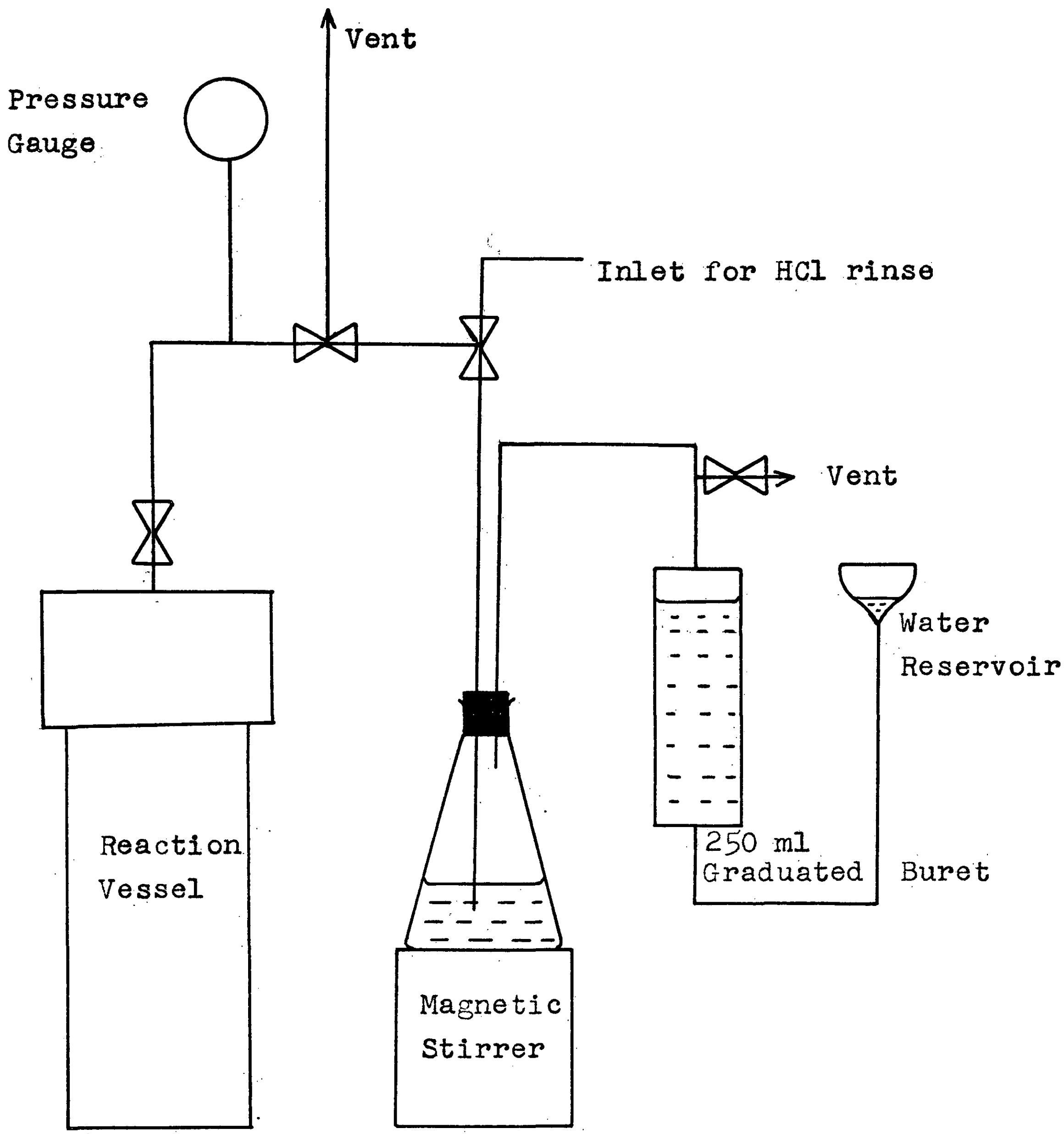
The shaking assembly was connected to purging-charging gas delivery systems. Each of these systems consisted of a nitrogen cylinder, a hydrogen cylinder with pressure regulators for each cylinder, and Aminco stainless steel tubing and fittings similar to those used on the shaking assembly.

Off-Gas Scrubber System

The scrubber system is shown in Figure 3. The tubing used was 304 stainless steel, 1/4-inch outside diameter and rated for operation at 100,000 psi at 100°F. A 0-3,000 psig

Figure 3

Scrubber Collecting Set-up



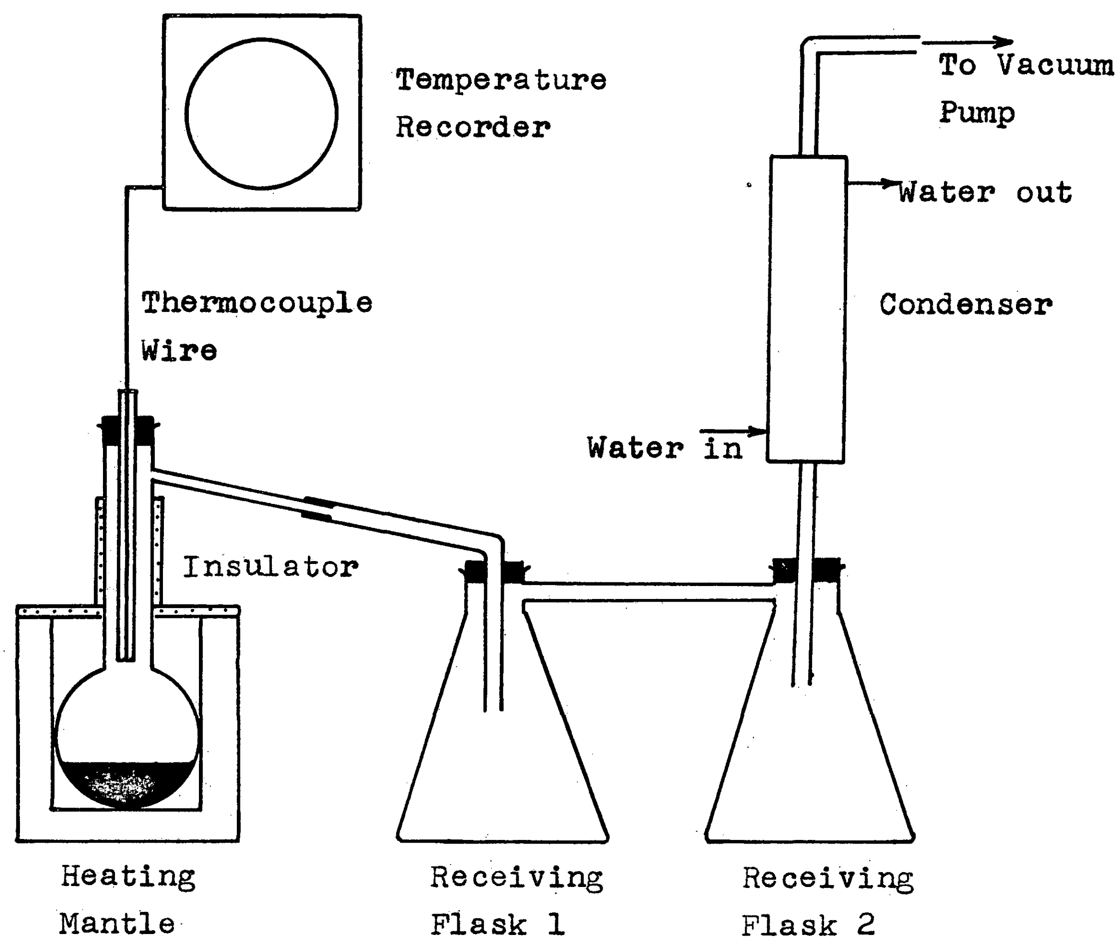
pressure gauge was used in the system to measure residual pressure in the reaction vessel. A Foxboro 6 point dynalog recorder was used to measure the residual temperature of the reaction vessel. A magnetic stirrer was used for better absorption of H_2S. A 250-ml graduated buret was used for measuring the gas sample volume by water displacement. Ammoniacal zinc sulfate was the solution used for scrubbing in a 250-ml Erlenmeyer flask.

Solvent Recovery System

The distillation vessel was a long-neck 500-ml distillation flask. It was heated by a 330-watt Glas-col Apparatus Co. heater. The heater was controlled by a 110-volt, 7-1/2 amp variable transformer. The temperature was measured using a 20 gauge iron-constantan type thermocouple and recorded on a Foxboro Dynalog 6-point circular chart recorder. Two flasks were used to trap the reclaimed solvent followed by a spiral condenser to trap any low boiling cuts and prevent these fractions from leaving the system. The vacuum was provided by a Cenco Pressovac 4 pump driven by a 1/4 hp, 110-volt electric motor, and was measured with a 0 to 30 in. Hg Duragauge vacuum gauge. Figure 4 shows the solvent recovery system.

Figure 4

Solvent Recovery System



PROCEDURE

The experimental procedure may be divided into four major areas: coal preparation, coal processing, solvent recovery, and analysis of sulfur content. A flow sheet indicating the treatment steps involved is given in Figure 5.

Coal Preparation

The raw coal was first crushed and then screened to a size smaller than 28-mesh and the process was repeated until 80% of the coal was in the usable size. The 28-mesh or finer fraction was dried for three hours at approximately $100^{o}C$ and then sealed in airtight jars until it was needed for processing.

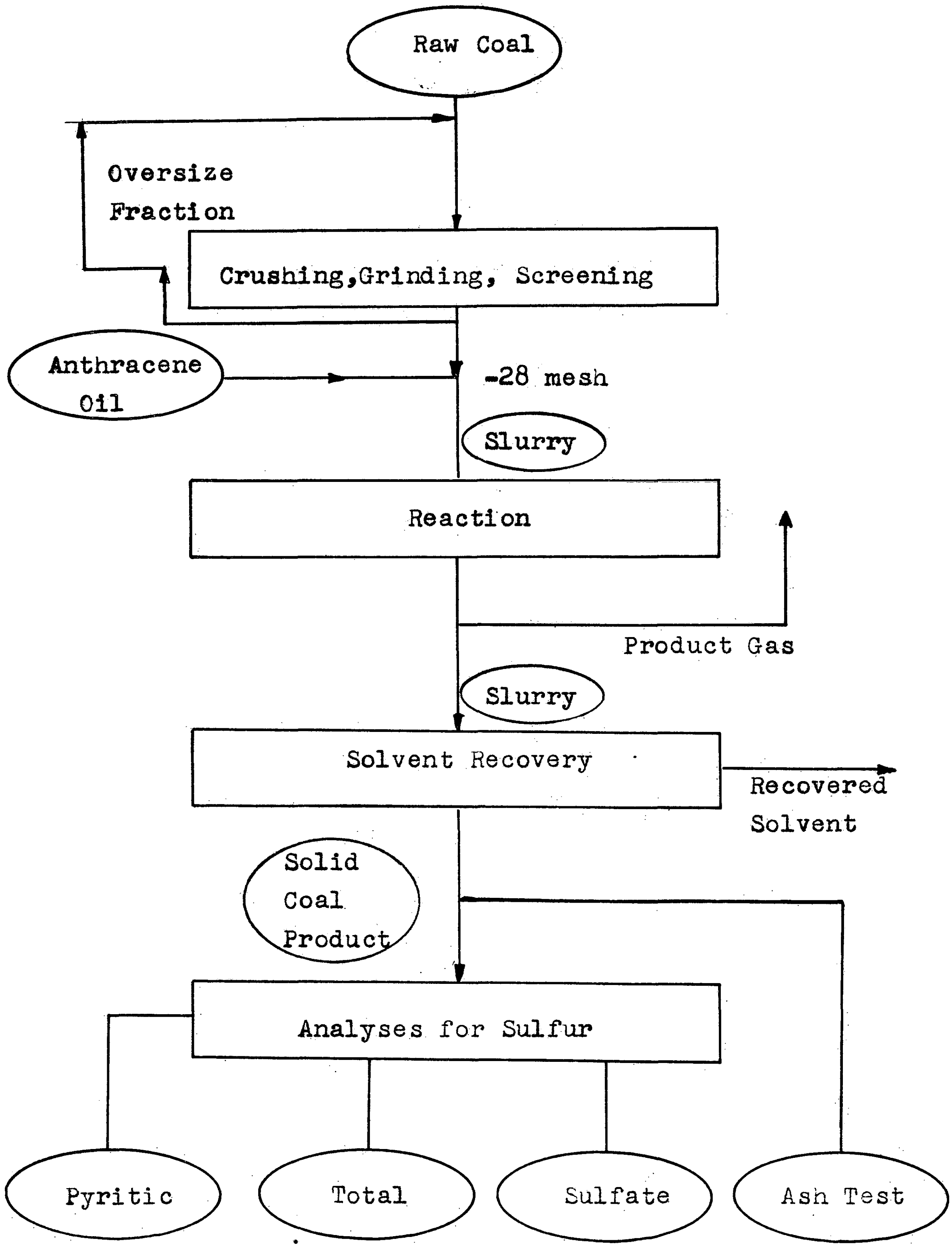
Coal Processing

Fifty grams of coal and 250 grams of anthracene oil were thoroughly mixed and then charged to the reaction vessel. The vessel was closed by placing the head and thrust ring on top of the vessel, turning the cap on, and tightening the thrust bolts. With the eye bolts screwed into the cap, the assembled reaction vessel was then inserted into the heating jacket of the shaker assembly, and the connecting lines were securely attached to the vessel and shaking assembly.

The reaction vessel was then purged and vented five times with nitrogen at a pressure of about 200 psig. Then

Figure 5

Flow Sheet for Procedure



the system was pressured with hydrogen at room temperature according to the table shown below:

Table 2

Initial Partial Hydrogen Pressure

Run Conditions T(°C)	P psig	Initial Partial Hydrogen Pressure at Room Temperature (psia)
325	600	320
325	1200	635
325	1800	950
360	600	300
360	1200	600
360	1800	900
400	600	285
400	1200	565
400	1800	845

When the shut-off valves on the shaking assembly were closed and the system isolated, the system was checked with soap solution for leakage.

If no leaks were found, the heater, the controller and the rocker were all turned on. The controller settings and the turn-off temperatures for the rapid heater are listed in Table 3.

Table 3
Controller Settings

Run Temperature °C	°F	Controller Setting °F	Rapid Heater Off at °F
400	751	800	680
360	680	710	580
325	616	620	520

When the reactor reached and leveled out at the reaction temperature, the shut off valve on the reaction vessel was opened and the total pressure at the reaction temperature was read. The reaction temperature was maintained for 15 minutes, at which time another pressure reading was taken.

With the shut off valve closed, the reaction vessel was disconnected from the shaking assembly by pulling the vessel from the heating jacket, and the vessel was cooled down on a stand with a fan. When the reaction vessel had cooled to room temperature, the vessel pressure was read. The off gas from the reactor vessel was then scrubbed for hydrogen sulfide.

Scrubbing

This method was developed by the Pittsburgh & Midway Coal Mining Company in their solvent refining process of coal. It is applicable in a concentration range of about 0.1 to 7 volume percent H_2S. Thirty ml of ammoniacal zinc sulfate solution was diluted to 150 ml in a 250 ml Erlenmeyer flask, and 200 ml of product gas was slowly injected while 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 1:1 HCl solution. The 250 ml flask was then rinsed with about 100 ml water into the 500 ml flask.

As quickly as possible the solution, while being stirred, was titrated with standardized 0.05 N sodium thiosulfate solution until the solution was yellow. Then 2 ml of 2% starch solution was added, and the end point of the titration was indicated by a permanent color change from blue to clear of the solution. The volume of sodium thiosulfate used was recorded. A blank test was run in the same manner without a gas sample. The blank and sample test were run triplicate. Since the blank values do not change very much, therefore only a weekly check was necessary if there had not been changes in the reagents, room temperature, etc. If the sample titration volume was less than half of the reagent blank, the test was rerun using a smaller gas sample.

The mole % of H_2S was calculated by the formula:

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

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_{gas} = volume (ml) of product gas used in test

F = Factor in milliliters of hydrogen sulfide 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 time of testing.

Solvent Recovery

After the off-gas had been vented, the reaction vessel was opened and the product was collected in a beaker for solvent recovery. With the weights of clean receiving flasks and the distillation flask recorded, the product was transferred to the distillation flask and weighed. The distillation flask was placed in the heating mantle, and the receiving apparatus was assembled and connected to the distillation flask and vacuum pump. A variable transformer was used to control the temperature of the heating mantle. The vacuum pump was turned on, pulling a vacuum of 10-in. Hg, when the distillation temperature had reached 150°C. The 10-in. Hg vacuum was maintained until at 270°C, full vacuum was applied to the system. Due to the evaporation of more solvent, the temperature dropped, but when the temperature reached 270°C again, the heater was turned off. Vacuum was maintained until the temperature started to drop.

The receivers and the distillation flask were then disconnected and weighed, and a small quantity of the recovered solvent was stored in a sample vial for later sulfur content analysis. When the solvent refined coal had cooled down in the flask, the flask was broken and the recovered coal was crushed with a mortar and pestle to a size suitable for the sulfur analysis procedures.

Analysis of Sulfur in the Coal Product

The sulfur content in the coal product was determined according to four sulfur types: sulfate, pyritic, organic, and total sulfur content by weight percent. The analyses are outlined in the ASTM Standards for gaseous fuels, coals and cokes (44).

Total sulfur content was determined by Eschka method and it is described in ASTM D271-68 (ASTM, 1970, pp. 23-25). However, the following changes to section 20(c) were made on the analysis of total sulfur content:

a) Instead of digesting, heat gently with 100 ml of water for one hour.

b) After treating with bromine water, the solution is acidified with 1:1 HCl, and the absence of bromine in the boiling solution is detected by the color change of methyl orange to pink.

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

d) Smoke off the filter paper below 500°C for about one and one-half hours.

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

a) Section 5.1.1 -- Instead of using cold finger condenser, let the coal-HCl mixture set in the Erlenmeyer flask overnight.

b) Section 5.1.2 -- After adding NH_4OH, set the beaker aside for 15 minutes and allow the precipitate to coagulate.

c) 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.

The pyritic sulfur content of the coal product was also determined by ASTM D2492-68 with Sections 5.1.5 and 5.2 replaced by the following: Weigh out 2.0 grams of the coal residue from the sulfate test (to 0.01 mg). 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. Filter the mixture through a medium texture filter paper. Pour the filtrate back into the flask and refilter the solution, removing additional coal residue. Wash the flask with 35 ml of 1:7 nitric acid solution.

Discard the coal residue. 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 five minutes. If some organic coloration remains, add more hydrogen peroxide (making sure that the solution boils for five minutes more before adding NaOH). With constant stirring, slowly add concentrated NaOH until a red iron precipitate forms. Add two ml excess NaOH, making sure that the stirring rod and sides of the beaker are washed. Set the beaker aside for 15 minutes, to allow the iron precipitate to coagulate.

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 NH_4Cl and a trace of NH_4OH. At this point there should be no iron precipitate left in the beaker. Discard the filtrate.

Place the filter paper containing the iron precipitate in a clean beaker. Add 25 to 50 ml of 2:3 HCl 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 up. Next, while stirring, add dropwise, $SnCl_2$ solution until the mixture is milky white. Then add two to three drops of $SnCl_2$ in excess. Wash the sides of the beaker with water and allow the solution to cool to room temperature.

While stirring, quickly add 10 ml of $HgCl_2$. Rewash the sides of the beaker with water. Let the solution set for two to three minutes (do not stir). After two or three minutes, begin stirring. Add 20 ml of H_3PO_4-H_2SO_4-H_2O solution, two to three drops of diphenylamine sulfonate indicator and water until there is 200 ml of solution. 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.

The organic sulfur content of the coal was then determined by difference by subtracting the pyritic and sulfate sulfur weight percents from the total sulfur weight percent.

INTERPRETATION OF RESULTS

Material and Sulfur Balances

1. Sulfur Content

The final sulfur content of the different forms (pyritic, sulfate, inorganic, organic and total) are listed in Table 4. All the numbers are in weight percent.

Due to the limitations of the analytical technique, only pyritic, sulfate and total sulfur contents can be analyzed. The inorganic sulfur content is the sum of pyritic and sulfate sulfur content, while organic sulfur content is the difference between total and inorganic sulfur content.

The following excerpt is from the Office of Coal Research, Report No. 77, Interim Report No. 1 (4):

> Although the inorganic sulfur removal was found to be essentially 100% complete using the solvent refining process, uncertainties in the analytical procedures should be noted that qualify this finding. The bulk of the inorganic sulfur found in coal occurs as FeS_2 or pyritic sulfur. During the solvent refining process, the following may take place:
>
> $$FeS_2 + H_2 \rightarrow FeS + H_2S$$
>
> This reaction results in the evolution of H_2S gas and the formation of FeS, an insoluble inorganic sulfur form. The ASTM technique for determining the pyritic sulfur content of coal accounts for only FeS_2 and not FeS. Thus, if appreciable amounts of FeS were present in the insoluble ash phase, the analysis would not reflect this fact and artificially high values for the removal of inorganic (pyritic) sulfur would result. It is, however, possible that during the vacuum distillation process, the FeS in

Table 4

Sulfur Content of Solvent Refined Coal

	Percent Sulfur				
Run	Pyritic	Sulfate	Inorganic	Total	Organic
CKH	1.277	0.245	1.522	3.496	1.974
IMH	0.474	0.610	1.084	4.417	3.333
1A	0.179	0.022	0.201	2.141	1.940
1B	0.715	0.021	0.736	2.459	1.723
2A	0.141	0.015	0.156	1.958	1.802
2B	0.128	0.017	0.145	1.973	1.828
3A	0.026	0.018	0.044	1.774	1.730
3B	0.056	0.017	0.073	1.775	1.702
4A	0.154	0.029	0.183	2.079	1.896
4B	0.161	0.027	0.188	2.070	1.882
5A	0.065	0.015	0.080	1.810	1.730
5B	0.096	0.004	0.100	1.901	1.801
6A	0.028	0.015	0.043	1.926	1.883
6B	0.033	0.039	0.072	1.743	1.671
7A	0.095	0.024	0.119	1.708	1.589
7B	0.094	0.026	0.120	1.980	1.860
8A	0.102	0.030	0.132	1.913	1.781
8B	0.096	0.027	0.123	2.038	1.915
9A	0.160	0.024	0.184	2.067	1.883
9B	0.081	0.024	0.105	1.949	1.844
10A	0.099	0.186	0.285	2.932	2.647
10B	0.207	0.197	0.404	2.954	2.550
11A	0.069	0.056	0.125	2.897	2.772
11B	0.189	0.127	0.316	2.800	2.484
12A	0.121	0.141	0.262	3.250	2.988
12B	0.111	0.146	0.257	3.510	3.253
13A	0.110	0.128	0.239	3.196	2.957
13B	0.074	0.127	0.201	3.284	3.083
14A	0.113	0.131	0.244	3.416	3.172
14B	0.123	0.109	0.232	3.471	3.239
15A	0.156	0.071	0.227	3.327	3.100
15B	0.132	0.064	0.196	3.159	2.963
16A	0.055	0.061	0.116	2.265	2.149
16B	0.190	0.096	0.286	2.829	2.543
17A	0.205	0.090	0.295	2.965	2.670
17B	0.147	0.088	0.235	2.578	2.343
18A	0.253	0.071	0.324	2.677	2.353
18B	0.184	0.070	0.254	2.462	2.208

the ash phase reacts further with residual hydrogen in the solvent as follows:

$$FeS + H_2 \rightarrow Fe + H_2S$$

The presence of this reaction would allow extremely high pyritic sulfur removals to be achieved by the solvent refining process. Since the insoluble matter was not filtered from the reaction product as extracted from the reaction vessel, and in light of the extremely severe conditions present in the distillation vessel (vacuum, 300°C), such a reaction may have occurred and the results not observed. At present, analytical techniques are not available which would allow this hypothesis to be experimentally confirmed by laboratory analysis, however, the hypothesis has been supported by an iron pyrite experiment in which the reaction of pyritic sulfur with hydrogen was continuing during the distillation step. An experimental run was made in the rocking bomb reactor using iron pyrite (FeS_2) mineral as the raw material. One hundred grams of the mineral and 150 grams of anthracene were charged to the reactor with 625 psig partial pressure of hydrogen at reaction temperature (383°C).

The product from the reactor was split into two parts; one was put through the distillation step under 24 in. Hg vacuum at a maximum temperature of 300°C. The other half of the reaction product was not taken through the distillation step but was filtered and washed with acetone to recover the iron pyrite from the anthracene. The results of chemical analysis of the iron pyrite run are given below:

Sample	% Pyritic Sulfur
Head	20.9
Reaction Product	13.6
Distillation Product	8.9

These preliminary results tend to reinforce the hypothesis that the pyritic sulfur content of the reaction product is further reduced during the vacuum distillation step.

2. Percent of Sulfur Removal and Surface Responses

Table 5 presents the percent sulfur removal for the total experimental program. In Table 5 the best desulfurization achieved for CK (subbituminous) coal is indicated by *, while that for IM (bituminous) coal is indicated by **. It is evident that for bituminous and subbituminous coals, the best desulfurization of organic and total sulfur was achieved in run 7 and run 16, respectively. Both runs 7 and 16 have the same pressure and temperature (600 psig and $400^{\circ}C$), which indicates the trend of best desulfurization found in this experiment. In order to study the direction of efficient desulfurization, response surfaces of total desulfurization were plotted. Figure 6 shows the response surfaces of CK and IM coals on total desulfurization with respect to temperature and pressure.

The CK coal gives a saddle-shaped surface with its ridge running along the diagonal that joins the high temperature and low pressure. This combined effect of temperature and pressure is further supported by the analysis of variance technique which is discussed in the following sections. The IM coal, however, gives a crater-shaped surface with a steep rise along the high temperature range. This trend is also reinforced in the analysis of variance on the data obtained from the IM coal products.

An explanation of the response surface shape requires additional study in view of the very complex desulfurization mechanism.

Table 5

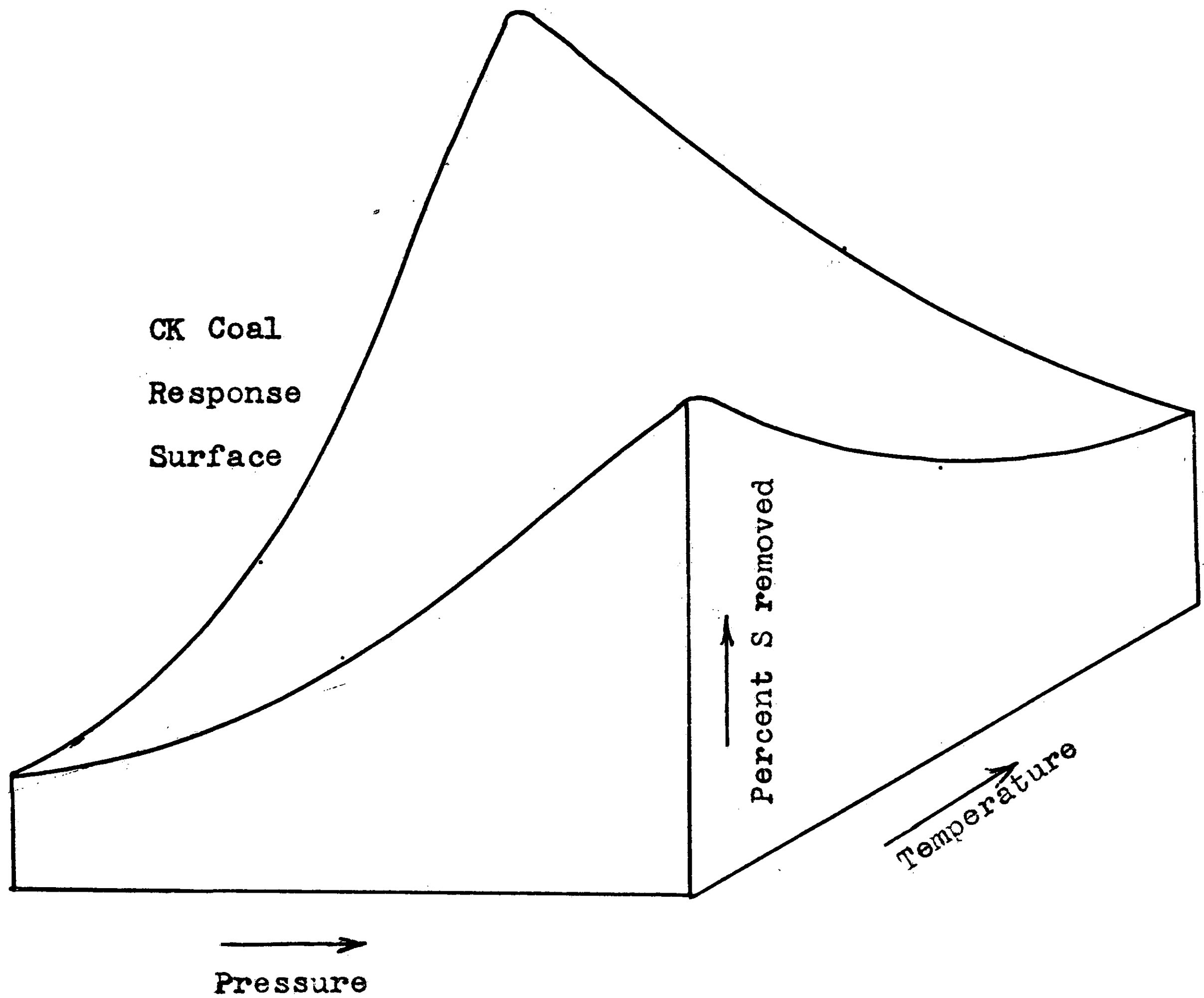
Percent Sulfur Removal

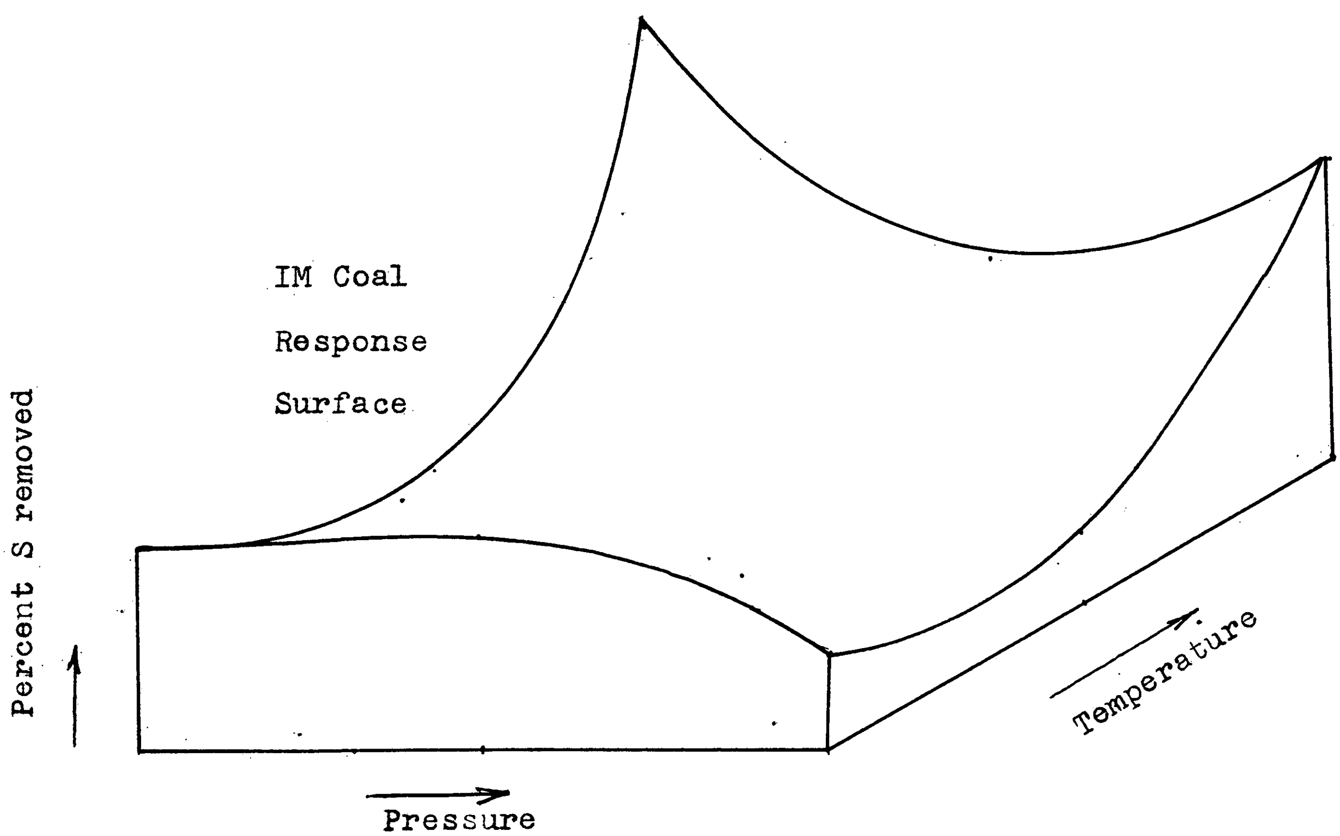
Run	Organic	Inorganic	Total
1A	1.72	86.80	38.76
1B	12.72	52.65	29.66
2A	8.71	89.75	43.99
2B	7.40	90.47	43.56
3A	12.36	97.11	49.26
3B	13.78	95.20	49.23
4A	3.95	87.98	40.53
4B	4.66	87.65	40.79
5A	12.36	94.74	48.23
5B	8.76	93.43	45.62
6A	4.61	97.18*	44.91
6B	15.35	95.27	50.14
7A	19.50*	92.18	51.14*
7B	5.78	92.12	43.36
8A	9.78	91.33	45.28
8B	2.99	91.92	41.71
9A	4.61	87.91	40.88
9B	4.56	93.10	44.25
10A	20.58	73.71	33.62
10B	23.49	62.73	33.12
11A	16.83	88.47	34.41
11B	25.47	70.85	36.61
12A	10.35	75.83	26.42
12B	2.40	76.29	20.53
13A	11.28	77.95	27.64
13B	7.50	81.46	25.65
14A	4.83	77.49	22.66
14B	2.82	78.60	21.42
15A	6.99	81.92	24.68
15B	11.10	72.69	28.48
16A	35.52**	89.30**	48.72**
16B	23.70	73.62	36.18
17A	19.89	72.79	32.87
17B	29.70	78.32	41.64
18A	29.40	70.11	39.39
18B	33.75	76.57	44.26

*Maximum percentage of sulfur removed in subbituminous coal.

**Maximum percentage of sulfur removed in bituminous coal.

Figure 6


CK Coal
Response
Surface
Percent S removed
Temperature
Pressure


IM Coal
Response
Surface
Percent S removed
Temperature
Pressure

3. Selected Sulfur Balances

Some effort was devoted to closing a sulfur balance for the experiments. A selected sulfur balance result is shown in Table 6. The best sulfur accountability was achieved in run 16A, which gives 90.4% sulfur accounted in the process of desulfurization. A better result may have been obtained on sulfur accountability if the scrubber sample data had been obtained for every run.

4. Mass Balance on Coal and Anthracene Oil

In Table 7, the percent of coal yield and percent solvent recovered were calculated based on the feed weights of coal and solvent, which are 50 and 250 gm, respectively. The percent of coal yield ranges from 90% to 136%. Theoretically the yield should be less than 100%, however, these figures indicate that there was some solvent left in the product coal.

The anthracene oil can be driven out of the product completely if it is severely coked during the vacuum distillation step. However, the recovery was subject to the vacuum constraints of the distillation system used and the desire not to coke the final coal product.

The percentage of solvent recovery in all cases was not 100%. This may be attributed to the losses incurred during transfer into and out of the reaction vessel and the distillation flask. The losses in all these transfer steps are neglected.

Table 6

Selected Sulfur Balance

Run	Reaction			Off-gas			% Sulfur
	In (g)	Out (g)	Difference (g)	Vol. H_2S at STP	n_{H_2S}	Wt. Sulfur (g)	Accounted
13B	2.209	1.609	0.599	0.231	0.010	0.320	53.4
16A	2.209	1.749	0.460	0.283	0.013	0.416	90.4

Table 7

Mass Balance on Coal and Solvent

Run	SRC (gm)	Anthracene Oil (gm)	% Coal Yield	% Solvent Recovered
1A	68	198	136	79
1B	52	215	104	86
2A	46	196	92	78
2B	55	206	110	82
3A	54	206	108	82
3B	64	189	128	76
4A	54	220	108	88
4B	53	222	106	89
5A	57	219	114	88
5B	51	207	102	83
6A	55	208	110	83
6B	57	206	114	82
7A	59	214	118	86
7B	43	220	86	88
8A	47	225	94	90
8B	47	209	94	84
9A	53	228	106	91
9B	58	216	116	86
10A	50	236	100	94
10B	51	228	102	91
11A	47	191	94	76
11B	59	212	118	85
12A	55	217	110	87
12B	55	212	110	85
13A	46	232	92	93
13B	49	220	98	88
14A	46	225	92	90
14B	49	236	98	94
15A	46	226	92	90
15B	43	228	86	91
16A	66	212	132	85
16B	52	230	104	92
17A	48	233	96	93
17B	51	227	102	91
18A	45	230	90	92
18B	60	217	120	87

5. Material Accountability on Vacuum Distillation

Table 8 shows the material accountability on the vacuum distillation. In all the runs, the best material balance was 100%, the least 97.2%. The loss is due to the vaporization of some low boiling cut of the anthracene oil under severe pressure and high temperature.

6. Ash Balance

An ash test was performed to see if desulfurization had an effect on the ash content of coal. In the conventional solvent refining process, ash is removed by steam filtering the reacted coal. However, desulfurization by solvent refining in hydrogen atmosphere without performing the deashing step appears to lower the ash content of the coal as demonstrated with several tests. A small quantity of the ash might be lost in the coal solution which adhered to the inner surface of the reaction vessel during the transfer of reacted coal solution to the distillation flask. Actual loss might be due to entrainment during the distillation step. However, not enough experimental evidence was collected to support the establishment of any hypothesis that could explain the reduction of ash content in the product coal.

Statistical Analysis

The analysis of variance tables for CK and IM coals are shown in Tables 9 and 10, respectively, each with analyses on percent of total, organic, and inorganic sulfur removal

Table 8

Material Accountability on Vacuum Distillation

Run	In (gm)	Out (gm)	Loss (gm)	Percent Accounted For
1A	271	266	5	98.2
1B	269	267	2	99.3
2A	243	242	1	99.6
2B	266	261	5	98.1
3A	264	260	4	98.5
3B	253	253	0	100.0
4A	277	274	3	98.9
4B	277	275	2	99.3
5A	279	276	3	98.9
5B	261	258	3	98.9
6A	267	263	4	98.5
6B	266	263	3	98.9
7A	275	273	2	99.3
7B	269	263	6	97.8
8A	276	272	4	98.6
8B	258	256	2	99.2
9A	281	281	0	100.0
9B	280	274	6	97.9
10A	286	286	0	100.0
10B	287	279	8	97.2
11A	242	238	4	98.3
11B	276	271	5	98.2
12A	273	272	1	99.6
12B	267	267	0	100.0
13A	280	278	2	99.3
13B	274	269	5	98.2
14A	271	271	0	100.0
14B	285	285	0	100.0
15A	278	272	6	97.8
15B	272	271	1	99.6
16A	279	278	1	99.6
16B	288	282	6	97.9
17A	286	281	5	98.3
17B	286	278	8	97.2
18A	279	275	4	98.6
18B	283	277	6	97.9

Table 9

Analysis of Variance Tables for CK Coal

Based on Total sulfur data

SØURCE	DF	SUM ØF SQUARES	MEAN SQUARES	MSR
TL	1	12.32	12.32	1.10
TQ	1	10.41	10.41	0.93
PL	1	98.79	98.79	8.81 *
PQ	1	5.34	5.34	0.48
(TP)	4	209.95	52.49	4.68 *
RESID	9	100.93	11.21	
TØTAL	17	437.74		

Based on Organic sulfur data

SØURCE	DF	SUM ØF SQUARES	MEAN SQUARES	MSR
TL	1	31.40	31.40	1.16
TQ	1	16.47	16.47	0.61
PL	1	106.92	106.92	3.94 *
PQ	1	17.75	17.75	0.65
(TP)	4	441.38	110.34	4.07 *
RESID	9	243.94	27.10	
TØTAL	17	857.86		

Based on Inorganic sulfur data

SØURCE	DF	SUM ØF SQUARES	MEAN SQUARES	MSR
TL	1	0.00	0.00	0.00
TQ	1	6.69	6.69	1.49
PL	1	74.75	74.75	16.64 *
PQ	1	0.08	0.08	0.02
(TP)	4	76.83	19.21	4.27 *
RESID	9	40.44	4.49	
TØTAL	17	198.79		

Table 10

Analysis of Variance Tables for IM Coal

Based on Total sulfur data

SOURCE	DF	SUM OF SQUARES	MEANSQUARES	MSR
TL	1	283.73	283.73	16.08 *
TQ	1	445.98	445.98	25.28 *
PL	1	37.35	37.35	2.12
PQ	1	2.49	2.49	0.14
(TP)	4	185.11	46.28	2.62
RESID	9	158.80	17.64	
TOTAL	17	1113.46		

Based on Organic sulfur data

SOURCE	DF	SUM OF SQUARES	MEANSQUARES	MSR
TL	1	442.14	442.14	18.24 *
TQ	1	920.52	920.52	37.97 *
PL	1	65.71	65.71	2.71
PQ	1	8.01	8.01	0.33
(TP)	4	323.40	80.85	3.33
RESID	9	218.21	24.25	
TOTAL	17	1977.97		

Based on Inorganic sulfur data

SOURCE	DF	SUM OF SQUARES	MEANSQUARES	MSR
TL	1	13.72	13.72	0.29
TQ	1	27.79	27.79	0.59
PL	1	2.39	2.39	0.05
PQ	1	12.09	12.09	0.26
(TP)	4	198.90	49.72	1.06
RESID	9	424.08	47.12	
TOTAL	17	678.97		

in the product coal. The F statistic at the 90% confidence level ($F_{1,9,.90} = 3.36$) was chosen as the test statistic for the experiment. Based on the comparison of the mean square ratio with the F statistic, it may be seen that CK (subbituminous) coal is responsive to the linear pressure effect and the temperature-pressure interaction. This finding is consistent in all forms of sulfur removal for the CK coal.

The total and organic sulfur removal analyses indicate that IM (bituminous) coal is responsive to a temperature (both quadratic and linear) effect while inorganic sulfur removal shows no significant response to pressure or temperature, either linear or quadratic.

Effect of Temperature

Generally, the rate is temperature dependent as described by the Arrhenius equation:

$$k = k_o \exp(-E/RT)$$

where k = rate constant, hr^{-1}

k_o = frequency factor, hr^{-1}

E = energy of activation, kcal/g-mole

R = gas law constant, kcal/g-mole ^oK

T = reaction temperature, ^oK

It is obvious from the equation that k is directly proportional to T. The experimental results in Table 5 have shown higher sulfur removal as the temperature increases. In addition to that, the analysis of variance and empirical modeling have both supported the idea that high temperature improves the desulfurization.

Effect of Pressure

Hydrogenation, particularly for desulfurization and denitrification, favors higher hydrogen partial pressure. However, in this study, the reverse tendency has been observed. Pressure is a factor significant in the analysis of variance for subbituminous coal. In the batch reactor, quite probably the reaction reaches equilibrium rapidly for desulfurization, thus higher initial hydrogen pressure would inhibit the shift of equilibrium towards the favorable direction.

Coal has very complicated chemical structure and breaks down into smaller structures during dissolution and reaction which results in a large number of individual reactions. They compete with each other to form the more stable intermediates or products. The mechanism is hypothesized as follows:

$$\text{Coal} \xrightarrow[\text{reaction}]{\text{dissolution}} C_1 + C_2 + C_3 + \ldots$$

$$C_1 + a_0\, H_2 \longrightarrow b_o\,(CG_1) + b_1\,(CL_1) + b_2\,(CS_1)$$

$$C_2 + a_1\, H_2 \longrightarrow b_3\,(CG_2) + b_4\,(CL_2) + b_5\,(CS_2)$$

$$\vdots \qquad\qquad\qquad \vdots$$

where C_i = smaller molecules or radicals decomposed from coal

a_i, b_i = stoichiometric constants

CG_i = gaseous intermediate or product from corresponding C_i

CL_i = liquid intermediate or product from corresponding C_i

CS_i = solid intermediate or product from corresponding C_i

The sum of coefficients for gaseous product (i.e. sum of b_i for gaseous compounds) for all these reactions might be larger than the sum of coefficients for hydrogen (i.e. sum of a_i). The hypothesis tends to explain why a lower initial hydrogen pressure gives better desulfurization than a higher one. However, the range of pressures studied is too small to draw a reliable conclusion.

Empirical Modeling

Statistically it is possible to model this process by considering a generalized model as

$$Y = a_0 + a_1T^2 + a_2T + a_3P^2 + a_4P + a_5(TP)$$

where Y = percent sulfur removed

T = temperature, ^{o}C

P = pressure, psia

a_i = coefficients to be determined.

The ranges of the temperature and pressure are restricted to 325-400^{o}C and 600-1800 psi, respectively.

Through statistical manipulation, the coefficients of the suggested model were evaluated. Table 11 summarizes the regression analysis results on these coefficients. The first three models are for CK (subbituminous) coal with correlation coefficients (R) of approximately 0.80 for all three models based on different types of sulfur forms considered. The second number in each bracket is the standard deviation of the determined coefficient. A glance at the coefficients of this data set indicates that the coefficients are consistent and correlated in order of magnitude. A final empirical model based on total sulfur removal is presented for each coal in Table 12.

<u>Activation Energy from Pseudo-First Order Fit</u>

It is impossible to perform the conventional reaction order analysis on the overall kinetic system. Through mathematical manipulations, the activation energy for the system was calculated from a pseudo-first order fit, but no meaningful results were obtained. However, through several mathematical manipulations, an attempt was made to calculate the activation energy for a pseudo-first reaction order fit. Unfortunately, for the coal solvent refining process no meaningful results were obtained.

Table 11

Summary of Empirical Models of Desulfurization Results from Regression Analysis

Designation	R	Empirical Model				
		a_o	a_2	a_4	a_5	a_3
CK-Total	.83	- 37.04	$.21 \pm .050$	$.061 \pm .013$	$-(1.6\text{x}10^{-4} \pm 3.8\text{x}10^{-5})$	$-(1.10\text{x}10^{-11} \pm 2.13\text{x}10^{-12})$
CK-Organic	.80	-110.06	$.32 \pm .075$	$.087 \pm .020$	$-(2.3\text{x}10^{-4} \pm 5.8\text{x}10^{-5})$	$-(1.40\text{x}10^{-11} \pm 3.2\text{x}10^{-12})$
CK-Inorganic	.77	56.29	$.089 \pm .038$	$.031 \pm .010$	$-(7.5\text{x}10^{-5} \pm 2.9\text{x}10^{-5})$	$-(6.7\text{x}10^{-12} \pm 1.6\text{x}10^{-12})$
		a_o	a_1	a_2	a_5	a_4
IM-Total	.81	578.19	$.0048 \pm .0011$	$-(3.27 \pm .74)$	--	--
IM-Organic	.90	868.46	$.0068 \pm .0011$	$-(4.84 \pm .80)$	$1.5\text{x}10^{-4} \pm 6.3\text{x}10^{-5}$	$-(.058 \pm .023)$
IM-Inorganic	.52	Nothing reliable				

The general model is:

$$y = a_o + a_1T^2 + a_2T + a_3P^2 + a_4P + a_5(TP)$$

Table 12

Empirical Desulfurization Model for

Bituminous and Subbituminous Coals

Coal	Model
Bituminous	$y = 578.19 + .0048\ T^2 - 3.27\ T$
Subbituminous	$y = -37.04 + .21\ T + .061\ P - .00016\ (TP)$

Key: y = Percent of sulfur removal

T = Temperature, $^{\circ}C$

P = Pressure, psia

General Discussion of the Data

Figures 7 and 8 present the data for total sulfur analysis for the two coals investigated in this study. In Figure 7a, percent total sulfur removal is plotted versus temperature with hydrogen partial pressure as a parameter for IM coal. In Figure 7b, percent total sulfur removal is plotted versus pressure with temperature as a parameter for IM coal. The same plots are done for CK coal in Figures 8a and 8b. In both plots, replicate sulfur analyses are plotted for each run conditions as well as replicate runs. For each point in the experimental matrix two replicate runs were completed while for each run at least three replicate sulfur analyses were completed. The data for replicate runs and replicate sulfur analysis are shown in Figures 7 and 8.

The data in both Figures 7 and 8 is scattered. However, it must be remembered that the maximum error in total sulfur analysis is $\pm 0.1\%$ sulfur. Consequently, the scatter is not too surprising. Efforts to determine the cause of the scatter led to the following potential causes:

1. Sampling
    a. Inhomogeneous sulfur charge in the reactant.
    b. Inhomogeneous sulfur out of the product.
    c. Inhomogeneous sulfur into the analytical test.

d. Inhomogeneous anthracene oil (mixed cut).

e. Sample size too small.

2. Reproducibility of experimental conditions.
3. Kinetic and mass transfer phenomena during reaction under different conditions.
4. Catalytic effects by metallic impurities in the coal or reaction vessel.

It was impossible to investigate all of the above causes during the course of this study and future effort should be devoted toward explaining the above phenomenon.

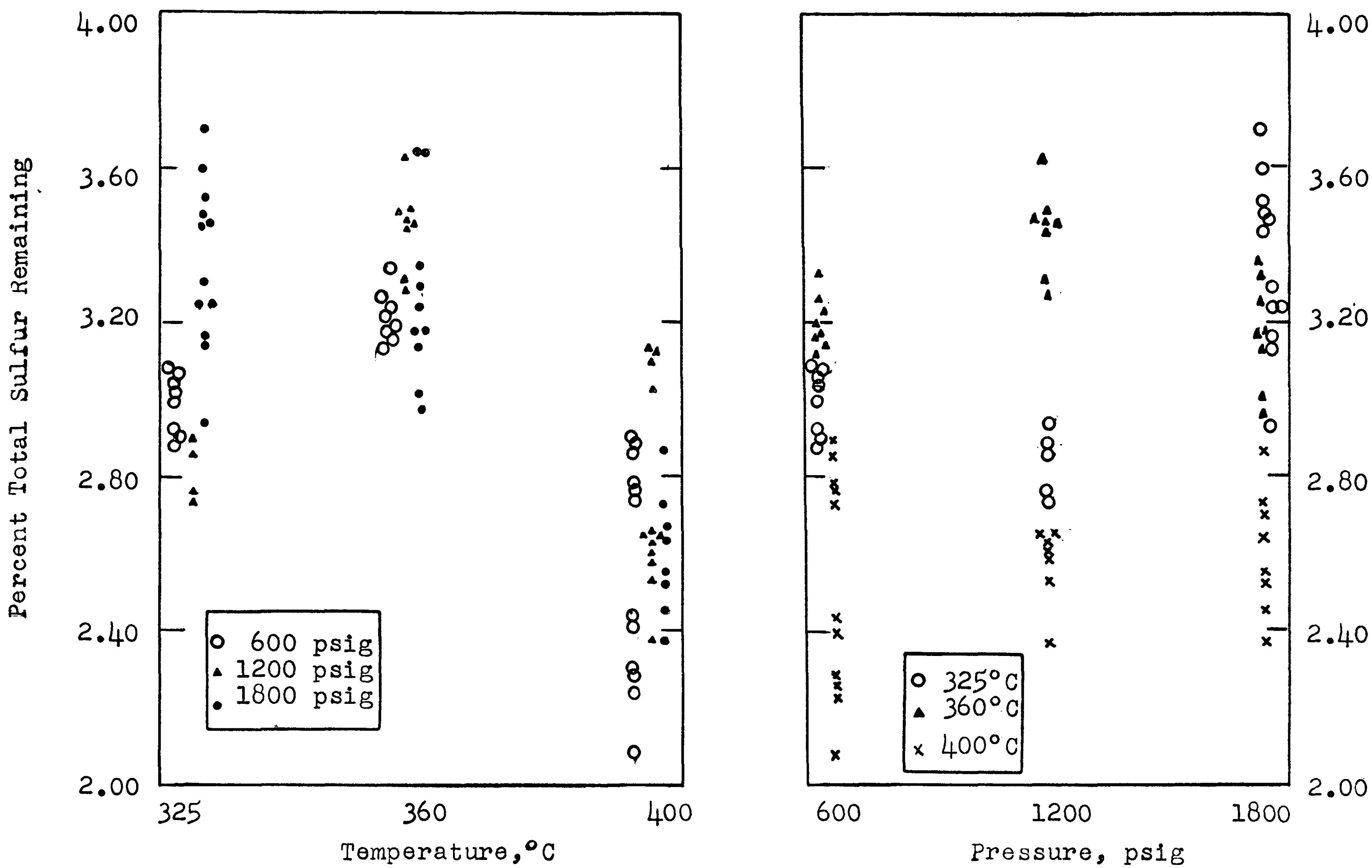
Even in view of the scatter, the data does suggest the following:

1. Higher temperature improves desulfurization for both the CK and IM coals.
2. The pressure effect is not clear although both coals show better desulfurization under high temperature and low hydrogen partial pressure.

Figure 7

Percent sulfur removal at different pressures vs. temperatures for IM coal

Percent sulfur removal at different temperatures vs. pressures for IM coal



(7a)

(7b)

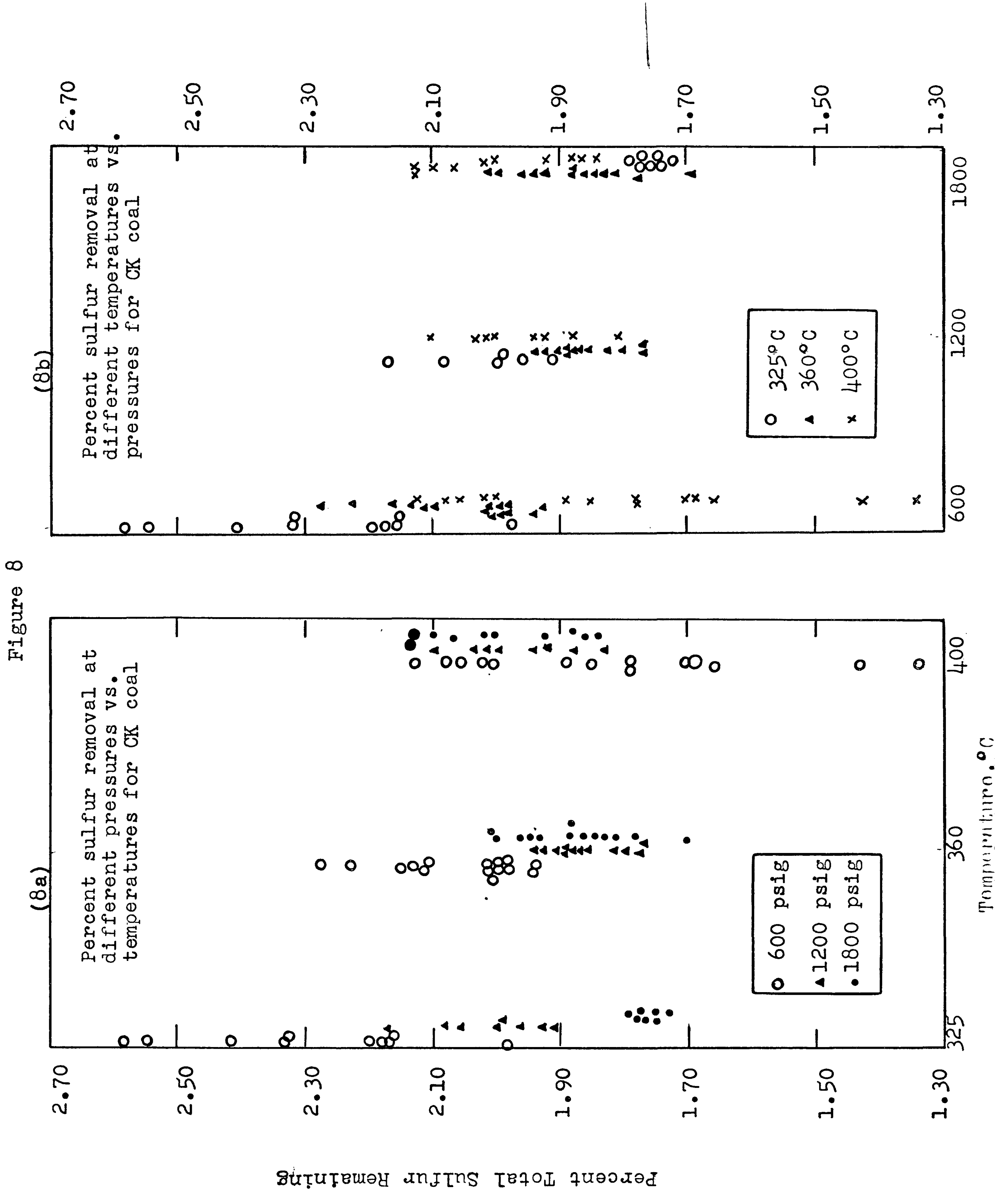

(8a)
Percent sulfur removal at different pressures vs. temperatures for CK coal
o 600 psig
▲1200 psig
•1800 psig
(8b)
Percent sulfur removal at different temperatures vs. pressures for CK coal
o 325°C
▲ 360°C
× 400°C
Percent Total Sulfur Remaining
Temperature, °C
2.70
2.50
2.30
2.10
1.90
1.70
1.50
1.30
325
360
400
600
1200
1800

Figure 8

CONCLUSIONS

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

1. At the 90% confidence level, the desulfurization of the bituminous coal is significantly affected by temperature (quadratic and linear effects).
2. At the 90% confidence level, the desulfurization of the subbituminous coal is significantly affected by pressure (linear effect) and temperature-pressure interaction.
3. Empirical models of desulfurization for bituminous and subbituminous coals are presented as follows:

   Bituminous coal: $y = 578.19 + 0.0048T^2 - 3.27\ T$

   Subbituminous coal: $y = -37.04 + 0.21\ T + 0.061\ P - 0.00016\ (TP)$

   where y = percent of total sulfur removal

   T = temperature, $^\circ$C (325-400°C)

   P = pressure, psi. (600-1800 psi)
4. A combination of low pressure and high temperature favors increased desulfurization for the variable ranges studied in this experimental research.
5. Treatment of coal in solution with hydrogen is a technically feasible method of removing both organic

and inorganic sulfur from coal. The maximum removal of organic, inorganic, and total sulfur from the coals studied was 35.52, 97.18, and 51.14 percent, respectively.

6. Inorganic sulfur removal is relatively high (70-98%) regardless of which combination of levels of the process variables are considered. This conclusion is true only if the hypothesized reaction $FeS + H_2 \rightarrow Fe + H_2S$ goes to completion. If this is not true then the inorganic sulfur removal is not as high as it is calculated.
7. Solvent recovery of the process ranges from 76-94% while the yield of solvent refined coal is higher than 90%.
8. Loss of vapor due to vacuum distillation is low; in every run the loss is well below 3%.
9. Due to the difficulty in direct analysis for FeS or organic sulfur in the coal samples, an error in the forms of sulfur analyses will show up in the organic sulfur content of the coal. As it is indicated in the ASTM Standards, for coals with sulfur content over 2%, the permissible differences for total sulfur analysis within the same laboratory is 0.1%. Based on this fact, the total sulfur content percentages are more reliable than the percentages of the other forms of sulfur.

RECOMMENDATIONS

Coal itself is a very complicated substance, to desulfurize it efficiently requires a thorough knowledge of the major effects. Besides temperature, pressure, and their interactions, other possible effects such as particle size of raw coal, solvent type, solvent to coal ratio, heating rate and recycling of solvent will probably affect desulfurization. Accordingly, these effects require additional study. During this investigation, difficulties were encountered in developing a reaction mechanism which will give reliable kinetic data for the process. This information is necessary for realistic economic evaluation of the commercial size plant and more effort should be directed in this area. An additional recommendation would be that chromatographic techniques should be used to analyze the gaseous products rather than the titration techniques used in this study.

Based on the findings of this investigation, it is recommended that an optimization study on desulfurization be conducted. From the trends indicated by this experiment, the temperature and pressure ranges of 350-450^{o}C and 500-2500 psig are recommended for further investigation. Concurrent with this, a study on reclaimed solvent with emphasis on hydrogen enrichment and mechanism of desulfurization will eventually lead to a better understanding of desulfurization process. Also a study on better techniques for direct analysis on FeS and organic sulfur will benefit further research on coal desulfurization. Finally, a study on the ash content with respect to the desulfurization parameters will be beneficial to the advancement of coal utilization industry.

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APPENDIX

COMPUTER PROGRAM ON ANALYSIS OF VARIANCE OF 3^2 CROSS, DOUBLE - REPLICATE FACTORIAL DESIGN

To illustrate the use of this computer program, the sample input is shown below:

```
INPUT A,B,C,D,E,F33.62,33.12,34.31,36.61,26.42,20.53
INPUT G,H,P,Q,R,S27.64,25.65,22.66,21.42,24.68,28.48
INPUT T,U,V,W,X,Y48.72,36.18,32.87,41.64,39.39,44.26
```

The printout of this analysis of variance is shown by ANOVA table for IM coal based on total sulfur removal in Table 10.

TYPE NØVA.F4

```
[11:02:25]
C       ANALYSIS ØF VARIANCE FØR 2 FACTØRS AT 3 LEVELS
1       FØRMAT(' INPUT A,B,C,D,E,F',$)
        WRITE(4,1)
        READ(4,6)A,B,C,D,E,F
        WRITE(4,2)
2       FØRMAT(' INPUT G,H,P,Q,R,S',$)
        READ(4,6)G,H,P,Q,R,S
        WRITE(4,3)
3       FØRMAT(' INPUT T,U,V,W,X,Y',$)
        READ(4,6)T,U,V,W,X,Y
6       FØRMAT(6F)
        RSUM1=A+B+G+H+T+U
        RSUM2=C+D+P+Q+V+W
        RSUM3=E+F+R+S+X+Y
        CSUM1=A+B+C+D+E+F
        CSUM2=G+H+P+Q+R+S
        CSUM3=T+U+V+W+X+Y
        SSTØ=A**2+B**2+C**2+D**2+E**2+F**2+G**2+H**2
     1+P**2+Q**2+R**2+S**2+T**2+U**2+V**2+W**2+X**2+Y**2
        SST1=CSUM1+CSUM2+CSUM3
        SST2=SST1**2/18.
        SST=SSTØ-SST2
        SSS=2.*(((A+B)/2.)**2+((C+D)/2.)**2+((E+F)/2.)**2
     1+((G+H)/2.)**2+((P+Q)/2.)**2+((R+S)/2.)**2+((T+U)/2.)**2
     1+((V+W)/2.)**2+((X+Y)/2.)**2)
        RES=SSTØ-SSS
        SSPL=((RSUM3-RSUM1)**2)/12.
        SSTL=((CSUM3-CSUM1)**2)/12.
        SSPQ=((RSUM1+RSUM3-2.*RSUM2)**2)/36.
        SSTQ=((CSUM1+CSUM3-2.*CSUM2)**2)/36.
        PT=SST-RES-SSTL-SSPL-SSPQ-SSTQ
        SPT=PT/4.
        SRES=RES/9.
        SRTL=SSTL/SRES
        SRPL=SSPL/SRES
        SRTQ=SSTQ/SRES
        SRPQ=SSPQ/SRES
        SRPT=SPT/SRES
        WRITE(4,7)
        WRITE(4,8)SSTL,SSTL,SRTL
        WRITE(4,9)SSTQ,SSTQ,SRTQ
        WRITE(4,10)SSPL,SSPL,SRPL
        WRITE(4,11)SSPQ,SSPQ,SRPQ
        WRITE(4,12)PT,SPT,SRPT
        WRITE(4,13)RES,SRES
        WRITE(4,14)SST
        WRITE(4,15)
7       FØRMAT(4X,'SØURCE   DF      SUM ØF SQUARES   MEAN
     1SQUARES',7X,'MSR',/)
8       FØRMAT(5X,'TL',6X,'1',3X,3F14.2,/)
9       FØRMAT(5X,'TQ',6X,'1',3X,3F14.2,/)
10      FØRMAT(5X,'PL',6X,'1',3X,3F14.2,/)
11      FØRMAT(5X,'PQ',6X,'1',3X,3F14.2,/)
12      FØRMAT(4X,'(TP)',5X,'4',3X,3F14.2,/)
13      FØRMAT(4X,'RESID',4X,'9',3X,2F14.2,/)
14      FØRMAT(4X,'TØTAL',3X,'17',3X,F14.2)
15      FØRMAT(4X,' TYPE 1 TØ RERUN,-1 TØ EXIT ',$)
        READ(4,16)Q
16      FØRMAT(F)
        IF(Q)20,1,1
20      STØP
        END.
```