

A PRELIMINARY STUDY OF NON-CATALYZED  
HYDRODESULFURIZATION OF COAL-  
DERIVED LIQUIDS

By

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## PREFACE

Coal-derived oils from two sources were hydrotreated in this experiment. They were the PAMCO (Pittsburg and Midway Coal Mining Company) oil and the FMC filtered oil (Colorado Bear Mine). Non-catalytic hydrodesulfurization studies were conducted at 500 and 1500 psig reaction pressures, 700° and 800°F temperatures and 1.18 and 3.14 liquid volume hourly space times in a trickle flow reactor.

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## NOMENCLATURE

### Abbreviations

bb1	petroleum barrel
cc	cubic centimeter
°F	degree Fahrenheit
hr	hour
ml	milliliter
SCF	standard cubic feet
sq. ft.	square feet
S.S.	stainless steel



## CHAPTER I

### INTRODUCTION

An intense research effort in coal liquefaction could not have been timed better. The production of fuels from coal is not a new endeavor. During World War II hydrogenation of coal by the Bergius process was widely used in Germany for the manufacture of motor fuels. The uneconomical processing and the related pollution problems stood in the way of development and utilization in the United States.

Energy is absolutely indispensable to life and growth. The rate of energy consumption is a direct deciding factor behind the economy and the well-being of every nation in the modern world. The per capita income and energy consumption are very closely linked through their fundamental nature. From the history of progress of a country like the United States, the overwhelming role that energy has in building a country's economy and life style shall not be underestimated. The cheaply available fuels have energized the United States towards the destiny of world leadership.

At present, oil and natural gas together contribute about 75% of the total energy requirements of the United States (17). But the domestic oil and gas reserves are dwindling and have proven to be inadequate to keep pace with the rising energy demands. The relatively recent oil embargo imposed by the Arabs subsequent to the Mid-East confrontation, has already portrayed the detrimental effects of excessive dependence on foreign oil sources.

The demand of energy on a total world basis is increasing from the equivalent of 100 to 170 million barrels (bbl) of crude oil per day during this decade; and by the year 2000, this demand is projected to rise to 400 million bbl of equivalent crude oil per day (37). Countries such as Japan and other nations of Western Europe are also competing with the United States to strengthen the seller's market. Beyond a doubt, the availability of a cheap source of oil will no longer exist.

Distressed by this dilemma, the United States is considering the various energy sources which may be necessary to cope with the basic requirements to maintain her active economy and life-style.

The environmental concerns, the pricing policy and the increasing population, coupled with some misuse of energy, are some of the key factors that led to an early drainage of the oil and gas wells and lack of exploration in the United States. The coal industry has been hard hit with the enactment of stringent environmental regulations, mine safety laws and lack of firm regulatory policies by certain governmental bodies. Consequently coal as a promising source of energy had been virtually written off and considered only as a monument.

Anticipating the unhealthy situation of an energy deficit, the nation started searching for new avenues leading to amenable solutions. Nuclear reactors have emerged as a plausible answer. The other cognizant sources such as solar energy, hydrogen and fusion are not developed to the extent that they could take up the energy task in the foreseeable future.

The start-up delays in nuclear plants have put the promises of peace-time nuclear energy far behind schedule. The recent upsets

in world politics have created a new perspective in the arena of diplomatic and domestic administration of the United States. This necessitated an urgent reshuffling and reformulation of the statutes adopted in related environmental and energy fields. The scenario is changing. Work with the Alaskan pipe line is being expedited, and the country is contemplating coal as again being a vital energy resource.

The United States has about 3.3 trillion tons of coal beneath her soil. This is a total estimated resource base without consideration of recovery technology, economics and such items. Research on coal has been going on since the last few decades to obtain energy in one form or another. Gasification and liquefaction are employed in the coal-conversion process now under development. An economic production of liquid fuels from coal would be most desirable if this could substitute as a crude oil to be used in conventional refinery operations.

This study has been confined to coal liquefaction. The coal-derived liquids contain undesirable sulfur and nitrogen compounds and hence, are to be eliminated before such liquids are further processed. The sulfur is poisonous to various catalysts used in the conventional refinery processing units. The removal of sulfur from coal liquids in a non-catalytic hydrotreating unit is the topic of this study.

In previous studies in the School of Chemical Engineering at the Oklahoma State University, coal-derived liquids had been hydrotreated in trickle flow reactors (1,30,36,38). Various studies were

conducted with the objectives oriented towards the development of a catalyst for the desulfurization and denitrogenation of coal liquids. Assessing the extent of sulfur removal from coal liquids in the absence of a catalyst in a hydrotreating reactor is the major effort of this work. A study of the non-catalytic desulfurization is significant as this could have a bearing on the kinetic modelling of the desulfurization reactions. Non-catalytic desulfurization will also serve to illustrate the relative advantages of catalysts. The results of these experiments could also be successfully employed to assess the performance of the various catalysts leading to their economic evaluation when used under similar circumstances. The specific objectives pertinent to this experimental study are:

1. To provide information towards the development of relevant kinetic modelling efforts on hydrodesulfurization of coal liquids.
2. To assess the effects of pressure, temperature and space time on the non-catalytic hydrodesulfurization reactions of certain coal-derived liquids.
3. More specifically, to show the extent of desulfurization that could be accomplished in an uncatalyzed hydrotreating unit, compared with a catalytic hydrotreating system.

## CHAPTER II

### LITERATURE SURVEY

The history of coal liquefaction by direct hydrogenation can be traced from 1911 when Bergius obtained oil from coal without a catalyst in his experiments conducted at Hanover, Germany (39). The introduction of catalysts in the coal hydrogenation processes in 1925 enabled the researchers to attain more yield of liquid products. This advance was followed by catalytic processing in coal liquefaction and much work has been conducted in this field since that time. Catalytic hydrotreating is an effective tool for removing sulfur from coal-derived liquids since sulfur has the potential to interfere with the conventional refining processes by way of catalyst poisoning and environmental pollution through off gases from the processing industries. Catalytic desulfurization in the presence of hydrogen has been extensively undertaken by many, and considerable information about this topic is available in the literature. The intention of this chapter is to present only the related literature discussions which are relevant to this experimental work.

#### Reactor

This study of non-catalyzed hydrotreating of coal-derived liquids has been carried out in a trickle flow reactor. In trickle flow operation, the liquid phase flows downward whereas the gaseous phase

moves in either co- or counter current flow to the trickling liquid. The performance of the trickle flow system has been studied by many researchers to evaluate the reliability and suitability of trickle flow processing. Liquid maldistribution due to channeling and back-mixing have been found to be major problems associated with trickle flow operation.

One of the criteria that could be countable towards alleviating the problem of the possible channeling through the trickle bed is the ratio of the reactor tube diameter to the particle diameter. Baker, Chilton and Vernon (2) in their investigation of an air-water system in a packed column, have noted a ratio of 10 to 1 as the column diameter to packing diameter being the minimum to establish good liquid distribution. But in another work, Schiesser and Lapidus (31) reported that liquid distribution problems persist, significantly, even with a ratio of column diameter to packing diameter of 16 to 1. A ratio of as high as 36 to 1 (33) has also been projected by other researchers to establish a good liquid distribution. Accordingly, the tendency of the liquid for channeling through packed beds is seen to be greater in smaller diameter reactors. But Rose (27) in his study on the performance of the trickle bed reactors has concluded that effective liquid distribution is much more difficult in large diameter commercial reactors and are less efficient than the small pilot plant reactors.

#### Backmixing

The assessment of the operation of trickle bed reactors is based on the assumption of plug flow and accordingly the residence time of the reactants are to be determined by the flow rate and the

bed volume. Deviation from plug flow can happen due to axial eddy flow which increases the effluent concentration of the reactants. This phenomenon is noted as backmixing and may be another problem that is involved with the trickle flow reactors. Mears (20), in his experiment on liquid flow distribution in trickle beds has suggested a ratio of 350 to 1 being the ratio of height of the packed bed to the particle diameter as a good estimate in first-order reactions to eliminate the problem of backmixing. However, Schwartz and Roberts (32) have reported that the liquid backmixing is frequently not found to be an important problem in trickle flow reactors.

Liquid maldistribution in trickle flow reactors has also been studied in terms of liquid flux (gallons per square feet per hour) at constant liquid space time (volume of reactor per volume of liquid per hour). The effect of liquid flux, over the range of 3.8 to 15.3 gallons per hour per square foot on a hydrotreating processing of COED (Char Oil Energy Development) oil conducted at a temperature of 720<sup>o</sup>F and 3000 psig pressure, was studied, and no significant change in the reactor performance was noted (23). Satchell (30) and Sooter (36) also devised their experiments to show the extent of influence of liquid flux on the catalytic hydrotreating study of coal liquids. They varied the liquid flux from 4.84 to 9.69 gallons per hour per square foot and over this range the effect of variations on the hydrotreating reactions were too small to be considered. However, in commercial scale hydrotreating processes liquid flux of 150-500 gallons per hour per square foot surface area is usually required to accomplish good liquid distribution all along the reactor (8).

In general, the conclusions of various studies on the liquid flow problems encountered in the trickle bed operations are contradictory. For many instances wide differences are evidenced (27) in the results of the pilot plant studies and the commercial units. Subsequently, a tangible approach in the design of the trickle bed reactors is difficult to be made. The above suggested parameters by the various researchers shall be viewed as guiding towards achieving an evenly distributed flow in the reactors. However, care must be taken in the design of commercial reactors to distribute the liquid uniformly through the packed bed.

#### Hydrogen Rate

The hydrogen rate is an important parameter governing the extent of the overall reaction by its concentration and flow velocity through the packed bed of the reactor. Adequate amount of  $H_2$  should be supplied to meet the sulfur removal and the  $H_2$  saturation reactions. The turbulence due to the  $H_2$  flow velocity affect the liquid film thickness over the inert particles. This indeed affects the overall reaction. Wan (38) and Sooter (36) assessed the influence of hydrogen flow during their experimental study on the catalytic hydrotreating of coal-derived liquids in trickle flow reactors. At an operating pressure of 1000 psig, temperature  $800^{\circ}F$  and 0.901 hour space time, Wan varied the hydrogen flow rate from 3980 to 39800 SCF of hydrogen per barrel of oil. This hydrogen flow variation had also been tried at a different operating condition of 2000 psig pressure,  $700^{\circ}F$  temperature and 0.901 hour space time. Sooter, in his study conducted at 1000 psig pressure,  $650^{\circ}F$  temperature and 1.5 hour space time,



increased the hydrogen flow rate from 1500 to 20,000 SCF per barrel of oil. In both of the studies no significant changes in the desulfurization had been observed. Hoog (9) had observed a slight effect on the desulfurization reaction at hydrogen flow rates between 250-1500 SCF of hydrogen per bbl of oil and beyond 1500 SCF of hydrogen per bbl of oil, no effect was noticed.

From the above information about the effect of hydrogen rate on the desulfurization reactions, a feed rate of higher than 1500 SCF of hydrogen per bbl of oil would be safe enough to meet the hydrotreating process requirements, which are mentioned previously.

### Kinetics

Desulfurization of both coal-derived liquids and petroleum feed stocks has been described by first-order, second-order and third-order kinetic models in the literature reviewed here. The catalytic desulfurization of petroleum stocks indicates a second-order reaction at the low temperature of 600<sup>o</sup>F, whereas at the higher temperatures of around 800<sup>o</sup>F the desulfurization reaction follows first-order kinetics overall (36). No work on non-catalytic desulfurization of coal liquids in the presence of hydrogen could be located in the recent literature.

Any reaction of molecular hydrogen with an organic compound is generally termed as hydrogenation (8). In this work of non-catalytic hydrodesulfurization of coal liquids, the involved thermal cracking due to the nonhydrogenative rupture of carbon-sulfur bonds or sulfur-sulfur bonds would be much more pronounced than in the catalytic process where hydrogenative sulfur removal is more dominating.

Generally the cracking reactions are accompanied by the formation of products of higher molecular weight through condensation reactions of the cracked products (11, 14). A Significant amount of work would be required to isolate the simple cracking, hydrocracking (cracking in presence of hydrogen), desulfurization and the possible condensation reactions from each other with the available information in the literature and this effort is beyond the scope of this study.

#### Pressure, Temperature, and Space Time Effects

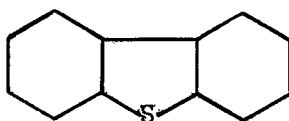
Hydrodesulfurization is usually carried out at pressures of 150 to 3000 psig (8). In the hydrotreating of coal-derived liquids Wan (38) has reported that no significant increment was seen in the sulfur removal upon a pressure increase from 1000 to 2500 psig. Sooter's work (36) on desulfurization has mentioned the pressure effect in the range of 500 to 1000 psig but no improvement in the sulfur removal was noticed beyond 1000 psig. In general, the pressure effects are reported to be influencing up to 1000 psig beyond which no significant effects are noticed in the catalytic hydrodesulfurization processes. This could be explained by the increased hydrogen concentration of the liquid phase at higher hydrogen partial pressures (36).

The temperature and reaction time are important process variables in both catalytic and non-catalytic hydrotreating desulfurization reactions. Increases in both temperature and reaction time favor the desulfurization and cracking reactions. The results of all the work reviewed here are consistent and follow the aforementioned trend. Generally hydrodesulfurization is carried out in the temperature range of 500 to 825°F and feed space velocities over the range of 0.5 to 5.0

volumes per hour per volume of packed bed, in catalytic hydrotreating studies. Hydrogen partial pressure is the most important parameter in the design of the desulfurization processes as the extent of sulfur removal is basically related to the amount of hydrogen required for the hydrogenation reactions. It is desirable to maintain high hydrogen partial pressures, almost equal to the total reaction pressure and can be achieved by maintaining substantially excess hydrogen flow than required for the desulfurization and other reactions.

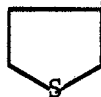
### Identification of Sulfur Compounds

A satisfactory design and successful operation of the desulfurization reactors are difficult due to the presence of a variety of sulfur compounds and incomplete knowledge of the reaction mechanisms (5). Sooter (36) in his thesis on the catalytic desulfurization of coal liquids has discussed and cited many references agreeing to the similarity of most of the sulfur compounds present in petroleum oils, shale oils, residuums and coal tars. Some typical reactions of the sulfur compounds that are commonly found in petroleum stocks, under hydrogenation conditions are discussed by Kobe and McKetta (16) and include mercaptans, organic sulfides, disulfides and thiophenes. In the discussion of the sulfur compounds of coal tar, the presence of dibenzothiophene.



being the largest of the fundamental structures of sulfur compounds has been reported (26, 36). In an analytical study on the nature

of sulfur groupings in Assam coals, India, Iyengar et al (10) noted that the presence of sulfides



in coal is not probable, whereas, the disulfides seem to exist only in very small amounts.

#### Literature Summary

A comprehensive discussion of the non-catalytic desulfurization of coal-derived liquids could not be located in the recent literature. Hence this summarization of the available information on desulfurization reactions is limited to the following points:

1. Liquid distribution is important in the trickle flow reactor operation. The maldistributions due to channeling and back-mixing are minimized by increasing the ratio of the reactor tube diameter to the particle diameter and the ratio of the height of the packed bed to the particle size, respectively.
2. The pressure effects are significant up to a pressure of 1000 psig beyond which this variable does not have important effects on the hydrodesulfurization reactions.
3. Temperature and reaction time are both important parameters and favor the desulfurization and the involved cracking reactions.

## CHAPTER III

### EXPERIMENTAL APPARATUS AND PROCEDURE

This study was carried out in the experimental system shown in Figure 1.

The main flow pattern of the process fluids are clearly understood from Figures 1 and 2 and is as follows:

Referring to Figure 2, the feed oil from Pump 24 joins the hydrogen supplied from the gas header. They meet at the top of Reactor 26 and flow downwards through the packed bed. The mixture comes out of the reactor and its pressure is decreased at the Back-Pressure Regulator 29, before entering the Separator 27. The cross section of the Separator is shown in Figure 3. In this Separator the gas and the liquid phases are disengaged. The liquid flows down through Valve 14 and is collected in the Receiver 28 from which it could be sampled. The gaseous products, along with excess hydrogen, escape through the line at the top of the Separator 27 and the pressure is further reduced across the secondary Pressure Controller 30. After scrubbing with caustic and with water, these gases are diverted to the hood through the wet gas meter.

The nucleus of the operational unit was a trickle flow reactor. For the smooth experimental runs and satisfactory results, the reactor with all the auxiliary equipment had been devised to meet the following requirements:

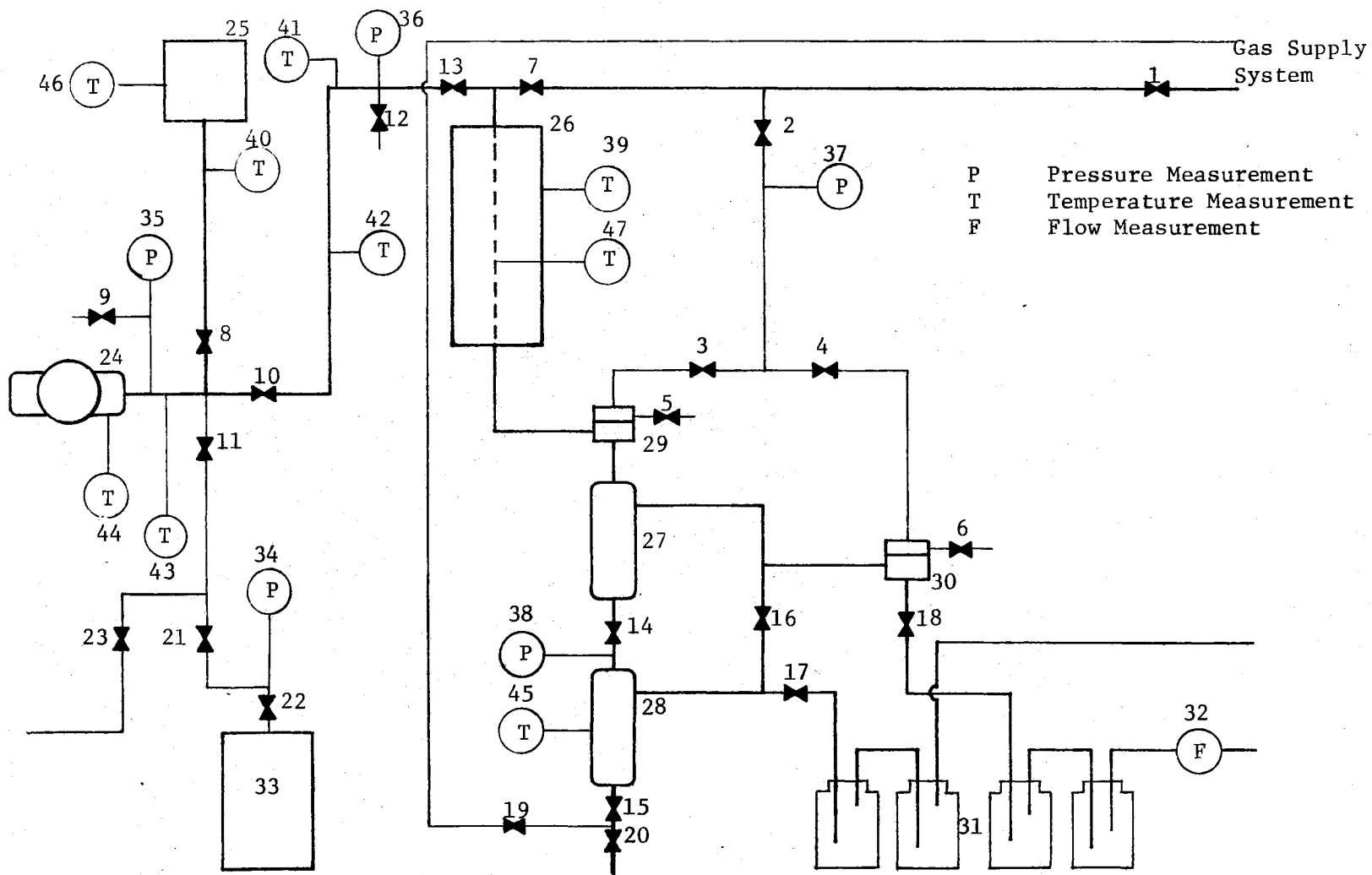


Figure 1. Engineering Flow Diagram

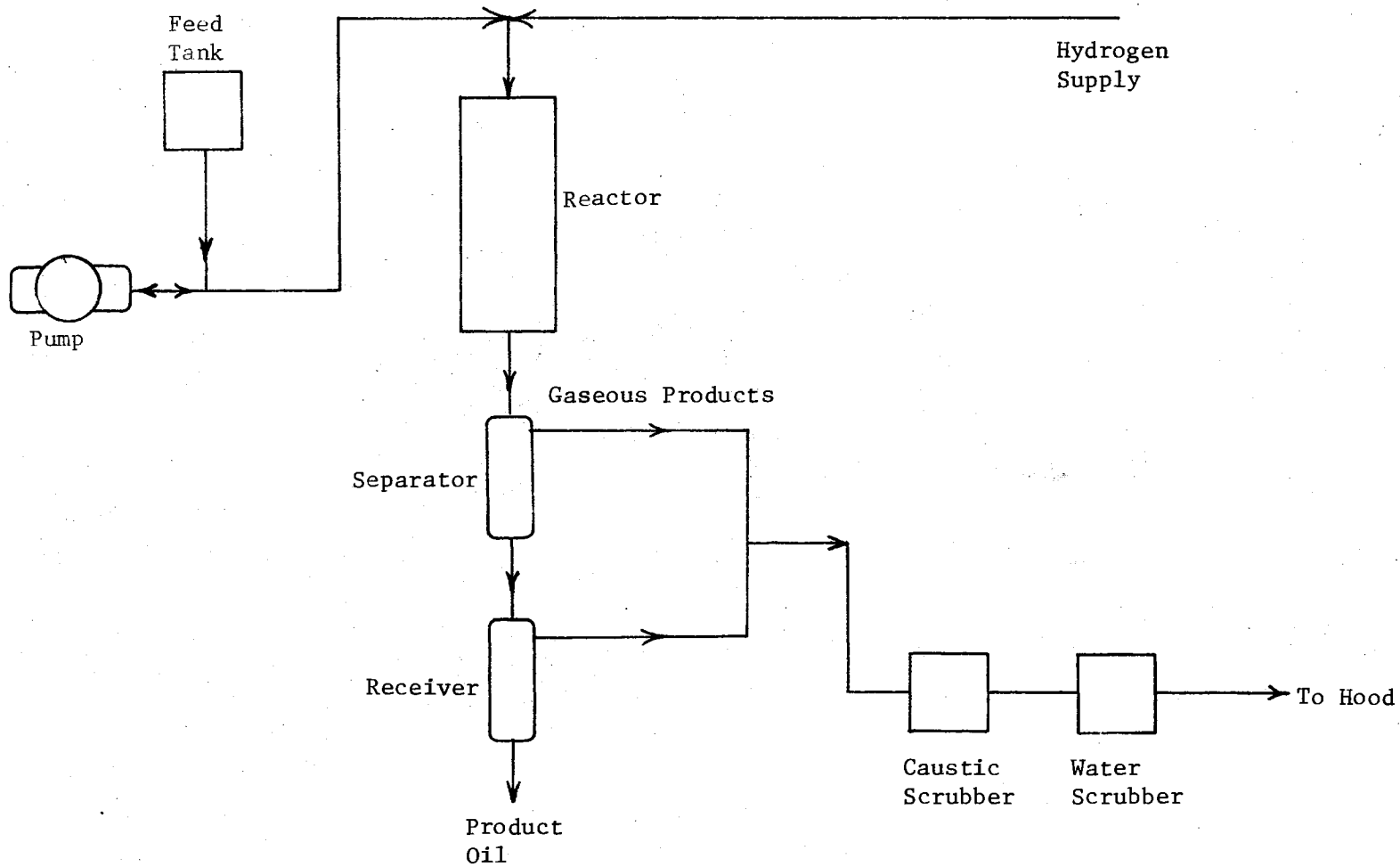


Figure 2. Process Flow Diagram

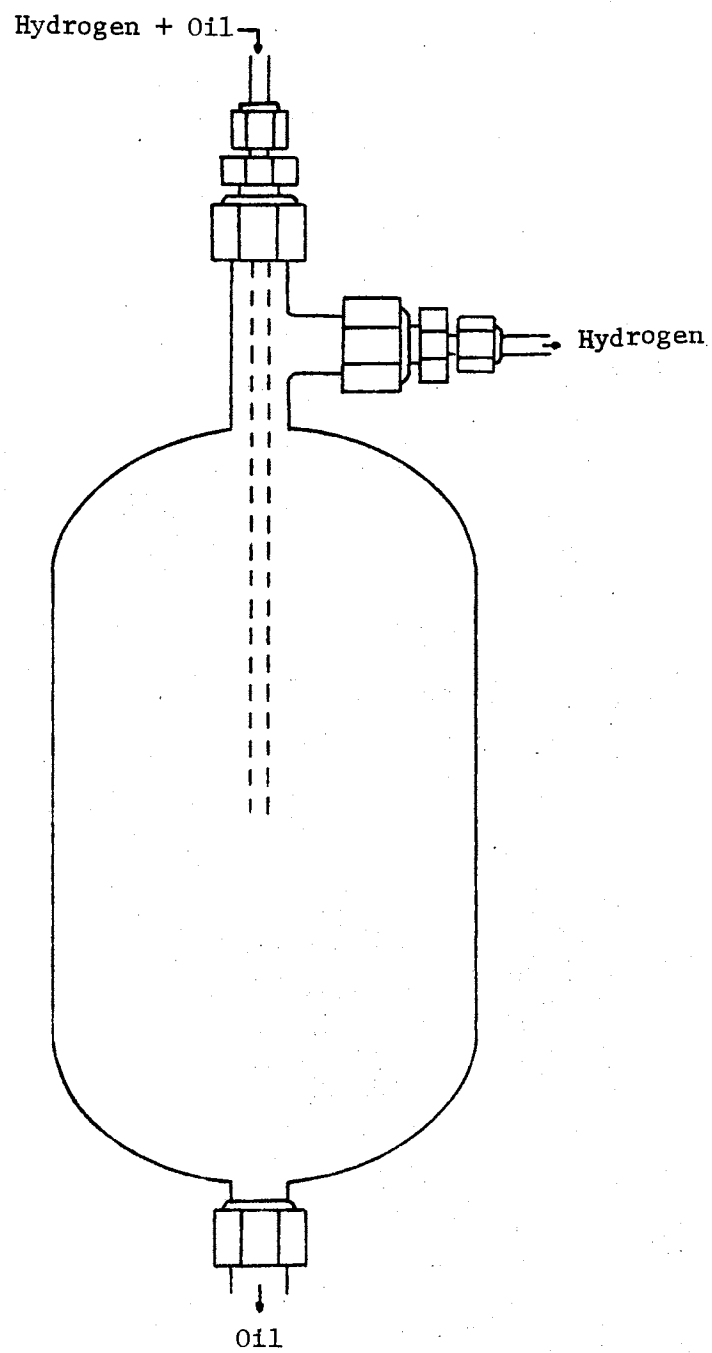


Figure 3. Separator



1. Flexibility and control of pressure between 0 - 2000 psig.
2. Control and maintenance of isothermal conditions along the length of the reactor for temperatures to at least 800<sup>o</sup>F.
3. Accessibility to sustain steady state conditions at different flow rates.

### Reactor

The reactor was a 23 inch long, 1/2 inch O.D., 316 Stainless Steel (S.S.) tube with a wall thickness of 0.049 inch. The top of this reactor had been provided with a 1/2 inch Swagelok cross that connected to 1/4 inch reducers (Figure 4). A 1/8 inch S.S. tube welded shut on the bottom served as the thermowell and provided for the measurement of the temperature from top to bottom of the reactor. A 23 inch iron-constantan thermocouple was moved along the thermowell. A reducer combination of 1/8 to 1/4 inch and 1/4 to 1/8 inch was assembled to fix the thermowell to the top section of the Swagelok cross. The bottom of the reactor was connected with an 1/2 inch union followed by an 1/2 inch to 1 inch reducer to join the reactor downstream lines. Small 50-mesh S.S. screens were secured at both ends of the reactor in order to hold the reactor packings. These holding screens were wedged in between the reactor tube and the fittings.

The reactor tube was packed with crushed berl saddles sized to 8-10 mesh. This size reduction for the packing material was done primarily to increase the ratio of tube-to-particle diameter and the length of the packed bed to the particle in order to promote uniform liquid distribution through the packed bed. This has been discussed

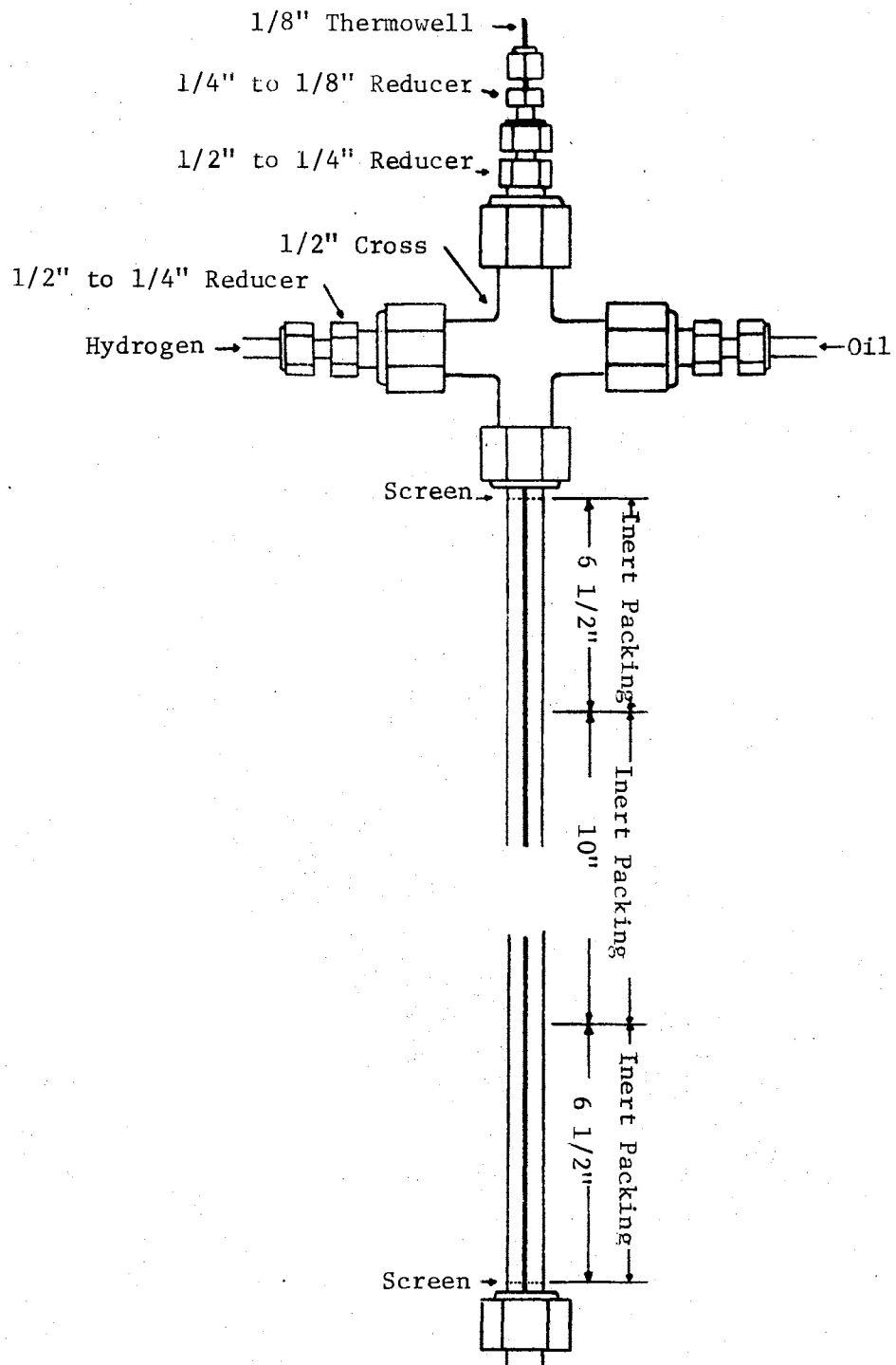


Figure 4. Reactor

in detail in the previous chapter. This 8-10 mesh size also matched the catalyst size used in the previous studies.

#### Reactor Heater

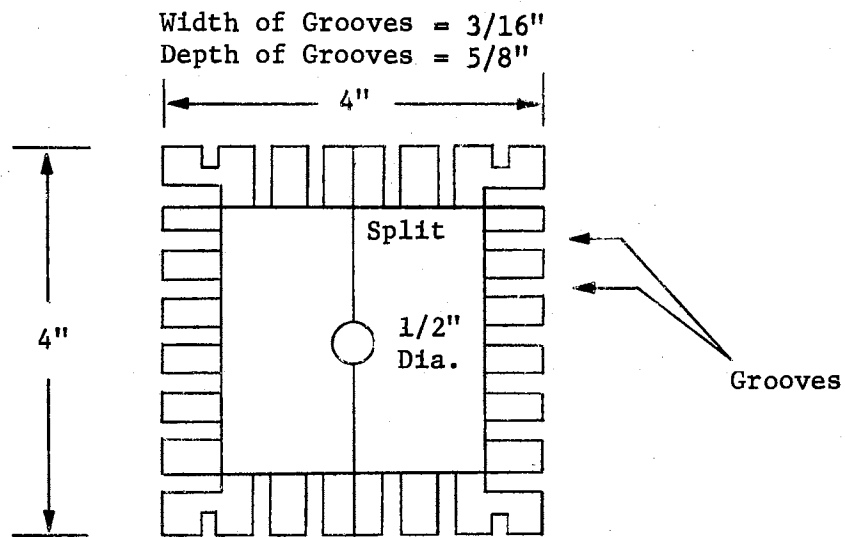
The reactor had been enfolded with three rectangular aluminum blocks of two different lengths, 5 and 8 inches, with the short ones positioned at both ends. The outer surfaces of these blocks were grooved longitudinally to accommodate beaded heating wires which were arranged vertically. (See Figure 5.) Each rectangular block was composed of two longitudinal halves hinged at one side facilitating easy assembly of the reactor and convenient handling.

The reactor with the surrounding heating blocks were wrapped completely with fibre glass insulating pads of an effective thickness of 3 inches.

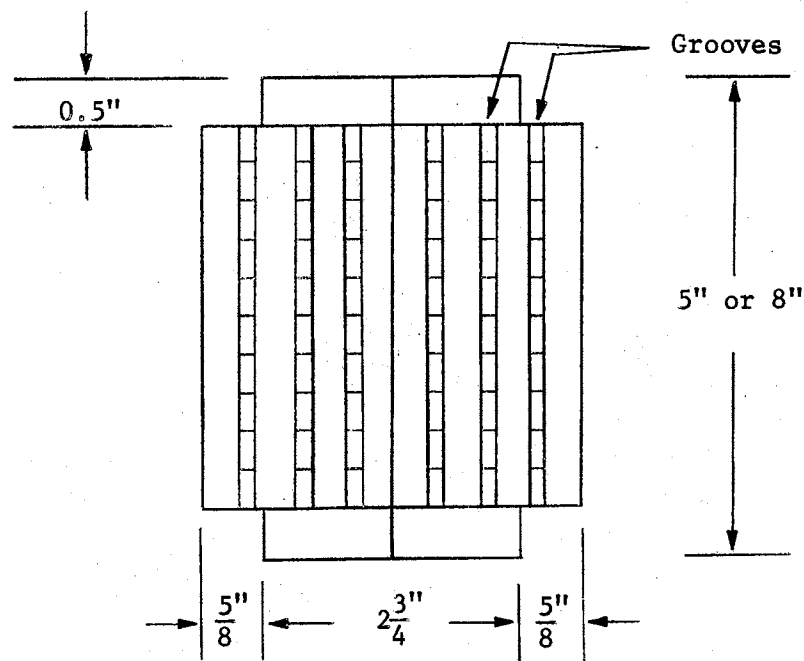
#### Pressure, Temperature and Flow Controls

The whole system was divided mainly into two sections, the high pressure and the low pressure sections. The lines and equipment downstream of the Pressure Regulator 29 (See Figure 1) were always maintained at 200 psig, irrespective of the reactor operating conditions. This was the low pressure loop. The upstream lines of this regulator were maintained either at 500 or 1500 psig.

The temperature of all the oil inlet and exit flow lines were maintained at approximately 200°F, by adjusting individual powerstats. This was necessary to facilitate pumping of the feed oil into the system. The reactor temperature was regulated by exercising individual control over the three heating blocks. The heat output of the top and bottom



(a) Top View of Heating Block



(b) Side View of Heating Block

Figure 5. Aluminum Heat Block

blocks were adjusted manually by two separate powerstats; whereas, the middle, long block was connected to a Hewlett Packard automatic temperature programmer controller.

The oil flow was also an important operational parameter since this provided the desired reaction time for a fixed reactor loading. The oil was drawn into the barrel of the Ruska pump and discharged at a pre-set rate through its metered pumping device. The main control of the hydrogen flow was regulated by a graduated micrometering needle Valve 1.

The operation of the unit can be broken into three main sequences: 1) start-up, 2) normal run and 3) shut down.

In start up, the whole unit was first pressure tested with  $N_2$  satisfactorily before the experiments were undertaken. To begin with, the scrubbers in series were filled with enough caustic solution and water respectively and the complete system was purged with nitrogen. Nitrogen was taken from commercial bottles through the supply manifold and sent into the system through Valve 1, while all remaining valves of the entire unit were kept open.

After purging for 10 minutes, the following sequence of operations were undertaken:

1. All drain and purge Valves 5, 6, 9, 12, 17, 20 and 23 were closed.
2. Valves 2, 8, 14, 16 and 18 remained open.
3. Valve 11 was always kept open as this gave access to the action of the safety rupture disc in the event of any excess pressure build-up during the course of experimentation.

4. The feed was introduced into Tank 25.
5. Valves 13 and 15 were closed.
6. All the heating elements were switched on and the temperature was increased at a rate not greater than 200<sup>o</sup>F per hour. This would avoid any possible thermal shock that could damage the lines and connections.
7. Valves 3 and 4 were closed and a small flow of nitrogen was maintained by keeping Valve 1 slightly open. This would promote uniform heating all along the reactor. The heating was continued until the respective lines and vessels are brought to the pre-set temperatures.

After bringing the system up to the desired level of temperature, the feed oil was drawn into the barrel of the Ruska-pump and Valve 8 was shut. The oil lines up to Valve 13 were filled with the feed oil by the simultaneous operation of the pump and drain Valve 12. Now the system was ready for pressurization. The following steps were taken before the unit was put to normal operation:

1. Valve 7 - closed
2. Valves 3 and 4 - opened
3. The pressure was raised to 200 psig, and Valve 4 was closed.
4. The pressure continued to increase to the set level of operation, Valve 3 was then closed.
5. Valve 7 was opened and gas supply was then changed to hydrogen.
6. Valve 1 was adjusted to maintain the required flow rate.
7. The oil side was pressurized by pumping the feed oil manually to the set gas pressure.

8. Valve 13 was next opened to pass oil into the line with the hydrogen.
9. The pump was coupled with the mechanical drive and the unit was in normal operation.

#### Sample Collection

While taking the sample Receiver 28 was isolated from the rest of the system and did not interfere with the normal operation of the unit. The following steps were undertaken:

1. Valves 14 and 16 - closed.
2. Valve 17 was cracked open to depressurize the vessel.
3. Valves 15 and 19 were opened to pass nitrogen through the Receiver 28 to purge off the gaseous products prior to oil sample collecting. No gas samples were taken.
4. Valve 19 was shut and the sample was taken with Valve 20 open.
5. Valves 17 and 20 - closed.
6. The sample Receiver 28 was pressurized to 200 psig with nitrogen by opening Valve 19.
7. Valves 15 and 19 - closed.
8. Valves 14 and 16 were opened to put the receiver in line with the rest of the unit for continued operation.

#### Change Over of Process Conditions

After collecting enough samples at a particular process condition, the whole unit had to be brought to a new pre-determined operating condition. This change-over from one set of variables to another was

done carefully without giving any pressure or thermal shocks to the process equipment or lines of the experimental unit. The changes of operational variables such as pressure, temperature and the feed oil rate were undertaken as follows:

In all the cases the Ruska-pump was stopped before any change in the process condition was executed.

Change of pressure:

1. Valve 7 - closed and Valve 3 opened.
2. (a) The pressure of the process system was raised by slowly opening the gas supply Valve 1 and setting the pressure at the desired level by closing Valve 3.  
(b) To lower the pressure, drain Valve 5 was opened to reduce, slowly, the pressure to the desired level.

Change of temperature:

The reactor temperature was adjusted by controlling the output of the reactor heating blocks. The powerstats connected to the upper and lower heating blocks together with the Hewlett Packard temperature programmer controller connected to the middle heating block were adjusted to regulate the heat output of the reactor system.

Change of feed oil rate:

The feed oil rate was adjusted by controlling the output of the Ruska-pump. The method is in the instruction manual supplied by the manufacturer (28).

Shut-down:

The following sequence of operations were performed to shut down the unit:



1. The Ruska-pump was switched off and Valve 13 closed.
2. The oil pressure was manually reduced by about 50 psi and Valve 13 was slightly opened. This was to clear the oil line beyond this valve by diverting hydrogen under pressure.
3. Valve 13 was closed and the oil pressure was again reduced. This was done manually.
4. Hydrogen flow was continued for about 1/2 hour to drain all the oil and products out into the receiver before the gas was changed over to nitrogen for final purging.
5. The contents of the receiver were flushed out and all the lines were purged thoroughly with nitrogen.
6. Valve 8 was opened and all heating elements were switched off.

Model numbers and other information about the equipment used in this project are given in Table I.

#### Sampling Frequency

The operational steps that were carried out to collect a sample have been orderly presented earlier in this chapter. Eight different process conditions were selected for each type of oil. The typical or representative sample of each process condition was taken for analysis. The necessary operational procedure to change over from one experimental condition to another process condition has been detailed in the previous section of this chapter. About one hour after the system had been normalized to the new process condition, the accumulated product oil in the receiver was drained and flushed well with nitrogen. The first oil product sample was then collected during the following hour or two. The treated oil that was accumulated in the receiver during either one

TABLE I  
LIST OF EXPERIMENTAL EQUIPMENT

---

Feed Tank 25 --8 1/2 in O.D. and 7 1/2 in high, stainless steel tank.
Reactor--1/2 in O.D., 0.049 in wall thickness, 316 stainless steel.
Separator 27 and Receiver 28--300 ml, max. pressure 1800 psig, 304 stainless steel, Matheson Model No. 6-645-2320.
Surge Tank 33--5 gal. tank.
Pump 24--Ruska positive displacement pump, Model No. 2242 BI, 500 cc cyr capacity, feed rates 2 to 240 cc/hr, max. pressure 4000 psi.
Tubing--1/8 in O.D., stainless steel, for carrying gas.
Tubing--1/4 in O.D., stainless steel, for carrying gas or liquid.
Valve 1--1/4 in, 316 stainless steel, micro-metering needle valve, Whitey Model No. 22S4.
Valves 2, 3, 4, 5, and 6--1/8 in, needle valves, max. pressure 11000 psi, Autoclave Engineers Model No. 10V-2001.
Valves 7, 14, 15, 16, and 17--1/4 in, gate valves, 316 stainless steel, max. pressure 3000 psig, Whitey Model No. IRS4.
Valve 8--1/4 in. gate valve, 316 stainless steel, extended stem type, Autoclave Engineers Model No. 6V-71U8.
Valves 9, 18, 19, and 20--1/4 in. gate valves, 316 stainless steel, Autoclave Engineers Model No. 6V-71U8.
Valves 10, 11, 12, 13, and 23--1/4 in. gate valves, 316 stainless steel, Whitey Model No. 6VS4.
Pressure Gauges 34, 35, 36, and 38--Crossby pressure gauge, 3000 psi. max.
Pressure Gauge 37--Heise Bourdon Tube, 3000 psig max.
Digital Temperature Indicator--Doric Scientific DS-300-T3, Temperature range 0-1595 <sup>o</sup> F.
Thermocouple 39--Chromel-Alumel, 0.04 in O.D., type 304, stainless steel sheath, grounded sensor tip configuration, 1/2 in. Conax.

TABLE I (Continued)

---

Thermocouples 40, 41, 42, 43, 44, 45, 46, and 47--Iron-constantan, 0.04 in. O.D., type 304, stainless steel sheath, bear sensor tip configuration, 1/2 in. Conax.

Wet Test Meter 32--Precision Scientific, 0.1 cu ft per revolution.

Back Pressure Regulators 29 and 30--Groove Regulator Co., Model No. 138416-1, pressure range 100-3000 psig at temp. 200<sup>o</sup>F.

Safety Valve 21--Rupture disc, stainless steel, bursting pressure 3000 psig at 70<sup>o</sup>F, Black Sivalis and Bryson Model No. 145563.

Safety Valve 22--Stainless steel rupture disc, bursting pressure 3000 psig. at 70<sup>o</sup>F, F. D. I. Model No. 19951.

Temp. Controller--Hewlett Packard temperature programmer, Model 240M-25, Temperature range 0-1832<sup>o</sup>F.

Power Stats--Superior Electric type 116, output voltage 0-140V.

Insulation Material--Fibre Glass, McMaster Carr.

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hour or two hours of operation after the first sample collection, was taken and considered as the representative sample of that particular process condition. This sequence of steps were followed to gather all samples at the respective chosen conditions of this study.

#### Feed Stock

Oils from two sources, FMC filtered oil (Colorado Bear Mines) and PAMCO composite oil, were used in this experimental project. The properties of these oils are shown in Tables I and II and were issued by the respective suppliers. The processes from which these feed oils were synthesized will be discussed in the next chapter. Note that the sulfur levels were 0.35% wt for the FMC oil and 1.2% wt for the PAMCO oil.

#### Sulfur Analysis

A Leco Automatic Sulfur Determinator was employed in the sulfur analysis of the product oils. The analytical system consisted of a Model 521-500 induction furnace and a Model 532-000 automatic titrator and was based on the ASTM combustion method E3065 (18) which specifies the potassium iodate titration of sulfur dioxide combustion products.

The sulfur in the sample oil was burned in an oxygen atmosphere. The combustion was conducted in the induction furnace at a high temperature to favor the formation of sulfur dioxide, which was titrated by the iodate method.

In the Leco iodate method, approximately 2 ml of starch-potassium iodide solution were added to 80 ml of 1% hydrochloric acid in the titration vessel. Potassium iodate solution in small amounts was introduced to form iodine as follows:

TABLE II  
PROPERTIES OF PAMCO COMPOSITE FEED OIL\*

---

Vacuum Bottoms wt%	45
Cut 2 solvent	55
Boiling Range: 100-230°C at less than 3 mm Hg	
The approximate analysis is:	
Carbon wt%	88.2
Hydrogen	7.34
Sulfur	1.2
Nitrogen	1.3
Oxygen	1.6
Ash	0.1 to 0.2

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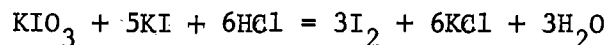
\*PAMCO Data

TABLE III  
ANALYSIS OF THE FMC FEED OIL

Oil Source	Colorado Bear Mines
Moisture, wt%	0.20
Quinoline Insoluble, wt%, dry	0.00
<u>Ultimate Analysis, wt%, dry</u>	
Carbon	83.05
Hydrogen	8.35
Nitrogen	1.13
Oxygen <sup>1</sup>	7.15
Sulfur	0.35
Ash	0.00
°API Gravity, 60°F/60°F	-4 to -5
Pour Point, °F	118
Flash Point, °F	350
Viscosity, SUS <sup>2</sup>	1090

<sup>1</sup> Oxygen determined by difference

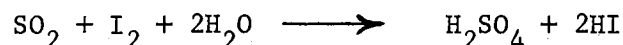
<sup>2</sup> Viscosity determined at 210°F.



The iodine and starch formed a blue complex:



Sulfur dioxide from the combustion reduced the iodine to iodide causing the destruction of the blue starch iodine complex.



Iodine solution was automatically added to the titration vessel in order to maintain the blue color of the solution mixture. The volume of the iodate solution that was needed to encounter the bleaching section of sulfur dioxide was calibrated to give the percent sulfur of the sample. The detailed procedure of this analytical technique along with the involved calculations are presented in Appendices A and B.

#### Specific Gravity Measurement

The specific gravities of the samples were calculated by the direct volume and weight measurements.

The samples were transferred into 5 ml. standard cylinders and the weights were taken. A mettler analytical balance Model B6 was used and the weight of each sample was read correctly up to the fifth decimal place with the provision of the micrometer read out. The recorded weight of each sample was an averaged value of three or more individual weights of the respective sample.

The volume measurements of the weighed samples were conducted in the same standard 5 ml. cylinders, used for weighing the samples. These

cylinders were kept in a water bath whose temperature was maintained at 173°F with the aid of heating bulbs.

#### Gases and Chemicals Used

The various chemicals and gases used in this experimental study have been given in Table IV.



TABLE IV  
LIST OF GASES AND CHEMICALS

---

Gases Used in the Process System:

Hydrogen - prepurified (99.95%) 3500 psig - Matheson

Nitrogen - prepurified (99.997%) 3500 psig - Matheson

Gases Used in Analytical Work:

Oxygen - 99.5% pure - Sooner Supply

Chemicals Used in the Process System:

Sodium Hydroxide Pellets - Fisher Scientific

Chemicals Used in Analytical Work:

MgO, Magnesium Oxide - Curtin Scientific

KIO<sub>3</sub>, Potassium Iodate - Curtin Scientific

HCL, Hydrochloric Acid - Fisher Scientific

Arrowroot Starch - Curtin Scientific

NaN<sub>3</sub>, Sodium Azide - Fisher Scientific

Distilled Water

Iron Chips - Curtin Scientific

Tin Granules - Curtin Scientific

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## CHAPTER IV

### EXPERIMENTAL RESULTS

The experiments were set up to study the effects of temperature, pressure, and space time on uncatalyzed desulfurization of coal derived liquids. The hydrotreating process was conducted at temperatures of 700°F and 800°F, total pressures of 500 and 1500 psig and volume hourly space times (cubic centimeters of inert packing per cubic centimeter of feed oil per hour) of 1.18 and 3.14 hours. Catalytic hydrotreating of the same feed oils used in this study had been carried out in an identical reactor by others in this laboratory unit. The height of the catalyst bed was 10 inches. In this non-catalytic process, this 10 inch catalyst bed was replaced with the inerts of the same size of 8-10 mesh and is shown in Figure 4. Only this replaced volume of catalyst bed by the inerts is referred to in the definition of space time of this study. The common reference volume adapted for the definition of space time in both studies, catalytic and non-catalytic, was devised to promote an effective comparative study between these two processes. The sulfur content of the product oils were analyzed by using the Leco Automatic Sulfur Determinator. The details of the analytical method and operational procedure of the equipment system are discussed in Appendix A and Chapter III.

The following definition of certain terms are also of importance in view of the better follow up of the presentation and understanding of this work:

#### Thermal Cracking

In this discussion, thermal cracking or simple cracking designates the pyrogenic decomposition reactions yielding light products due to non-hydrogenative cleavage of carbon-sulfur, sulfur-sulfur and carbon-carbon bonds.

#### Hydrocracking

In this work, hydrocracking is defined as the process of simultaneous cracking and hydrogenation of both the cracked fragments and the unsaturated compounds to varying extents.

#### Hydrodesulfurization

Hydrodesulfurization, with reference to this discussion, is the hydrotreating process which has as its sole objective the removal of sulfur from the feed oil by the reaction of hydrogen with the sulfur compounds to form hydrogen sulfide and the respective hydrocarbon molecule or molecules.

Oil from two sources were hydrotreated in this experimental work. These two coal derived feeds were the PAMCO composite oil and the FMC filtered (Colorado Bear Mines) oil. The process developed by the Pittsburg and Midway Coal Company (PAMCO), called the Solvent Refined Coal process (SRC) was used to produce the former oil (22); whereas, the latter was manufactured in the Char Oil Energy Development (COED) process developed by the FMC corporation (28).

In the SRC process, pulverized coal is mixed with a solvent and this slurry is sent into a dissolver along with hydrogen under

pressure. The dissolver effluent is filtered to remove the ash. This de-ashed fuel is hydrotreated to produce oil with a lower nitrogen and sulfur content.

The production of FMC oil involves the heating of dried coal in several stages without the presence of air. The evolved volatile matter is condensed and subsequently heated with hydrogen at higher pressures to produce oil.

The details of both the above processes are given in the reports. The properties of these feed oils are presented in Tables II and III.

The pressure, temperature, and space time effects during hydro-treating both of the coal liquids are presented in the respective figures and tables given in this chapter. The primary intention of this chapter is to identify the various experimental conditions and the corresponding results. The detailed discussion of these results will be given in the following chapter.

#### Effect of Process Variables on PAMCO Oil

The effect of temperature and space time on PAMCO oil at a total operating pressure of 1500 psig is depicted in Figure 6. The product oil with minimum sulfur content of 1.049 percent was noted at 800°F operating temperature and 3.14 hours space time. The results of the experiments conducted at a lower pressure of 500 spig with the same oil are shown in Figure 7 and are for both 700°F and 800°F operating temperatures. At 1.18 hour space time more desulfurization was accomplished at higher temperature of 800°F. But this was not the case with the treated oils at 3.14 hour space time. As shown in Figure 7,

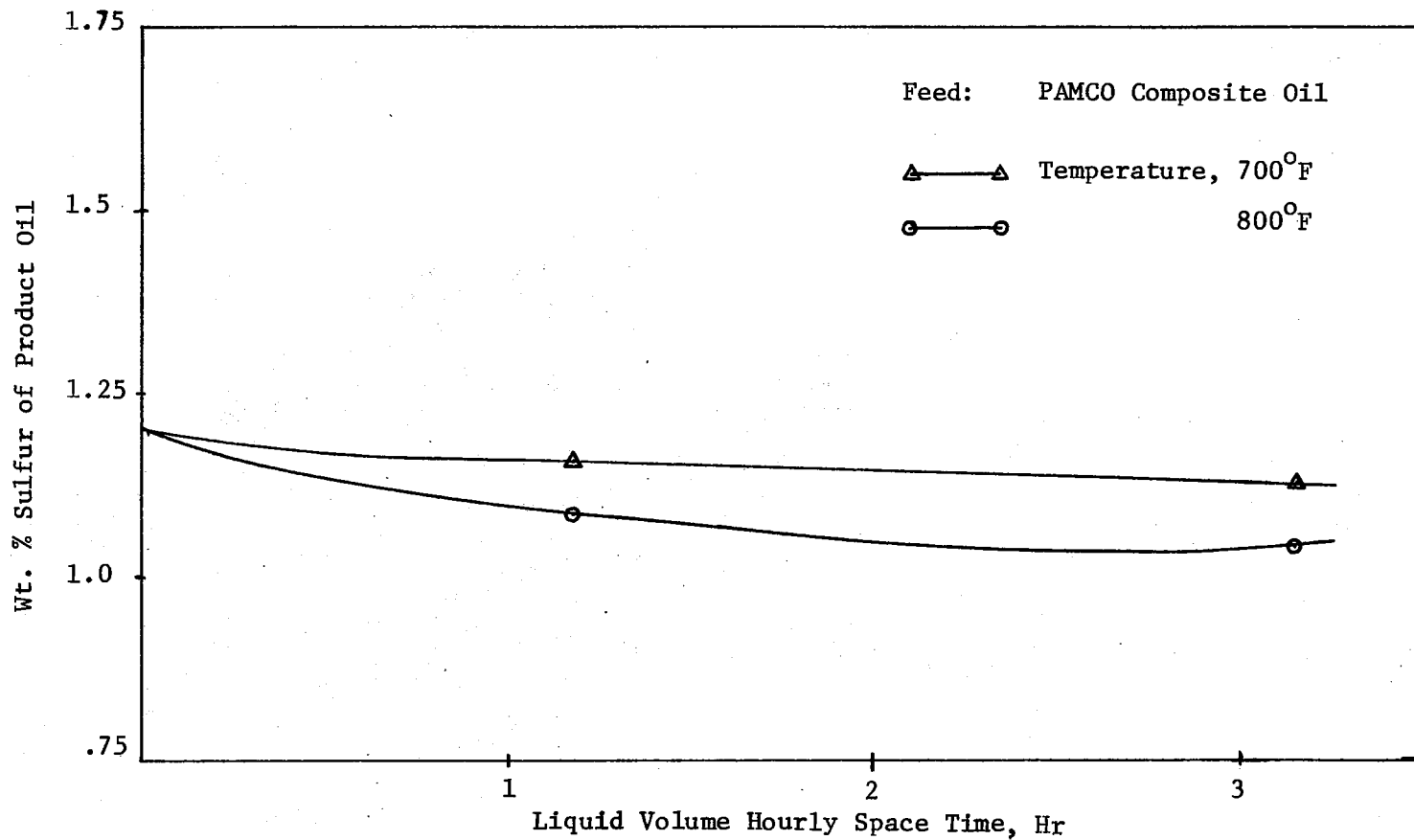


Figure 6. Effect of Temperature on Sulfur Removal from PAMCO Composite Oil at 1500 Psig

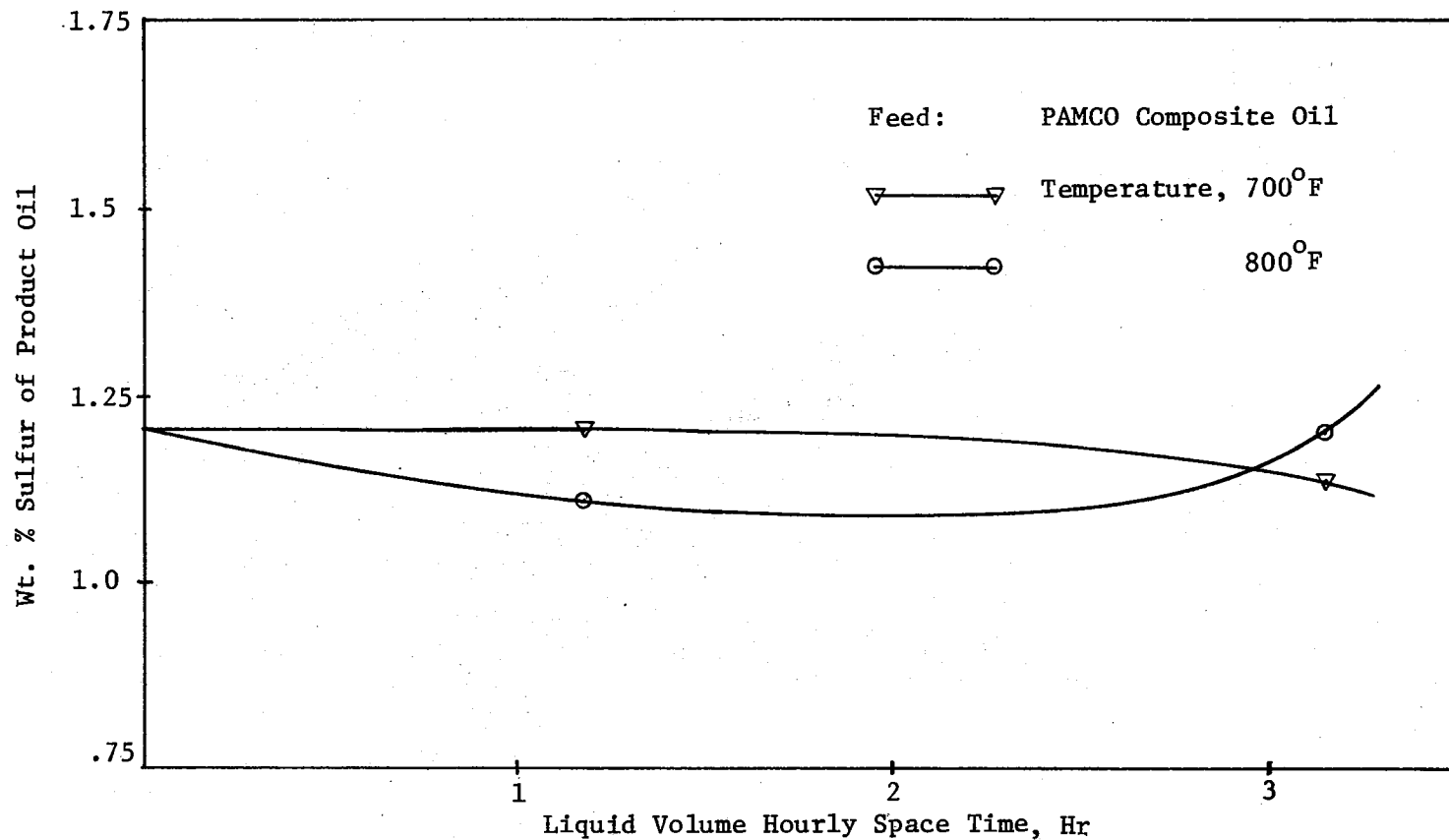


Figure 7. Effect of Temperature on Sulfur Removal from PAMCO Composite Oil at 500 Psig

the product oil of 800°F contained more percent sulfur than the product sample from 700°F operation. In addition to this, the 800°F curve shows the product oil at 3.14 hour space time contained more sulfur than the treated oil at 1.18 hour reaction time. The sulfur concentration of this product sample from 3.14 hour space time condition is almost equal to that of the feed. The lower pressure of 500 psig and higher temperature of 800°F at increased reaction time promoted the simple cracking of the nonsulfur compounds of the PAMCO feed oil. These lighter fragments should have escaped from the system as gaseous products thus effectively concentrating the oil with respect to sulfur levels. This could be explained with the observed decrease in the specific gravity of the product sample S-43 (Table V), which is presented in Figure 8. Note that only at 800°F, 500 psig and at the maximum space time of 3.14 hours space time was there a significant variation in specific gravity from that of the feed. The effect of reaction pressure on the PAMCO feed oil at 700°F and 800°F temperatures are better seen in Figures 9 and 10 respectively. The effect of pressure increase on the reaction was only slight at 700°F temperature drawn in Figure 9. But at the higher reaction temperature of 800°F the effect of pressure increase was clearly seen especially at 3.14 hour space time (Figure 10). At this condition the sulfur content of the product oil was reduced from 1.193 to 1.049 percent when the pressure was increased from 500 psig to 1500 psig. The results of the hydrodesulfurization of PAMCO composite oil are summarized in Table V.

TABLE V  
PAMCO - PRODUCT OIL CHARACTERISTICS

Sample	Pressure Psig	Temperature °F	Space Time Hour	% Sulfur	Sp. Gravity*
S-31	1500	700	3.14	1.136	1.013
S-28	1500	700	1.18	1.163	1.009
S-33	1500	800	3.14	1.049	1.021
S-35	1500	800	1.18	1.082	1.013
S-37	500	700	1.18	1.200	1.018
S-39	500	700	3.14	1.130	1.013
S-41	500	800	1.18	1.113	1.019
S-43	500	800	3.14	1.193	0.979

\*Specific gravity was conducted at 173°F



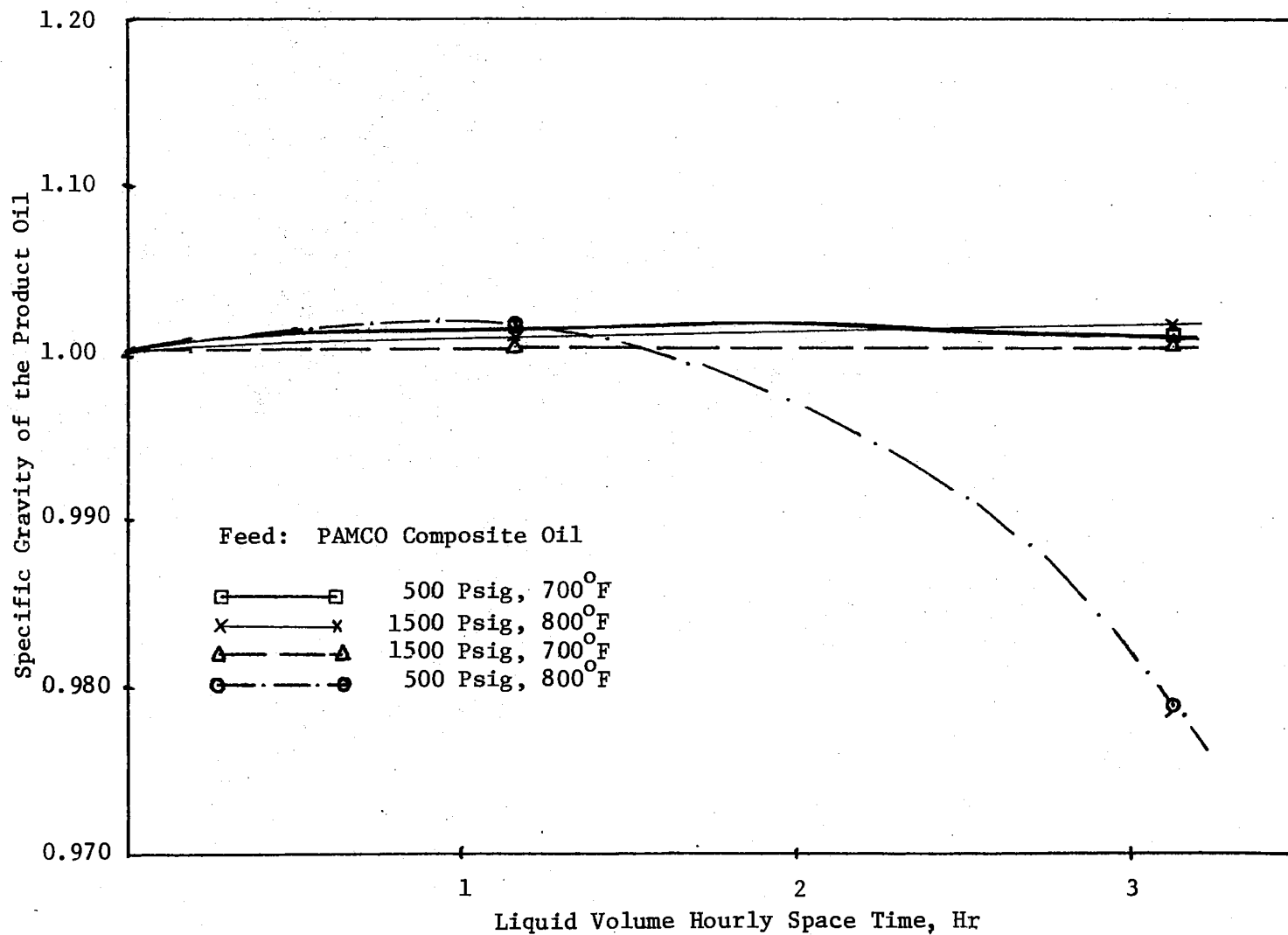


Figure 8. Effect of Temperature and Pressure on Specific Gravity of PAMCO Composite Oil

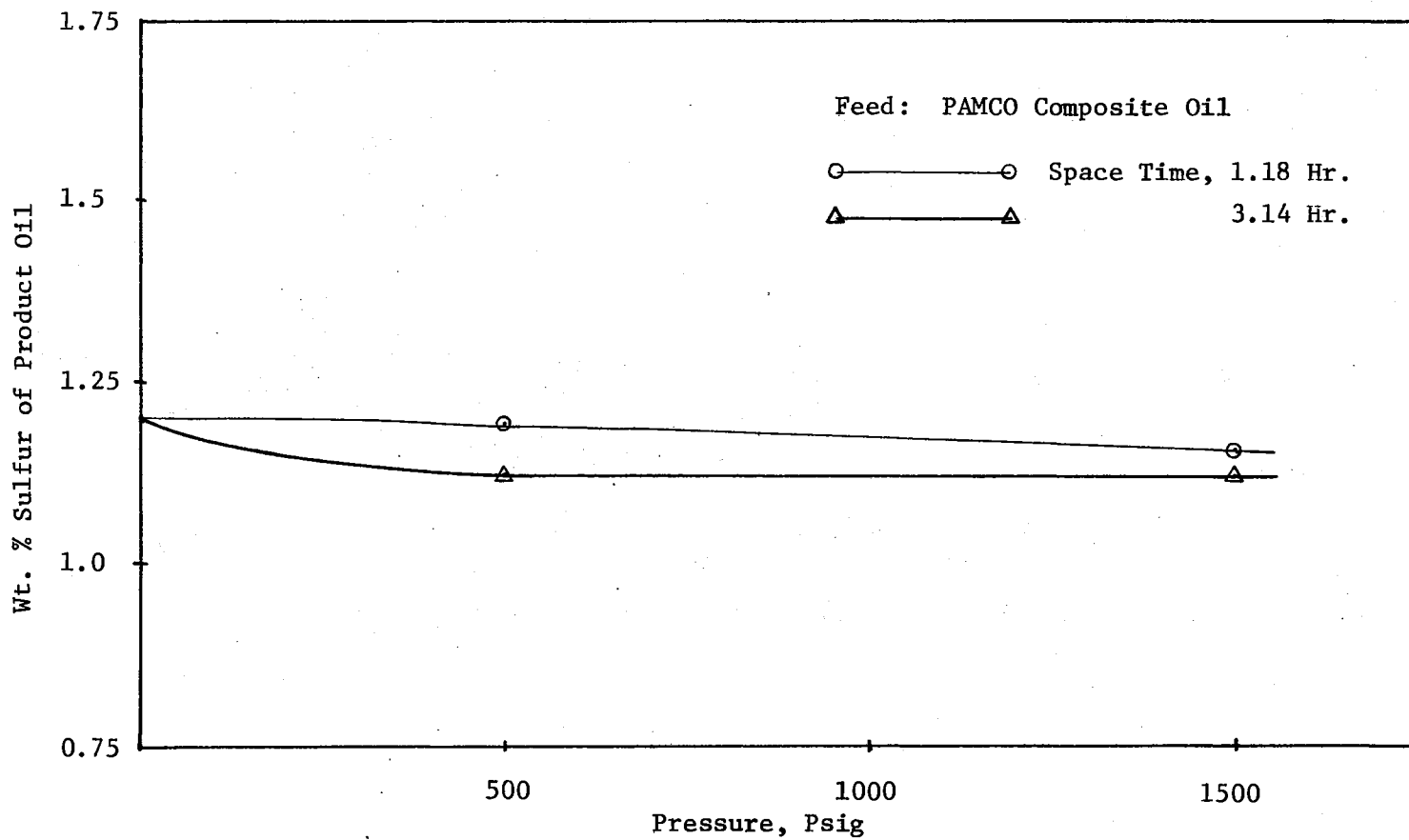


Figure 9. Effect of Space Time on Sulfur Removal from PAMCO Composite Oil at 700°F

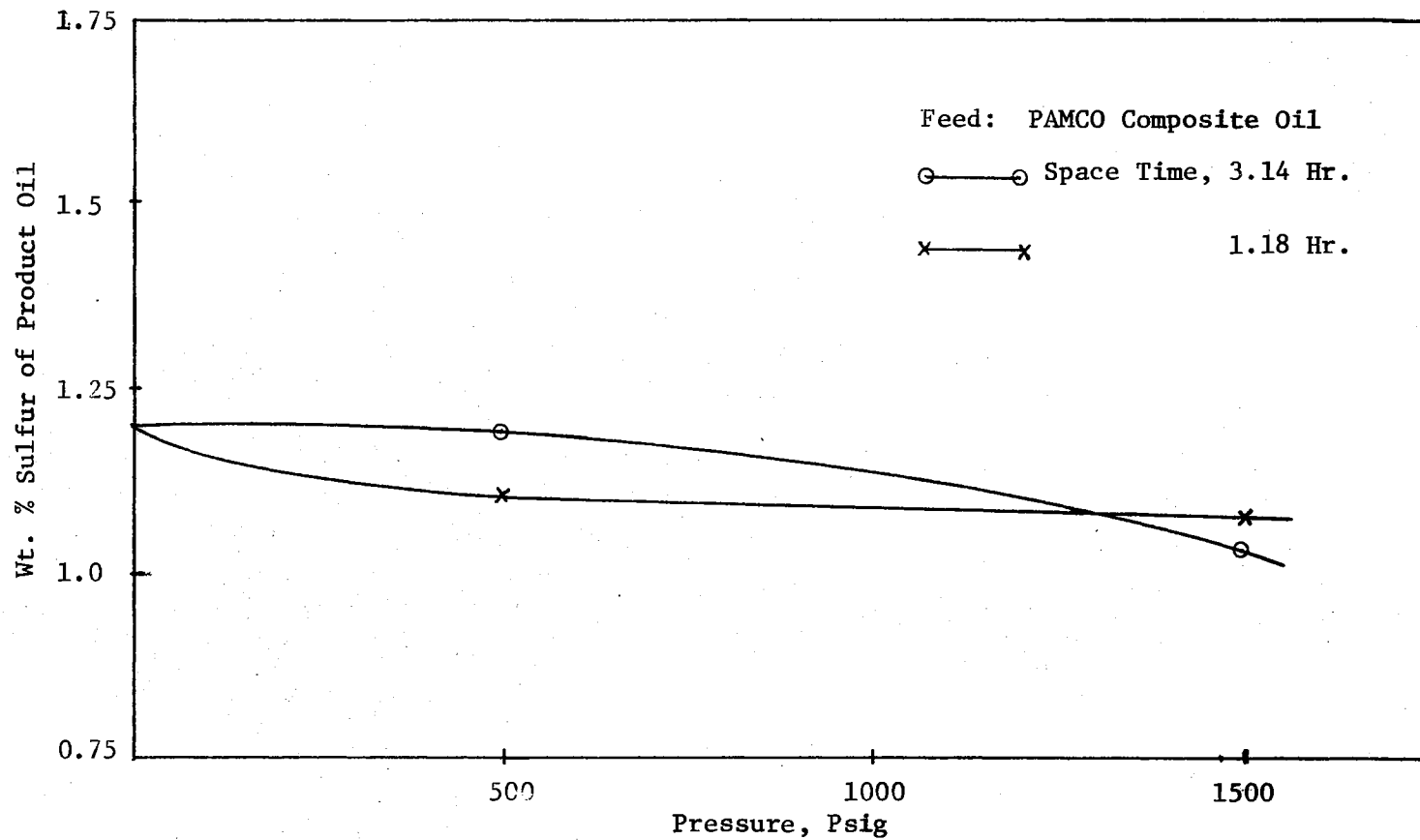


Figure 10. Effect of Space Time on Sulfur Removal from PAMCO Composite Oil at 800°F

### Effect of Process Variables on FMC Oil

The effect of the temperature and space time on the hydrodesulfurization reaction of the FMC oil at two operating pressures of 1500 psig and 500 psig are presented in Figures 11 and 12 respectively. The analysis of the samples S-7, S-9, and S-12 (See Table VI) revealed a higher sulfur percentage than that of the feed oil. Samples 7 and 9 were the treated oils of 700<sup>o</sup>F and 500 psig at two different space times of 3.14 and 1.18 hours, respectively. The other sample S-12 was a product of 700<sup>o</sup>F operating temperature, 1500 psig pressure and 1.18 hours space time. Certain non-sulfur compounds present in the feed oil had cracked at these process conditions and the resulting light fragments escaped from the system in the gaseous phase. This increased the sulfur percentage of the product samples over that of the feed oil. The involved specific gravity changes of the FMC oil are shown in Figure 13. In general FMC oil was found to be very sensitive to temperature and pressure variations and subsequently reaction time did not seem to be comparatively significant on the cracking of feed oil (Figure 13). Also in Figure 13, the specific gravity variations of the product samples from higher operating temperature of 800<sup>o</sup>F are relatively higher than those of the product oil, processed at 700<sup>o</sup>F. More sulfur removal was noted at higher temperature of 800<sup>o</sup>F. The effect of pressure increase on desulfurization reaction is better seen in Figures 14 and 15. At 700<sup>o</sup>F reaction temperature the pressure increase did not have significant effect on desulfurization reaction (Figure 14). But the influence of reaction time at both pressures of 500 psig and 1500 psig can be clearly seen. In

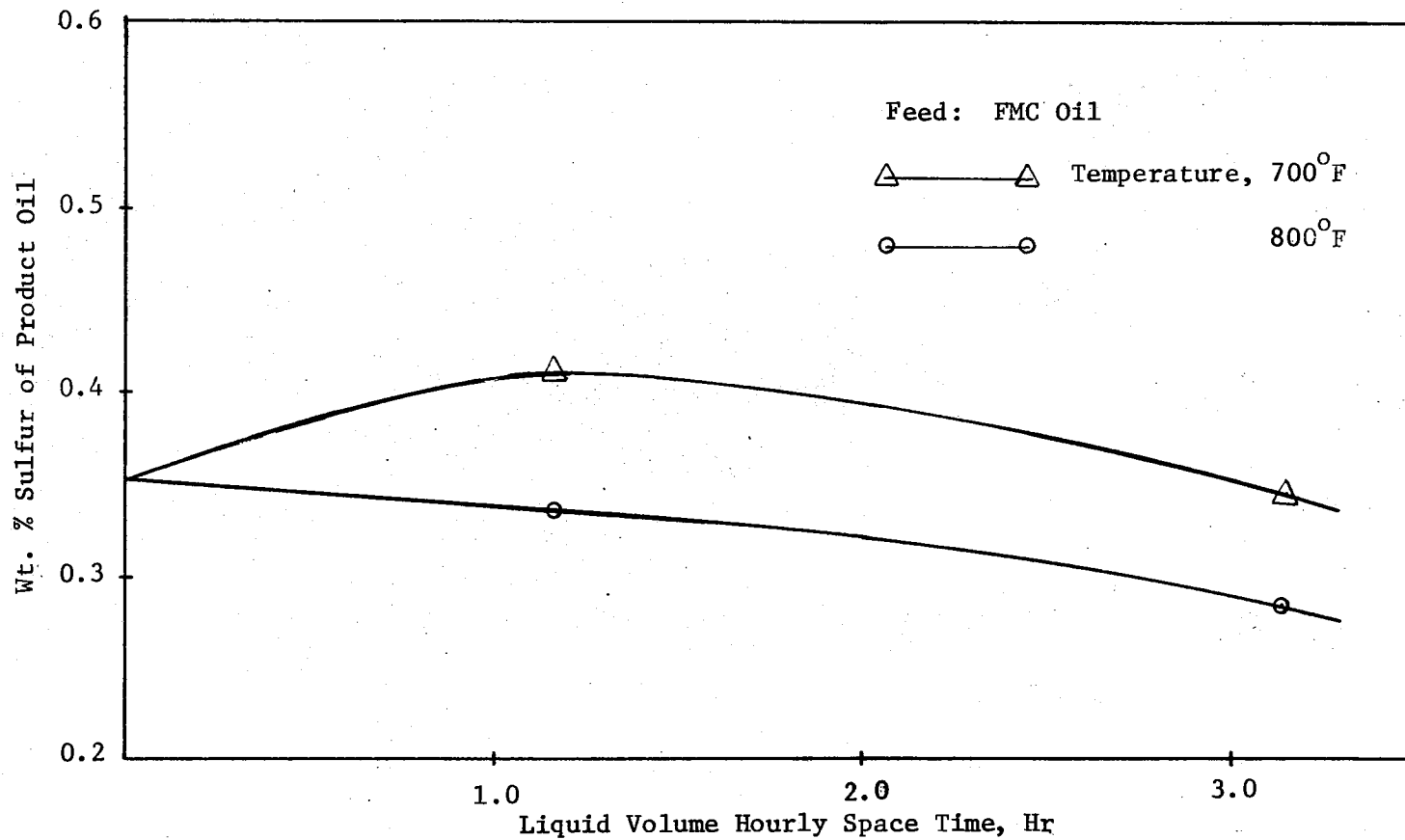


Figure 11. Effect of Temperature on Sulfur Removal from FMC Oil at 1500 Psig

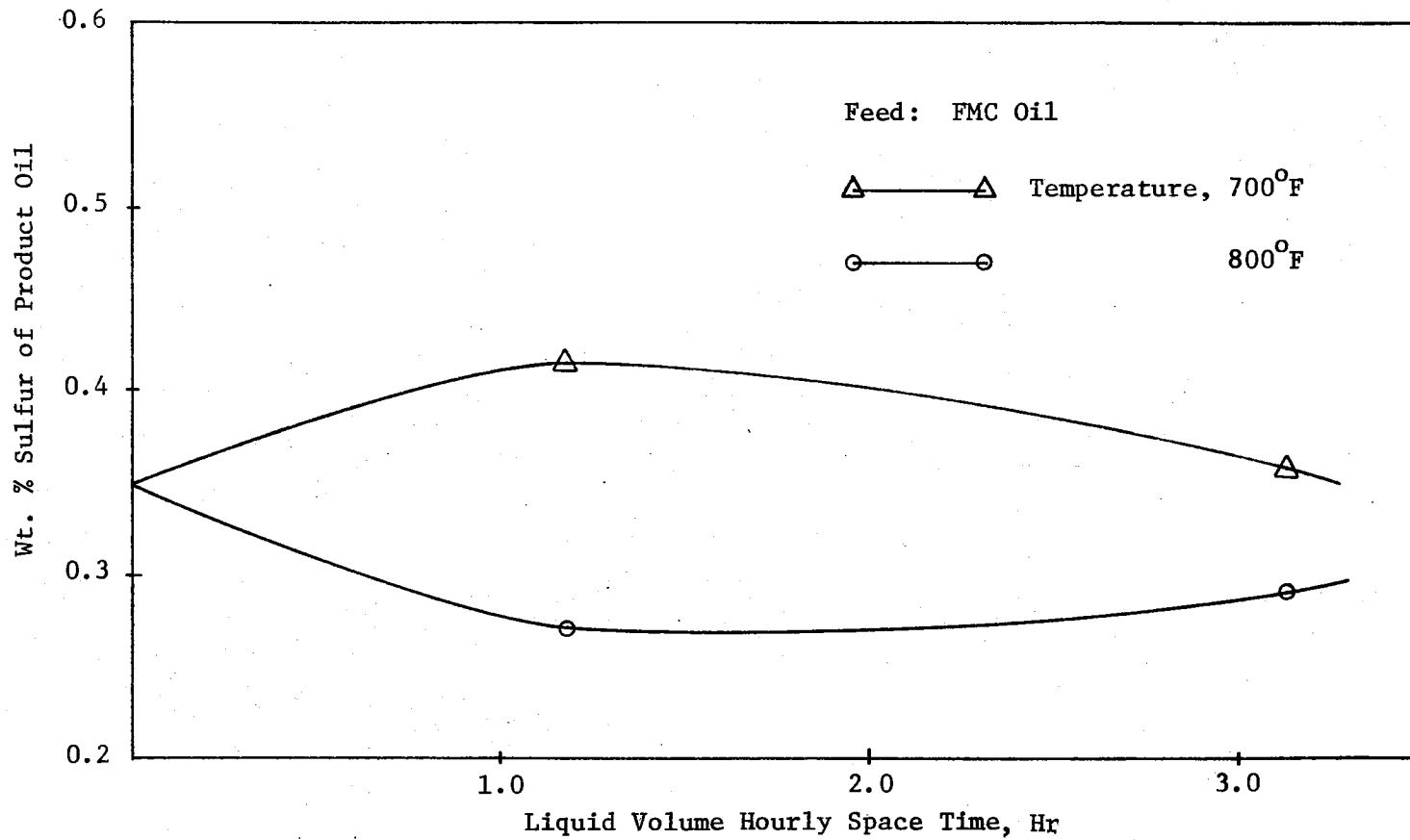


Figure 12. Effect of Temperature on Sulfur Removal from FMC Oil at 500 Psig

TABLE VI  
FMC - PRODUCT OIL CHARACTERISTICS

Sample	Pressure Psig	Temperature °F	Space Time Hour	% Sulfur	Sp. Gravity*
S-12	1500	700	1.18	0.411	1.009
S-14	1500	700	3.14	0.342	0.989
S-18	1500	800	3.14	0.282	0.964
S-21	1500	800	1.18	0.336	0.974
S-7	500	700	3.14	0.36	0.990
S-9	500	700	1.18	0.419	0.992
S-22	500	800	3.14	0.288	0.902
S-24	500	800	1.18	0.272	0.906

\*Specific gravity was conducted at 173°F.

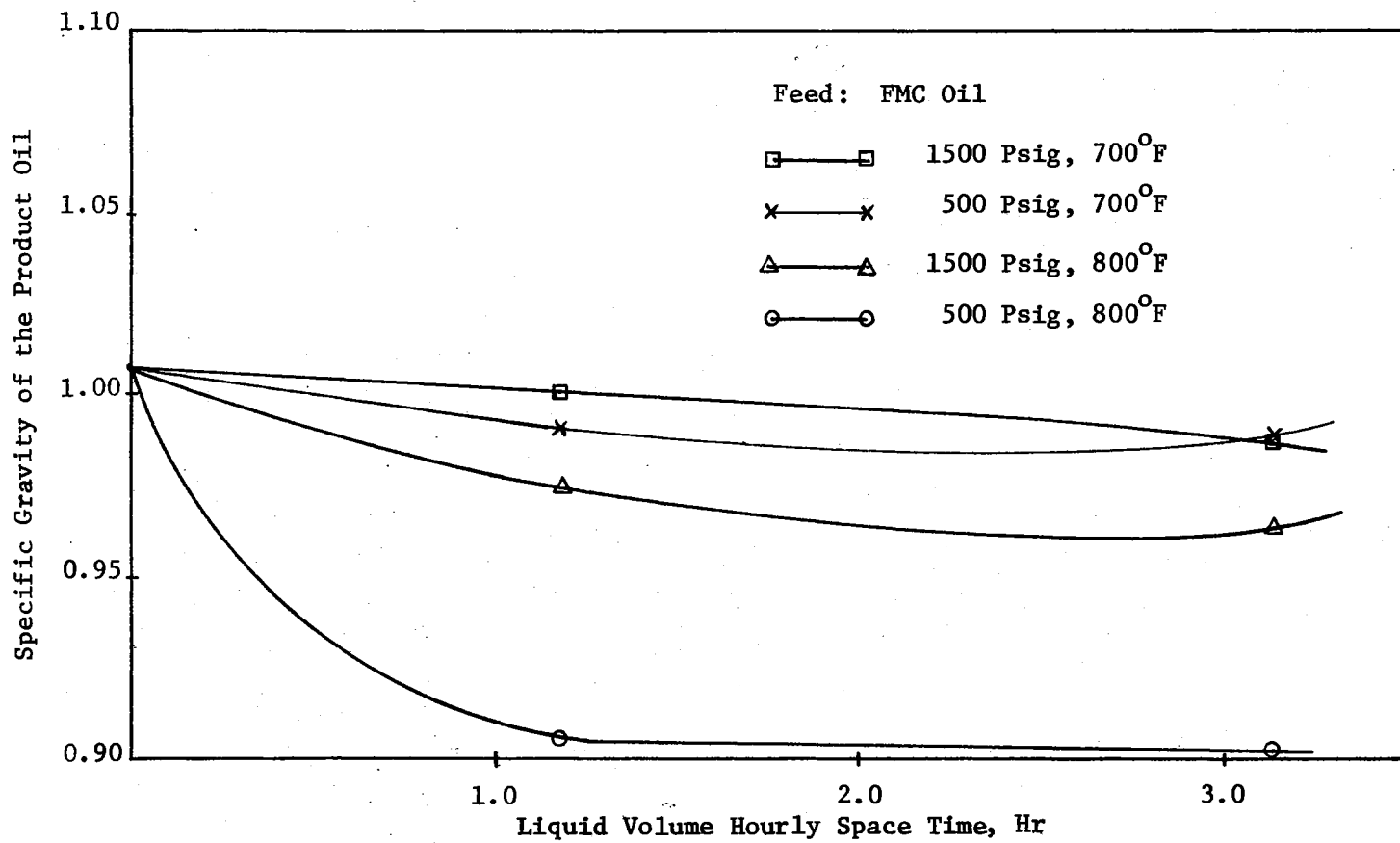


Figure 13. Effect of Temperature and Pressure on Specific Gravity of FMC Oil



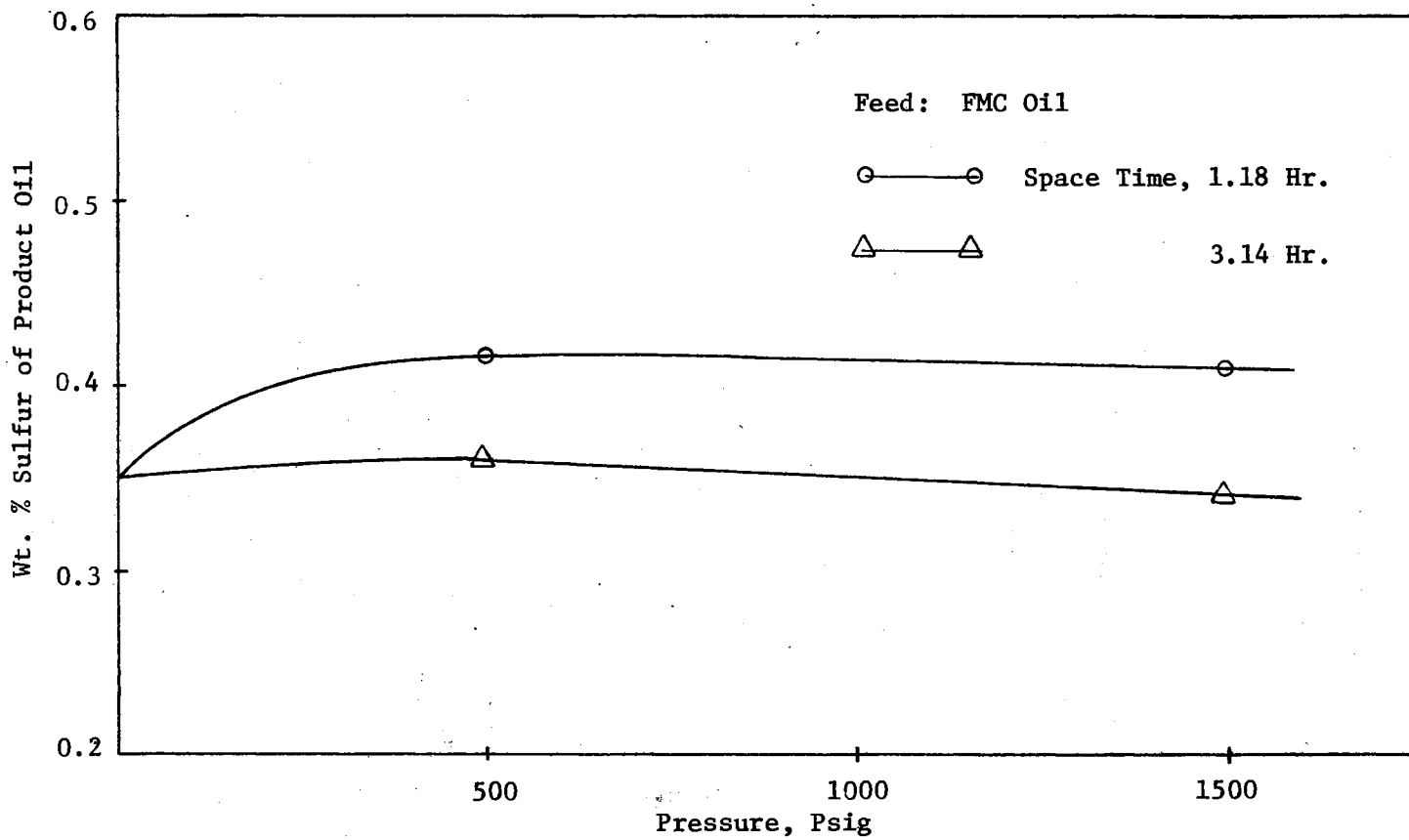


Figure 14. Effect of Space Time on Sulfur Removal from FMC Oil at 700°F

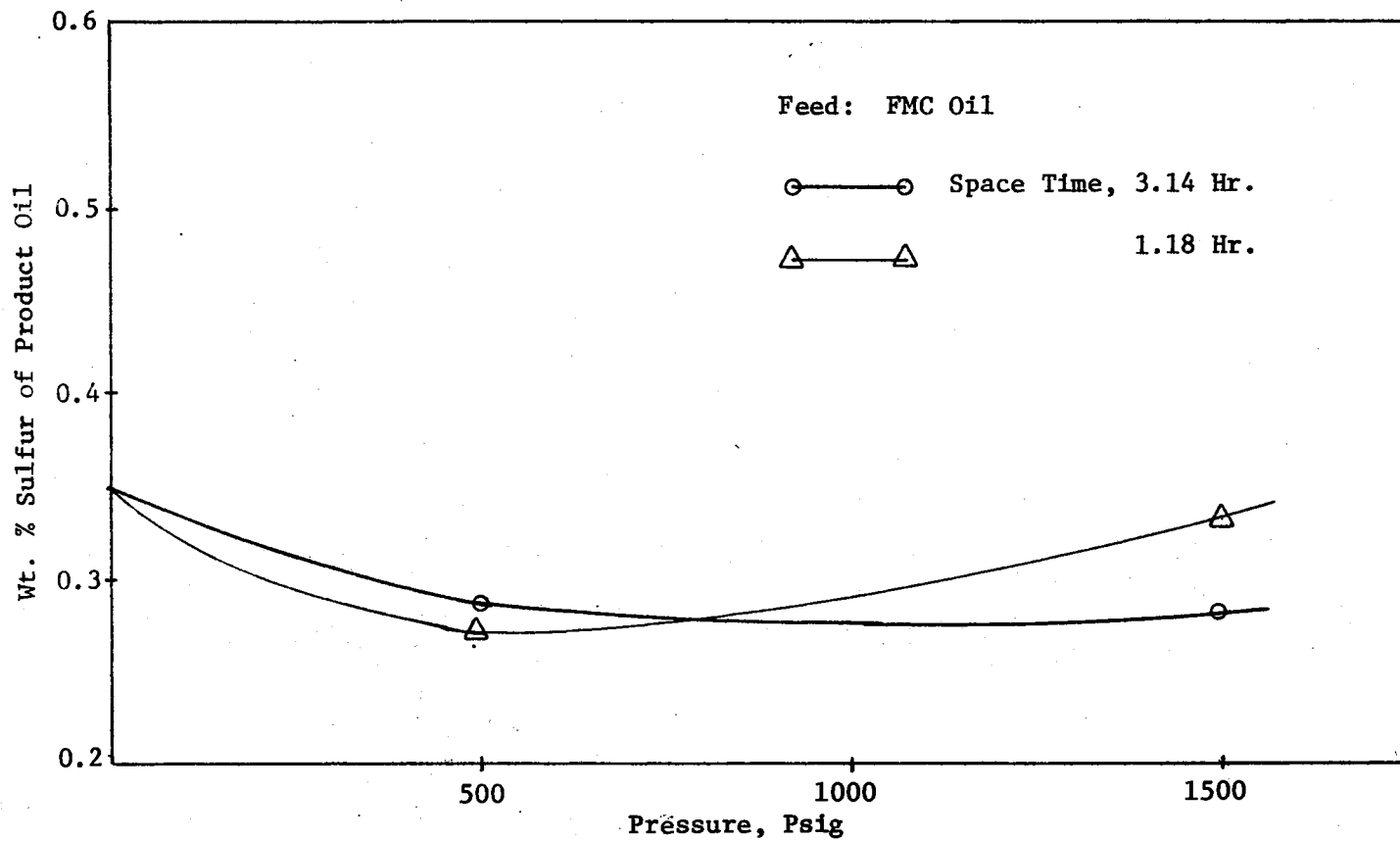


Figure 15. Effect of Space Time on Sulfur Removal from FMC Oil at 800°F

Figure 15, the pressure effect on sulfur removal at 800<sup>o</sup>F operating temperature is shown. At higher reaction time of 3.14 hours, the product oil contained 0.282 percent sulfur at 1500 psig pressure; whereas at 500 psig the sample oil was found to have 0.336 percent sulfur. The curve of low reaction time of 1.18 hours show an increase of sulfur content at higher pressure of 1500 psig than the oil processed at 500 psig.

The results of the experiment on PAMCO and FMC oils are summarized in Tables V and VI respectively. A detailed discussion of the observed results will be presented in the following chapter. The precision of the operational and the analytical work of this experimental study will also be considered.

## CHAPTER V

### DISCUSSION

Heterogeneous, uncatalyzed reactions are complicated since the compounds in each phase are liable to undergo extensive changes due to certain physical factors before they react. These factors include amount of interfacial surface area and the rate of diffusion of fluids from one phase to another. Consequently, the overall rate of non-catalytic hydrotreating reactions is affected by both kinetics and the rate of mass transfer between the phases (24). From the results in Chapter IV, it is evident that the thermal decomposition is at times pre-dominant over the desulfurization reactions, depending upon the operating conditions and composition of the feeds that have been processed. The contrasting features of the two oils, the PAMCO oil and the FMC filtered oil (Colorado Bear Mine), upon hydrodesulfurization in the absence of a catalyst were shown in Figure 6 through Figure 15.

For the better understanding and evaluation of the collected data, it is quite reasonable to review and discuss the effect of various limiting factors that were involved during the experimental operation and analytical work.

The desulfurization study was conducted in a trickle flow reactor (Figure 4). The performance of the trickle flow reactor can be affected by the poor distribution characteristics of the involved media causing inefficient conversion (27). Many researchers have

conducted various studies on the problems associated with the trickle bed reactors (20,32,34). Liquid maldistribution due to back mixing and channeling may be a problem. A method for assuring the absence of back mixing has been formulated by Mears (20). In his work he has also projected an estimated value of 350 to 1 being the ratio of height of the packed bed to the particle diameter as a good guide to ensure freedom from backmixing for first-order reactions. In this work the height to the particle diameter of the fixed bed was 291, however, the reaction order had not been determined. But Schwartz and Roberts (32) in their recent paper on evaluation of models for liquid backmixing in trickle bed reactors have concluded that liquid backmixing is not often found to be a major problem in trickle bed reactors.

A ratio of reactor tube to the particle diameter has also been considered as a criterion by some other researchers in the study on liquid flow pattern (20,21,22). Accordingly, the tendency of the liquid to flow out of the packing and down the wall surface where the packing is least dense is greater in small diameter reactors. However, commercial reactors where the ratio of the diameter of the tube to the diameter of the particle is usually greater, are less efficient than the pilot plant reactors (27).

The liquid maldistribution has also been looked into in terms of changing liquid flux at constant space time. The effect of liquid flux on reactor performance over the range of 3.8 to 15.3 gallons per hour per sq. ft. was studied (12) at 3000 psig pressure and 729<sup>o</sup>F temperature. The variations were too small to be considered. Satchell (30)

and Sooter (36) in their recent work on hydrotreating of coal liquids also found that the effect of liquid flux on the conversion was insignificant over the range of 4.84 to 9.69 gallons per hour per sq. ft. This experiment was done over the range of 2 to 5.25 gallons per hour per sq. ft. surface of the packed bed. Any conclusive decision on the extent of liquid maldistribution problem could not be reached on this uncatalyzed hydrotreating reactions as these experimental runs did not include a special study devised on this problem.

The gas distribution is another variable that may be of consideration in trickle flow reactor operation. Wan (38), in his work, studied the effect of superficial gas velocities in the hydrotreating experiments of coal derived liquids conducted in the trickle bed reactors. He found that superficial gas velocity over the range of 0.6 to 6.0 normal cubic feet per hour has no direct bearing on trickle flow operation. These flow rates are equivalent to 3980 to 39800 normal cubic feet of hydrogen per barrel of oil. This experiment had been conducted in an identical reactor with a hydrogen supply of 10,000 cubic feet of hydrogen per barrel of oil.

Temperature control is a tedious problem associated with catalytic exothermic reactions. But this did not contribute any stumbling block in this non-catalytic work due to the limited hydrodesulfurization reactions and the competing thermal cracking which is endothermic. In addition, to this, the flexible heat control device enabled, to great extent, to maintain a smooth temperature profile. A typical temperature curve is shown in Figure 16.

The Leco 532-000 Automatic Sulfur Analyzer was employed in determining the sulfur content of the product samples. The operational

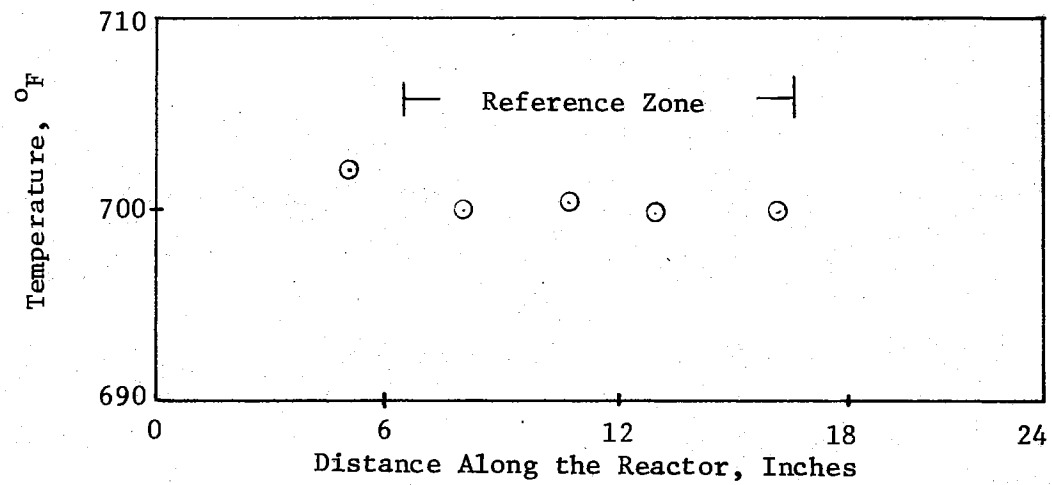


Figure 16. Typical Reactor Temperature Profile

procedure and computational methods are detailed in Appendix A. The performance of the analytical system had been verified with the sulfur content of the feed oils. For the FMC filtered oil a variation of  $\pm 1.7$  to 2.5 percent from the specification, shown in Table II was noticed and for the PAMCO oil the variation was  $\pm 1.6$  to 2.5 percent from the supplier's specification given in Table III. The specific gravities of the product samples were also determined and the procedure is presented in Chapter IV. The specific gravity of the FMC feed oil was determined and the method showed a deviation of  $\pm 2.78$  percent from the supplier's specifications. The precision of the overall operation was verified. The reproducibility of the samples was  $\pm 2.3$  percent for sulfur content and  $\pm 0.61$  percent for the specific gravity.

The temperature was found to have relatively marked effects on the uncatalyzed hydrodesulfurization reaction over the conditions chosen for this experimental work. At 1500 psig pressure, more sulfur removal was noted with the increase of temperature from 700°F to 800°F. Figure 6 depicts the desulfurization reaction behavior of PAMCO oil at these process conditions. At both space times of 1.18 hr. and 3.14 hrs., increases of sulfur removal were noticed with the increase of temperature from 700°F to 800°F. At 1.18 hour space time, the sample oil of 700°F reaction temperature contained 1.163 percent sulfur; whereas the product oil of 800°F showed 1.082 percent sulfur. At the higher space time of 3.14 hour space time the sulfur content of the product oils processed at 700°F and 800°F were 1.136 percent and 1.049 percent, respectively. The effect of the temperature increase on the desulfurization of PAMCO oil at the lower pressure of 500 psig is seen in Figure 7. As shown in the figure, at 1.18 hrs. reaction



time there was no change in the sulfur content of the oil treated at 700°F. But when the temperature was increased to 800°F, a slight desulfurization had taken place to reduce the sulfur content of the oil to 1.1 percent. The 700°F curve shows that the desulfurization was favored by space time. But, raising the temperature to 800°F, the reaction time was found to accelerate the overall thermal cracking more than the overall desulfurization reactions. This was evidenced by the accompanied specific gravity variation of the product oil when the reaction time was increased from 1.18 hrs. to 3.14 hrs. (Figure 8). Also the product oil processed at 800°F contains more sulfur than the oil processed at 700°F. In general, the rates of both the hydrogenation and cracking reactions were promoted with the increase of temperature, but the extent to which hydrogenation can proceed decrease, due to the low pressure conditions (13).

The specific gravity of the product oils forms a qualitative measure of the involved cracking and hydrogenation reactions during processing. The specific gravity correlation of PAMCO oil is depicted in Figure 8. The observed reduction of the specific gravity may be accounted for by the pronounced thermal cracking at the lower pressure operating condition. The combined effect of high temperature and low pressure had contributed to the thermal cracking (16,19). The increased thermal cracking with temperature has also been reported by Quader and Hill (25) in their work on hydrocracking of low temperature coal tar.

For the PAMCO oil, the maximum sulfur removal was obtained at the most severe reaction condition of 1500 psig pressure, 800°F temperature and 3.14 hours space time (See sample No. S-33, Table V).

FMC coal liquid (Colorado Bear Mine) was found to be more sensitive to temperature variations than the PAMCO composite oil (Figures

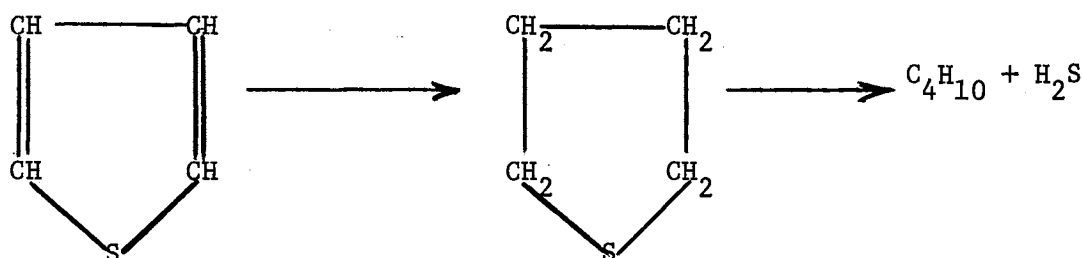
8 and 12). In almost all cases the thermal cracking seemed to prevail over the hydrodesulfurization reactions except at 1500 psig pressure and 800°F temperature operating condition. The highest sulfur removal was achieved at the lower pressure of 500 psig and temperature of 800°F with 3.14 hours space time. On a comparative basis, the extent of sulfur removal attained with reference to FMC oil was more than that with PAMCO oil. The observed variations in specific gravity of the oils at the respective process conditions show the possibility of cracking and hydrogenation of the substituents including the sulfur compounds present in the feed oil. An effort to set apart the desulfurization due to simple cracking and hydrocracking is impossible here with the collected data.

The reaction time was found to have effect on the hydrotreating reactions of the PAMCO oil, especially when the conditions are favorable to crack (Figure 8). This variable was influencing in the desulfurization of FMC oil especially at the higher operating pressure of 1500 psig (See sample S-18 and S-21, Table VI). The effect of space time on the cracking of the FMC oil was negligible and could be seen in Figure 12.

The effect of pressure increase from 500 psig to 1500 psig on both the desulfurization and cracking of the feed oils was found to be insignificant at 700°F temperature (Figure 9, 13 and Tables V and VI). But at the higher temperature of 800°F, this was not found to be the case. The pressure had significant influence on both the cracking and desulfurization reactions of both the feed oils. This can be seen clearly in Figures 10 and 15, Tables V and VI. Figure 10 depicts the effect of pressure on PAMCO oil treated at 800°F. When

the reaction pressure was raised from 500 to 1500 psig, no considerable variation in the desulfurization was noted at the lower space time of 1.18 hours. But at 3.14 hours space time, the sulfur content of the product oil was dropped when the pressure was increased from 500 to 1500 psig (Table V). This pressure effect on the desulfurization reaction in this non-catalytic process was mainly due to the non-hydrogenative cracking tendency of the feed oil at low pressure condition. The thermal cracking of PAMCO oil, at 500 psig was favored by the high temperature of 800<sup>o</sup>F and 3.14 hours reaction time was evidenced by specific gravity measurement of product oils (See Table V). In the case of FMC oil, the pressure increase from 500 to 1500 psig did not show notable improvement in the desulfurization at a higher reaction time of 3.14 hours. But at 1.18 hours space time, the sulfur removal was seen to decrease with the increase of pressure from 500 to 1500 psig. This showed that the progress of desulfurization reaction was not limited by the hydrogen depletion consequent to the hydrogen consuming reactions in the liquid phase. The increased desulfurization at 500 psig was mainly due to the hydrogenative cracking of the sulfur compounds of the feed oil. The variations in specific gravity of the treated FMC oil at the respective operating condition are shown in Table VI.

The major reactions of the involved sulfur compounds known to occur in presence of hydrogen have been demonstrated by a number of studies on pure sulfur compounds. The primary reaction is the carbon-sulfur bond rupture and the addition of hydrogen to the residual fragments. The reaction of the thiophenes, which is found to be one of the major sulfur compound groups is typified as follows:



In general an evaluation of the possible reaction of the sulfur compounds is difficult due to the complex and relatively unknown composition of both the reactants and the products.

The hydrodesulfurization of the same feed oils, PAMCO composite oil and FMC filtered oil, had been conducted catalytically by others in the same laboratory equipment. The results of one experiment on PAMCO oil with Nalco 474 (8-10 mesh) catalyst, conducted under identical conditions are shown in Figure 17. The feed oil containing 1.2 percent sulfur was hydrotreated at 1500 psig pressure, 800°F temperature and 3.14 hours space time. The product oil in the catalytic process contained only 0.149 percent sulfur; whereas, in the non-catalytic study, the oil processed under identical conditions contained 1.049 percent sulfur in its product. This shows that catalytic hydrotreating markedly reduces the sulfur content of the oils over the non-catalytic hydrotreating process. A similar comparative study between the catalytic and the non-catalytic hydrodesulfurization of FMC oil could not be attempted here as the evaluation of the former study is not yet completed.

Following this discussion, the conclusion of this study based on the observed experimental results are summarized in the next chapter.

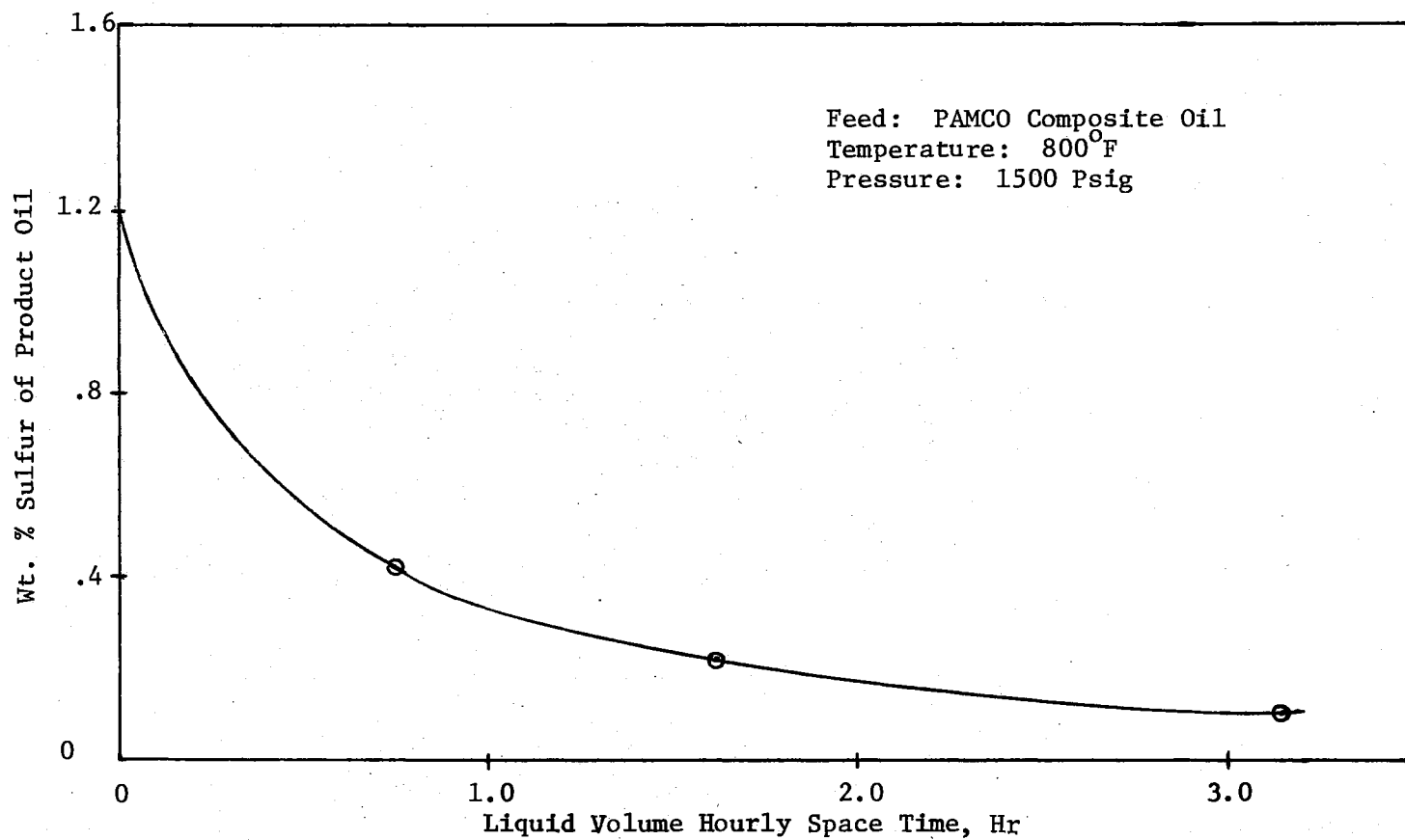


Figure 17. Catalytic Hydrodesulfurization of PAMCO Composite Oil, 800°F

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

#### Conclusions

1. The experimental system was satisfactorily operable with regard to flexibility in control of temperature, pressure and feed rate within the range of variables investigated.
2. The temperature was seen to have effect on the non-catalyzed hydrotreating process. Both the desulfurization and cracking reactions were increased with the increase of temperature.
3. Pressure increase, in general, favored the desulfurization reactions, whereas, a decrease of pressure promoted the overall cracking of the feed stock.
4. The desulfurization and the thermal cracking reactions were favored with the increase of space time.
5. The extent of non-catalyzed sulfur removal was relatively low compared to the catalyzed removal. The PAMCO oil at 800<sup>o</sup>F, 1500 psig and 3.14 hours yielded a product oil of 1.05 wt% for non-catalyzed removal compared to 0.15 wt% in catalyzed removal.
6. The FMC oil seemed to be somewhat more difficult to process in the trickle flow reactor than the PAMCO oil.
7. These data can serve as a basis of further work to help assess the catalyzed and non-catalyzed reactions occurring during hydroprocessing of coal liquids.

### Recommendations

1. The hydrogen flow rate should be measured by devising a convenient unit on the hydrogen line prior to the entry of the gas into the reactor.
2. Thermal experiments shall be conducted without the hydrogen supply into the reactor, to estimate the effect of hydrocracking on the uncatalyzed desulfurization reactions.
3. Kinetic studies on the non-catalytic desulfurization reactions are possible by conducting the experiments over a wide range of the selected process variables.

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## APPENDIX A

### SULFUR ANALYSIS

The total sulfur content of the product samples and the feed oils were analyzed by employing the Leco Automatic Sulfur Determinator. The whole analytical system comprised of three component units, an induction furnace (Model 521-500), an automatic titrator (Model 532-000), and an oxygen purification train (Model 516-000). The purifying train consisted of a sulfuric acid tower, a reagent tower filled with Ascarite and magnesium perchlorate, and finally a rotameter for measuring the oxygen flow rate. The moisture in the oxygen was removed in the sulfuric acid tower and the acid gases were eliminated in the reagent tower.

The working principles of the Leco Automatic Sulfur Determinator had already been discussed in Chapter III. The general procedure for the operation of this analytical system had been clearly described in the Leco bulletin (18).

The reagents used in this analytical work were prepared as follows:

#### Starch Solution

The starch solution was prepared by adding two grams of Arrow root starch to 5 ml of distilled water. This was poured into a 150 ml of boiling distilled water. The boiling of the mixture was maintained 2 minutes and then the solution was cooled to room temperature. Six grams of potassium iodide were added to this cooled solution and stirred well to desolve completely.

Fresh starch solution was prepared each day for the analysis. The other reagents used in this work were potassium iodate solution and the hydrochloric acid solution. These were stable solutions and considerable amounts were made at a time to be used up to one month.

#### Potassium Iodate Solution

The potassium iodate solution was prepared by desolving 111 gms of 100% potassium iodate in distilled water and made up to 1 liter in a flask.

#### Hydrochloric Acid Solution

The hydrochloric solution was prepared by diluting 15 ml. of 100% hydrochloric acid to 1 liter with distilled water.

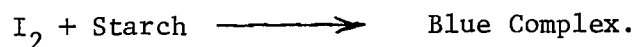
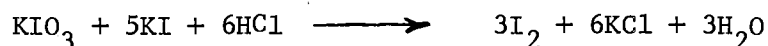
The Leco induction furnace and the automatic titrator were switched on approximately 45 minutes before the analytical work was initiated. This was to warm up the equipment system. There was an electrically heated glass delivery tube that carried the exhaust gases from the induction furnace chamber to the automatic titrator. This had to be switched on approximately 15 minutes prior to the analysis. In addition to this, a mark at the middle of the bell-shaped wall of the titration vessel was made. This served as a guide to supply constant volume of hydrochloric acid solution into the vessel for each analysis. Oxygen flow was commenced approximately 5 minutes before the analysis was begun and the flow rate was set at a rate of 1 to 1.2 liters per minute (STP). This was to drive off the air from the conduits and equipments.

Next the sample was prepared for the combustion in the Leco crucible, Model 528-25. About 0.282 gms of magnesium oxide were taken in the crucible and the sample oil weighing less than 0.1 gms was

transferred on to the magnesium oxide layer in the crucible. Another 0.282 gms of magnesium oxide were weighed and spread over the sample. About 1.5 gms of iron chips were added onto the crucible contents. Then finally the tin metal accelerators weighing 0.77 gms were put over the contents and the crucible was covered with the Leco porous cover, Model 528-42. The sequence of steps described as above were strictly followed to prepare the sample for combustion.

After the sample preparation, the analysis was performed as follows:

The titration vessel was filled with hydrochloric acid up to the level marked on its bell shaped wall. Then 5 mls of starch solution were added to the hydrochloric acid solution and oxygen was bubbled through the mixture. Then the button of the titrator double throw switch was turned on to the end point with the control knob set at the extreme left position (refer to the Leco instruction manual (18)). This knob was then moved slowly in the clockwise direction until it had added required volume of potassium iodate solution from the buret to the titration vessel to turn the color of the mixture to a solid medium blue. This indicated the end point of the solution mixture and the knob was set at this point. The following were the reactions involved in these steps:



Also 0.7 gms of sodium azide were added to the contents of the titration vessel. This prevented the interaction of the sample nitrogen compounds with the titration and determination of sulfur.

Now the crucible with its contents were placed in the combustion tube of the induction furnace. At the same time the titrator switch was also turned to the "titrate" position. The evolved sulfur dioxide from the combustion tube reacted with the iodine. The blue complex thence was destructed and subsequently potassium iodate solution from the buret was added automatically to maintain the blue color of the solution mixture at the pre-set end point. The volume of the added potassium iodate solution was used to determine the sulfur percentage of the sample. A typical calculation is shown in Appendix B.

A blank determination and furnace constant calculation were made before the final computations on the percent sulfur were attempted due to the following reasons:

#### Blank Determination

A blank was the crucible with all its contents, except for the sample, made by strictly following the sequence of steps as described in the sample preparation procedure. The blank was analyzed for sulfur present in the crucible with the accelerator. The sulfur content of the blank had to be deducted from the total percent sulfur computed directly from the buret reading while the samples were analyzed.

#### Furnace Factor

The reliability and accuracy of this analytical work was solely based on the extent that the sulfur present in the sample could be converted to sulfur trioxide in the product gases of the furnace could lead to inconsistent results. Even with the high temperature combustion, all the sulfur in the sample might not be completely converted to sulfur

dioxide. The extent of error due to this was minimized by incorporating a correction factor called Furnace factor, 'F' in the final calculations (18). The 'F' factor was found by analyzing a standardized oil sample whose sulfur content was known. This factor was determined as follows:

$$F = \frac{(\% \text{ Sulfur of the Std. Sample}) \times (\text{Wt. of the Std. Sample})}{(\text{Buret Reading} - \text{Blank})}$$

The detailed calculations relevant to this analytical work is shown in Appendix B.

Normally, three or four analyses of each sample were conducted and the average value was reported as the sulfur content of the respective sample. The typical calculations that were involved with the determination of the percent sulfur of the product oils are given in Appendix B.

## APPENDIX B

### SAMPLE CALCULATIONS

A standard sample of known sulfur concentration was analyzed in the Automatic Sulfur Determinator and the furnace factor 'F' was calculated as noted in Appendix A.

Weight of the standard oil :  $9.245 \times 10^{-2}$  gms.

Volume of Potassium iodate solution used for the Blank : 0.18 ml.

Volume of Potassium iodate solution used for the standard sample : 1.83 ml.

Sulfur concentration of the standard sample : 0.453%

Furnace factor 'F' :  $\frac{(0.453) \times (9.245 \times 10^{-2}) \text{ gms}}{(1.83 - 0.18) \text{ ml}}$

:  $\frac{2.54 \times 10^{-2} \text{ gms}}{\text{ml}}$

Weight percent of the sample:

Wt. % S =  $\frac{F \times (\text{Vol. of Sample} - \text{Vol. Blank})}{\text{Wt. of the Sample}}$

Weight of the Sample :  $8.529 \times 10^{-2}$  gms.

Volume of Potassium iodate solution used for the sample : 1.05 ml.

Wt. % sulfur of the sample :  $\frac{(2.54 \times 10^{-2}) \times (1.05 - 0.18)}{8.529 \times 10^{-2}}$

: 0.259



TABLE VII

## EXPERIMENTAL DATA

Sample Number	Temperature °F	Pressure Psig	Hydrogen Flow Rate cu ft/hr.	Oil Flow Rate cc/Hr.	Space Time cc Inert/ cc Oil/Hr.	% Sulfur Removal	Specific Gravity
S-7-1	700	500	3.77	6.0	3.14	0.354	0.992
S-7-2	700	500	3.77	6.0	3.14	0.361	0.987
S-7-3	700	500	3.77	6.0	3.14	0.365	0.991
S-8-1	700	500	3.77	6.0	3.14	0.361	0.995
S-8-2	700	500	3.77	6.0	3.14	0.362	0.991
S-9-1	700	500	10.1	16.0	1.18	0.411	0.994
S-9-2	700	500	10.1	16.0	1.18	0.425	0.991
S-9-3	700	500	10.1	16.0	1.18	0.421	0.991
S-10-1	700	500	10.1	16.0	1.18	0.410	0.988
S-10-2	700	500	10.1	16.0	1.18	0.420	0.990
S-12-1	700	1500	10.1	16.0	1.18	0.410	1.011
S-12-2	700	1500	10.1	16.0	1.18	0.404	1.005
S-12-3	700	1500	10.1	16.0	1.18	0.418	1.011
S-14-1	700	1500	10.1	16.0	1.18	0.341	0.989
S-14-2	700	1500	10.1	16.0	1.18	0.346	0.992
S-14-3	700	1500	10.1	16.0	1.18	0.340	0.986
S-18-1	800	1500	3.77	6.0	3.14	0.278	0.963
S-18-2	800	1500	3.77	6.0	3.14	0.281	0.966
S-18-3	800	1500	3.77	6.0	3.14	0.287	0.965
S-21-1	800	1500	10.1	16.0	1.18	0.343	0.974
S-21-2	800	1500	10.1	16.0	1.18	0.335	0.978
S-21-3	800	1500	10.1	16.0	1.18	0.330	0.970
S-22-1	800	500	3.77	6.0	3.14	0.293	0.901
S-22-2	800	500	3.77	6.0	3.14	0.286	0.901
S-22-3	800	500	3.77	6.0	3.14	0.285	0.904

TABLE VII (Continued)

Sample Number	Temperature °F	Pressure Psig	Hydrogen Flow Rate cu, ft/hr.	Oil Flow Rate cc/Hr.	Space Time cc Inert/ cc Oil/Hr.	% Sulfur Removal	Specific Gravity
S-24-1	800	500	10.1	16.0	1.18	0.276	0.908
S-24-2	800	500	10.1	16.0	1.18	0.271	0.903
S-24-3	800	500	10.1	16.0	1.18	0.269	0.907
S-28-1	700	1500	10.1	16.0	1.18	1.187	1.007
S-28-2	700	1500	10.1	16.0	1.18	1.161	1.012
S-28-3	700	1500	10.1	16.0	1.18	1.141	1.008
S-31-1	700	1500	3.77	6.0	3.14	1.156	1.011
S-31-2	700	1500	3.77	6.0	3.14	1.116	1.016
S-31-3	700	1500	3.77	6.0	3.14	1.136	1.012
S-32-1	800	1500	3.77	6.0	3.14	1.067	1.018
S-32-2	800	1500	3.77	6.0	3.14	1.028	1.018
S-32-3	800	1500	3.77	6.0	3.14	1.055	--
S-33-1	800	1500	3.77	6.0	3.14	1.044	1.020
S-33-2	800	1500	3.77	6.0	3.14	1.062	1.026
S-33-3	800	1500	3.77	6.0	3.14	1.041	1.017
S-35-1	800	1500	10.1	16.0	1.18	1.100	1.015
S-35-2	800	1500	10.1	16.0	1.18	1.040	1.010
S-35-3	800	1500	10.1	16.0	1.18	1.106	1.014
S-37-1	700	500	10.1	16.0	1.18	1.20	1.02
S-37-2	700	500	10.1	16.0	1.18	1.201	1.015
S-37-3	700	500	10.1	16.0	1.18	1.199	1.019
S-39-1	700	500	3.77	6.0	3.14	1.141	1.012
S-39-2	700	500	3.77	6.0	3.14	1.092	1.018
S-39-3	700	500	3.77	6.0	3.14	1.157	1.009
S-41-1	800	500	10.1	16.0	1.18	1.129	1.016
S-41-2	800	500	10.1	16.0	1.18	0.99	1.018
S-41-3	800	500	10.1	16.0	1.18	1.22	1.023

TABLE VII (Continued)

Sample Number	Temperature °F	Pressure Psig	Hydrogen Flow Rate cu ft/hr	Oil Flow Rate cc/Hr.	Space Time cc Inert/ cc Oil/Hr.	% Sulfur Removal	Specific Gravity
S-43-1	800	500	3.77	6.0	3.14	1.198	0.979
S-43-2	800	500	3.77	6.0	3.14	1.191	0.979
S-543-3	800	500	3.77	6.0	3.14	1.190	--

VITA

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