AN INVESTIGATION OF THE ACTIVITY OF TWO COBALT-MOLYBDENUM-ALUMINA CATALYSTS FOR HYDRODESULFURIZATION OF FMC OIL, A COAL-DERIVED LIQUID

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Bachelor of Technology

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Hyderabad, India

1974

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
December, 1975

In the research work at Oklahoma State University by Wan (46) and Sooter (43), four Co-Mo-Alumina catalysts were studied for hydrodesulfurizing raw anthracene oil. These catalysts had the same metallic composition but different support properties. They observed that at 1000 psig, $650^{\circ}F$ ($343^{\circ}F$) and liquid volume hourly space time of 0.3-1.5 hours, a decrease in the most frequent pore size from 33 to 25 Å resulted in slightly decreased hydrodesulfurization activity of the catalyst. Others (31) in this laboratory unit observed that for FMC oil, a catalyst having the most frequent pore radius of 33 Å to be better than a catalyst with 25 Å as the most frequent pore size.

Catalyst Deactivation

In the hydrodesulfurization of liquid feedstocks, carbonaceous and metallic depositions are the two main causes for the catalyst deactivation. Van Deemter (45) observed that the hydrodesulfurization activity of the catalyst decreases rapidly after processing $1.5\text{x}10^7$ kg of gas oil. Schuit and Gates (39) in their review summarized from various sources that the deposition of solids in fixed-bed voids presents a major engineering problem. The depositions of organometallic compounds have a more severe effect on the catalyst activity than the carbonaceous deposits. These deposits block the pores of the catalyst, hence reduce the effective surface area, resulting in decreased activity.

Sooter (43) in his hydrodesulfurization studies with raw anthracene oil observed no appreciable loss in catalyst activity. The maximum period of operation in his studies was 200 hours. In studies with FMC oil and PAMCO composite oil, Others (31) observed significant loss in catalyst activity.

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PREFACE

Two Cobalt-Molybdenum-Alumina catalysts, Sphericat Nalco 474 and Nalcomo 474 were studied for hydrodesulfurization of FMC oil (coal-derived liquid) in a trickle bed reactor. Experimental data were taken at 1500 psig, 2.99 liquid volume hourly space time and 7500 scf Hydrogen/bbl FMC oil for temperatures of $700^{o}F$ ($371^{o}C$), $800^{o}F$ ($427^{o}C$) and $850^{o}F$ ($454^{o}C$) using Sphericat Nalco 474 catalyst and for $700^{o}F$ ($371^{o}C$) and $800^{o}F$ ($427^{o}C$) using Nalcomo 474 catalyst. Six experimental runs were conducted, the duration of which varied from 100 to 200 hours. An attempt was made for the preliminary assessment of carbon build-up on the catalyst as well as the effect on catalyst activity caused by the amount of H_2S supplied during catalyst presulfiding.

I am deeply indebted to my thesis adviser, Professor B. L. Crynes, for his intelligent guidance and timely help in enabling me to complete my M.S. degree requirements earlier than usual, his inspirational dedication to research and encouragement, his cooperation and great human understanding, and the excellent art of developing even the hidden talents of his graduate students. I am very thankful to all the Faculty members for their encouragement and particularly to Dr. R. N. Maddox for his patience with the project. A special note of thanks is due Messors D. C. Mehta and Sivasubramanian for their valuable suggestions and cooperation in completing this work.

I am very grateful to Mr. Dorsey Payne and Messors Vaikuntam Raghavan, Jack Wright, Anthony Jones, Kerry Scott and Nitin Mehta for their help in operating the equipment.

A special note of thanks is due Mr. E. E. McCroskey, the Storeroom Manager, and all the office Secretaries in the School of Chemical Engineering for their cooperation in completing the research and needed paper work.

Financial support from the School of Chemical Engineering and funds furnished by the Office of Coal Research, Department of Interior, and Pittsburg and Midway Coal Mining Company is gratefully received.

Finally, I express my deepest gratitude to my parents, brothers, sisters and all other family members for their constant support and sacrifices in making this achievement a reality.

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INTRODUCTION

The U. S., with its large energy resources, consumes about one-third of the total energy produced in the world. The gap between the domestic energy consumption and production of the U. S. emerged in the 1950's and has grown rapidly since 1970. The domestic energy consumption during the period 1960 to 1973 has grown at the rate of 4.2% per year while domestic energy production increased only at about 3.7% per year. The energy imports, mainly oil, increased at the rate of 7 to 10% per year. Energy conservation efforts are being made for bridging the gap between domestic energy consumption and production. The first healthy sign of these efforts became obvious from a decrease in the annual domestic energy consumption rate of 2.2% in 1974 (6).

In 1973 oil and gas supplied more than 75% of the energy required, of which 23% was imported. In 1974 oil supplied 45.8% of the total energy consumed, which is slightly less than its contribution of 46.6% made in 1973. Natural gas contribution remained constant at 30.4% while coal and lignite increased their share slightly from 17.6% in 1973 to 17.8% in 1974. The ratio of proven resources to annual production of natural gas has been decreasing rapidly from 20/1 in 1960 to 13.3/1 in 1970 and to 11.1/1 in 1974. The proved reserves of natural gas at the end of 1973 were 250 Trillion cubic feet (Tcf) and these dropped to 237.1 Tcf as of December 31, 1974. The natural gas liquid reserves declined by less than 2%, from 6455 million barrels in 1973 to 6350 million barrels in 1974.

The annual production rate of natural gas after remaining constant at 22.6 Tcf during the period 1970-73 dropped to 21.3 Tcf in 1974. The production of natural gas liquids also dropped from 741 million barrels in 1973 to 724 million barrels in 1974. The crude petroleum output also fell by 4.5% to 3.2 billion barrels in 1974.

In a recent study an estimate made on the basis of recent trends in the energy consumption indicated that the demand could reach an equivalent of 55 million barrels per day (MBPD) of oil by 1985, which is 55% greater than the 1973 consumption of 37.2 MBPD (27). The same study forecasts that proper energy conservation efforts can reduce the demand by 1985 to as low a value as 49 MBPD, as shown in Figure 1. The forecast made for the maximum production of liquid hydrocarbons from domestic resources is about 13.6 MBPD by 1985. This is still far short of the 1973 consumption of 16.2 MBPD.

In competition with oil and gas, the traditional coal markets were lost one by one with coal and lignite becoming under-utilized fuels. Coal is the most abundant fossil fuel having a limited capability for substituting for oil and gas. But it does have the potential to be converted to oil and gas. Coal production in 1974 was 600 million tons, which is 1.4% higher than that in 1973. Most of the forecasts suggest an expanded coal production to about 1260 million tons per year (MTPY) by 1985 in order to utilize more coal in the U. S. (27). This effort is a part of an attempt to achieve an increase

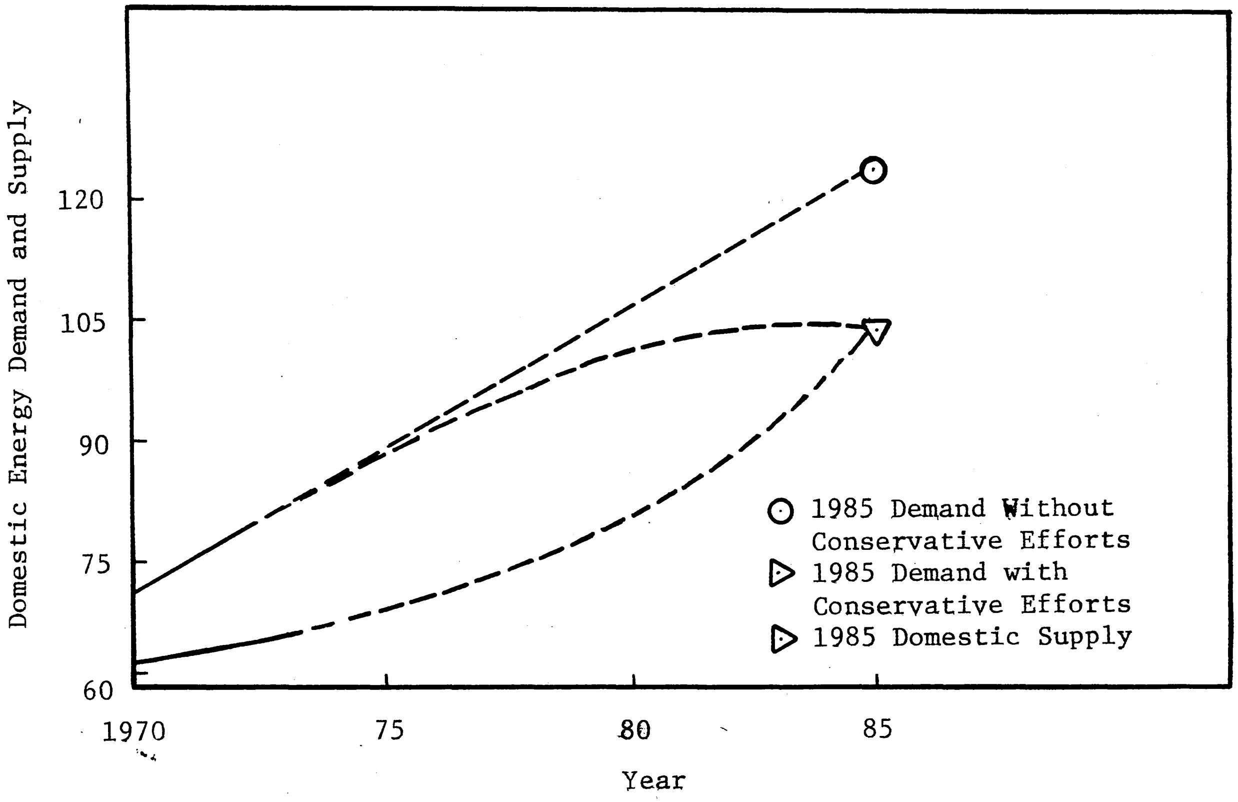

Figure 1. U. S. Domestic Energy Demand and Supply

Source: Reference (27)

of 20 MBPD of oil equivalent from all the domestic resources during the next eleven years.

The demand of energy from coal resources has been fluctuating since 1940 as shown in Figure 2. The coal resources were not able to increase their share in meeting the demand because of the tough competition with petroleum and natural gas. The demand of energy from petroleum resources has been increasing steadily from 7.67 Q Btu (3.62 MBPD) in 1942 to 36.8 Q Btu (17.38 MBPD) in 1974. The largest contribution made by coal was 17 Q Btu in 1943 compared to 8.23 Q Btu by petroleum in the same year. The demand of energy from coal seems to be increasing steadily from 12.86 Q Btu in 1967 to 14.4 Q Btu in 1973 and to 14.6 Q Btu in 1974. The irony of the situation is that the demand of energy from coal resources was twice that from petroleum in 1942, about equal in 1950 (12 Q Btu), but less than half in 1974. If proper steps are taken for increasing the coal production then, according to a forecast, the potential 1985 domestic coal production resources will be as shown in Table I.

As shown in Table I, the production of energy from coal resources will be the equivalent of about 11.7 MBPD of oil, about 23.8% of the total energy production compared to 17.8% in 1974. Natural gas resources will be producing an equivalent of 14.5 MBPD of oil, about 28.6 Tcf compared to 21.3 Tcf in 1974. Oil resources will be producing 12.5 MBPD, about 25.4% of the total energy production compared to 45.8% in 1974.

Synthetic fuels from coal are estimated to supply 3.46% of the total energy produced by 1985, of which 0.6% (0.3 MBPD) will be in the form of synthetic crude. Shale oil contribution in the form of

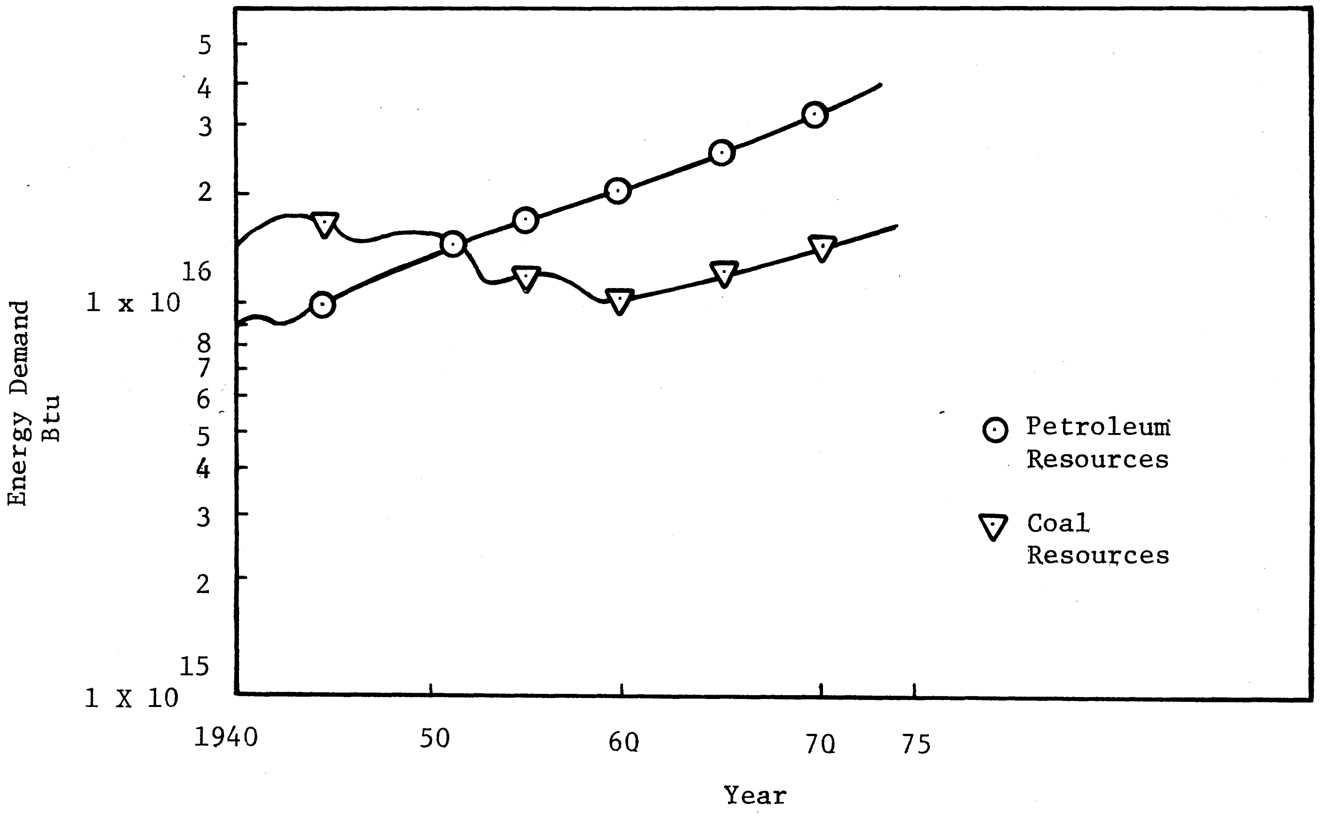

Figure 2. Energy Demand from Coal and Petroleum Resources

Source: Reference (24)

TABLE I

POTENTIAL 1985 U. S. ENERGY PRODUCTION RESOURCES

Energy Form	Production		Total		% Total
	MBPD	Q Btu	MBPD	Q Btu	
Coal:					
Coal solids	10.0	21.17			
Pipe line quality SNG*	0.8	1.69			
Methanol*	0.3	0.64			
Synthetic crude*	0.3	0.64			
Medium-Btu gas*	0.3	0.64			
			11.7	24.78	23.79
Nuclear:					
Uranium-Plutonium	8.3	17.57			
			8.3	17.57	16.87
Renewable:					
Hydroelectric	1.5	3.17			
Geothermal	0.2	0.42			
			1.7	3.59	3.44
Oil Shale:					
Synthetic crude	0.5	1.06			
			0.5	1.06	1.03
Natural gas:	14.5	30.70			
			14.5	30.70	29.47
Petroleum	12.5	26.46			
			12.5	26.46	25.40
	Total		49.2	104.16	100.00

* Based on the use of 8,500 Btu/lb U. S. western coal
Source: Reference (27)

synthetic crude will be 1.03% of the total. The major increase in contribution will be that of coal. To achieve this increase the estimated production and utilization will be as shown in Table II. Most of the additions, about 520 MTPY will be from Western surface mining. By 1985 about one-fourth of the total coal production, 310 MTPY will be utilized in the form of synthetic fuels compared to 950 MTPY in the form of coal solids.

TABLE II

ESTIMATED 1985 COAL PRODUCTION AND UTILIZATION IN THE U. S.

Source	1974-85 Additions (MTPY)	1985 Production (MTPY)	Fuel	1985 Utilization (MTPY)
Existing (1973) Mine depletion	(200)	--		
Eastern underground	280	480	Coal Solids	950
Eastern surface	60	220		
Western surface	520	560	Synthetic fuels	310
Total	660	1260		1260

Source: Reference (27)

The value of oil imports and even marginal oil wells at home will have importance as the future price setters and will affect the commercial production of these coal-based synthetic fuels. This particular forecast may not turn out to be true, but it does indicate the significantly more important role that coal must have and can play in the U. S.

The present study is concerned with the coal-derived liquids and hence with liquefaction of coal. Considering the more important role coal can play, the technology for commercializing coal liquefaction processes has not yet fully developed. Several processes have been proposed, some of which are still at the bench scale or pilot plant scale. The primary objective of these processes is to produce a substitute refinery crude and/or a suitable low-cost clean fuel for direct use in boilers. The coal liquefaction processes can be characterized as follows:

1) Hydrogen-Additon methods: In these methods, dried and sized coal is mixed with an internally generated coal-derived solvent (heavy aromatic) to form a slurry and then allowed to react with hydrogen under suitable conditions of temperature and pressure. If a catalyst is used, then these methods are also referred to as solvation coupled with catalytic hydrogenation processes, H-coal and Synthoil processes are some of the typical examples. If the processes are non-catalytic, then they are also referred to as solvent refined or extractive hydrogenation processes. Solvent refined coal (SRC) and Conslidation Coal Company (CSF) processes are some of the typical examples.

2) Carbon-Rejection methods: In these methods, dried and sized coal is heated to successively higher temperatures to remove valuable

liquids before the product char is burned. The processing conditions, and the coal type used, determine the amount of char and liquid obtained. Char is the major product in these methods and a typical example is the Char Oil Energy Development (COED) process developed by FMC Corporation.

Several companies are also working on the development of their own processes, but the details are yet to be released. Some of the companies actively involved at present include Gulf Oil Co., Exxon, and Oil Shale Corp.

The coal-derived liquids as produced have a low hydrogen content and relatively high concentration of hetero-atoms. Some of these liquids require further hydrotreating before subjecting it to refinery processing or use as a boiler fuel. Hydrogenation of coal-derived liquids relative to the petroleum crudes takes place at a slower rate because of the presence of large amounts of polynuclear aromatic structures. Desulfurization is an important step before further processing coal-derived liquids because of the poisioning effect of sulfur on catalysts to be used in subsequent operations such as reforming, etc. The air pollution control regulations regarding the fuel sulfur content also emphasizes the need for desulfurization at an earlier stage. Those in industry also believe that the removal of sulfur from liquid and gaseous fuels is relatively more easy than from the flue gases.

Experience with petroleum feedstocks has led to the development of catalytic hydrodesulfurization processes. Most of the commercially available catalysts for hydrodesulfurization have been developed with the petroleum feedstocks, which consist mostly of paraffins and olefins compared to the coal-derived liquids. These coal-derived liquids consist primarily of polynuclear aromatic structures and relatively little is known about the hydrodesulfurization of such a complex mixture of these structures. The catalyst type most commonly used in industry for hydrodesulfurizing petroleum feedstocks is Cobalt-Molybdenum on a Alumina support. Industrially, hydrodesulfurization is carried out in trickle or fluidized bed reactors. In these reactors hydrogen and liquid feedstock contact the catalyst under controlled conditions of temperature, pressure and time of contact.

Some of the important factors to be considered in the selection of catalysts for the hydrodesulfurization of coal-derived liquids are:

1) Activity: The activity of catalyst determine the economics of processes in terms of the total productivity during its life (active period) and the loss of productivity during the shut down required for its replacement.

2) Selectivity: The selectivity towards sulfur removal in particular and hetero-atom removal in general is of prime consideration. In some cases cracking of the feedstock is undesirable. Moreover selectivity and hydrogen consumption are closely related.

3) Sintering: Most of the hydrodesulfurization processes are carried out at high temperatures and pressures. Such high temperature operations over a long period of time causes the crystals making up the active surface of the catalyst to grow in size, thus reducing the surface area and hence the activity.

4) Fouling: Depositions of metals and carbonaceous material on the catalyst results in its deactivation. This deactivation may also

be due to the pore blockage of the catalyst.

5) Mechanical strength: The catalyst particles should be strong enough to withstand the severe operational conditions of high temperature and high pressure. There should be minimum loss due to attrition resulting in fines.

6) Particle size: In petroleum industry, decrease in particle size resulted in increased sulfur removal indicating pore diffusional limitations. A compromise is necessary between the particle size and the pressure drop across the catalyst bed.

7) Geometrical factors: Surface area, pore diameter and pore volume of the catalyst in general and of the support in particular determines the overall activity of the catalyst loading to a major extent. The pore size should be considerably bigger than the size of the reacting molecules. In some cases presence of macro pores in a catalyst has been observed to be an advantage.

8) Diffusional limitations: Concentration gradients across gas-liquid, liquid-solid and gas-solid interface may exist. Concentration and thermal gradients may also exist within the catalyst pores. These gradients can result in fractional utilization of the catalyst active area.

In general the characteristic features of the feedstocks and the capital investment required will determine the relative importance of the factors mentioned above. The present study is a part of a research program at the School of Chemical Engineering, Oklahoma State University on the development of catalysts for hydrodesulfurizing coal-derived liquids. The objectives of the present study were as follows:

1) In the long run, to be capable of developing catalysts, specifically selective for the hydrodesulfurization of coal-derived liquids.

2) To establish the effects of temperature, pressure, space time and catalyst pore size on the activity of catalysts in the hydrodesulfurization of coal-derived liquids.

3) In particular, to establish the effect of temperature, pressure, space time and pore size on the short term deactivation of two presently available, commercial Cobalt-Molybdenum-Alumina catalysts in the hydrodesulfurization of FMC oil (coal-derived liquid). The reference for this establishment is the sulfur concentration in the feed and product oils.

CHAPTER II

LITERATURE REVIEW

Earlier in the development of technology for hydroprocessing petroleum feedstocks, simultaneous hetero-atom removal was achieved successfully. In commercial practice, removal of sulfur in the form of H_2S by the catalytic hydrotreatment of the feedstock is commonly referred to as hydrodesulfurization. This process is selective to the removal of sulfur present in the organic as well as non-organic form in the feedstock. The high cost of hydrogen remained a major bottleneck in the commercialization of hydrodesulfurization technology for a long time, until the widespread use of hydroreformers.

In commercial practice throughout the world, production of low sulfur concentration fuels as well as refinery feedstocks containing sulfur, of the order of a few parts per million (ppm) from petroleum is practiced by hydrotreatment operations. The similarity between petroleum feedstocks and coal-derived liquids with respect to the chemical composition and physical properties suggest hydrotreatment operations for the production of low sulfur fuels and refinery feedstocks from coal-derived liquids.

Hydrodesulfurization of petroleum feedstocks is practiced commercially in most of the cases in fixed bed operations, trickle bed reactors. Relatively little is known about the hydrodesulfurization of coal-derived liquids. In a trickle bed reactor the nature of the feedstock and the catalyst used together with the process variables such as temperature, pressure, space time and hydrogen to oil feed ratio determines the success of hydrodesulfurization process.

The observed performance of a catalyst and the effect of its physical properties such as surface area, pore volume and pore size distribution are determined by the severity of the hydrotreating conditions as well as the behaviour of the trickle bed reactor. Some of the pertinent literature will be reviewed briefly, first with respect to the trickle bed reactor and then with respect to the process variables. This is done to get a better understanding of the severity of operational conditions while keeping in view the limited knowledge available about the trickle bed reactors for such operations.

Trickle Bed Reactors

In trickle bed reactors, the liquid phase flows down through a fixed catalyst bed while the gaseous phase flows either co-current or counter-current to it. Another type of reactor, sometimes used in the residual oil hydrodesulfurization, is the ebullating bed or fluidized bed reactor, also commonly referred to as slurry-bed reactor. In this, the catalyst is fluidized by the liquid phase while the gas flows co-currently as discrete bubble through the liquid-solid fluidized bed.

Earlier in the research program at Oklahoma State University a decision was made to use the trickle bed reactor design in the hydrodesulfurization of coal-derived liquids. The success of Wan (46), Sooter (43), and Chirakaparambil (5) in using a trickle bed reactor design in their theses work has been encouraging. Hence, for direct comparison of catalyst activity and percent desulfurization with their work, a trickle bed reactor has been chosen for the present study. Moreover, a trickle bed reactor has the following advantages over the slurry-bed reactor in the hydrodesulfurization operations:

1) Residence time distribution patterns close to plug flow.

2) Effect of backmixing leading to higher temperatures and/or lower space velocities is relatively less significant.

3) Possibility of undesirable homogenous side reactions leading to a higher hydrogen consumption at lower space velocities is relatively low.

4) Favorable effect on economics because of less hydrogen consumption and an increase in capacity due to a more nearly plug flow operation.

5) Operational and maintenance simplicity.

In the case of heterocatalytic reactions the effective utilization of the reactor and hence the catalyst is determined to a great extent by the flow pattern and the backmixing effects. These factors are also important in the design of a commercial unit from the results of a laboratory scale unit. In most of the cases the magnitude of nonideality of flow in the commercial unit and the laboratory unit differs widely. This difference can be due to the different magnitudes of channeling, recycling and holdup effects of the fluids in the two units.

Liquid and Gas Distribution

Most of the earlier literature reports studies in packed beds for gas-liquid systems. The hydrodynamics associated with trickle bed reactors resemble, to a certain extent, that in packed bed absorbers.

The distribution of liquid and gaseous phases in packed beds has drawn the attention of many people for a long time.

Schwartz and Smith (41) in their experimental work with air flowing through a bed packed with 0.125 - 0.5 inches (0.32 - 1.27 centimeters) spherical and cylindrical pellets at an average velocity of 0.42 to 3.59 ft/sec observed radial variations in the velocity profile. However, they concluded that the assumption of uniform flow can be made for a tube to particle diameter ratio (D_t/D_p) of more than 30. Schiesser and Lapidus (38) in their residence time distribution studies, with a liquid trickling through a packed bed, reported significant radial variations in flow rate for D_t/D_p as large as 16. Ross (35) studied the residence time distribution in different sized trickle bed reactors with a gas superficial velocity of 188 ft/hr. He varied the liquid superficial velocity from 9.2 to 47.2 ft/hr in a model reactor, 9.7 to 10.5 ft/hr in a pilot plant unit and 27.9 to 68.6 ft/hr in a commercial reactor. The catalyst pellets used were 3/16 inch (0.48 cm) in diameter and 0.188 in. (0.48 cm) in length. He concluded that effective liquid distribution is much more difficult in commercial units.

Satterfield (37) in a recent review on trickle bed reactors reported that in narrow diameter laboratory and pilot plant units liquid migrates to the wall. The liquid flowing down the wall is a function of the flow rate and D_t/D_p ratio. At D_t/D_p ratio as high as 10 the liquid flowing down the wall may be 30-60% of the total liquid.

Liquid holdup is another parameter gaining importance in explaining the behaviour of liquid phase in trickle bed reactors. Lapidus (16) in his residence time distribution studies with co-current air-water and air-hydrocarbon systems in a 2 inch (5.08 cm) diameter bed packed with 0.125 inch (0.48 cm) diameter Co-Mo catalyst pellets reported that at air flow rate of 38 $lb/hr.ft^2$, water flow rate of 1600-3900 $lb/hr.ft^2$ and hydrocarbon (benzene) flow rate of 1550-2060 $lb/hr.ft^2$ the total liquid holdup to be about 30% of the total volume of the bed. He further calculated that approximately 50% of the intraparticle voids were filled with liquids which indicates poor liquid-catalyst contacting. Ross (35) in his studies with pilot-scale and commercial units attributed the poor performance of commercial units to the liquid holdup which was 2/3 of that in a pilot-scale unit. Henry and Gilbert (10) in their hydrogenation studies reported that at constant conditions the increased utilization of catalyst by decreasing the catalyst size can be due to increased liquid holdup. LeNobel and Choufer (17) however, attributed the effect of decreasing catalyst size to pore diffusion limitations.

There exists close agreements as well as contradictions in the literature reviewed above. These contradictions may be mainly due to the differences in objectives in obtaining the data and the relative importance given to the effects of flow maldistribution in interpreting the data.

Axial Dispersion and Mass Transfer Effects

Lapidus (16) in his studies with 0.125 inch (0.48 cm) dia. Co-Mo catalyst pellets reported that plug flow of liquid can be a good approximation in trickle bed reactors. Mears (22) suggested a criteria for predicting flow pattern within 5% of plug flow. He reported that if $h/D_p > (20n/Pe_L)(\ln \frac{C_{in}}{C_{out}})$, where n is the order of the reaction and

Pe_L is the liquid Peclet number (D_pL/D_L), then the assumption of plug flow can be a good approximation.

This criteria requires the calculation of liquid Peclet number and hence the liquid diffusion coefficient. The uncertainty involved in predicting the diffusion coefficient is the major bottleneck in the use of this criteria. However, Mears (22) in his bench-scale hydrotreating work with straight run gas oil at 700°F (371°C), 1500 psig, and LHSV (liquid hourly space velocity) of 2.0 $(\text{hours})^{-1}$ calculated a minimum h/D_p of 350.

Satterfield (37) in his recent review of trickle bed reactors reported that mass transfer through the liquid film seems to have negligible affects in hydrodesulfurization. He concluded that for the effectiveness factors normally encountered in the hydrodesulfurization of petroleum feedstocks, the mass transfer effects can be neglected for catalyst particles bigger than the average liquid film thickness. Van Deemter (45) in the hydrodesulfurization studies with straight run gas oil at 707°F (375°C), 735 psig and WHSV (weight hourly space velocity) of 2.0 $(\text{hours})^{-1}$ calculated an effectiveness factor of 0.99 for 0.0138 inches (0.035 cm) diameter Co-Mo-Alumina catalysts, and an effectiveness factor of 0.36 for 0.197 inches (0.5 cm) diameter catalyst particles. Van Deemter (45) also estimated the average liquid film thickness to be 0.00039 to 0.0039 inches (0.001 to 0.01 cm). Addlington and Thompson (1) in the hydrodesulfurization of gas oils at 780°F (416°C), and 500 psig reported an effectiveness factor of 0.6 for 0.125 inches (0.32 cm) diameter Co-Mo-Alumina catalyst particles. Sooter (43) in his hydrodesulfurization studies with raw anthracene oil estimated an effectiveness factor of about one based on the liquid diffusion coefficient for thiophene in anthracene oil.

The characterization of the feedstock and the product oils in estimating their physical as well as transport properties is mostly empirical. This factor should be considered in the design and evaluation of the performance of the trickle bed reactor.

The other important factors to be considered for the effective utilization of the reactor as well as the catalyst are the process variables such as temperature, pressure, space time and hydrogen to oil feed ratio. These will be considered next.

Temperature and Space Time Effects

The effect of feedstock characteristics should be kept in view while determining the effect of process variables in hydrodesulfurization processes. The main objective of this review is to obtain an idea about the different operational conditions as reported, hence no attempt will be made to draw conclusions regarding these operating conditions.

An excellent review of the hydrodesulfurization technology was given by McKinley (20), and Schuman and Shalit (40). They have reported the temperature range of 500-825^{o}F (260-440^{o}C) for the hydrodesulfurization of petroleum feedstocks. Van Deemter (45) reported hydrodesulfurization of straight run gas oil at 707^{o}F (375^{o}C) in the trickle bed reactor design developed by Shell Oil company. The hydroprocessing of cracked gas oil in the same reactor at temperatures approaching 752^{o}F (400^{o}C) revealed a tendency for increased coke formation.

Residual oils containing a relatively lower hydrogen to carbon ratio with more contaminates than distillate or straight run gas oils are processed at slightly higher temperatures. Galbreath and Driesen (8) reported hydrodesulfurization of residual oils at 700-800^{o}F (371-427^{o}C). McKinney and Stipanovich (21) also reported hydrodesulfurization of residual oils at 800^{o}F (427^{o}C) in ebullated bed reactor. In a recent review Tominaga and Kunugi (44) reported the temperature range for the hydrodesulfurization of residual oils in commercial practice to be 752-806^{o}F (400-430^{o}C).

Most of the work reported for coal-derived liquids is not aimed specifically at hydrodesulfurization, but deals with the broader aspect of hydrogenation. Qader, et al. (33) reported the hydrotreatment of a coal-derived liquid in a fixed bed reactor at 788^{o}F (420^{o}C) with more than 90% desulfurization. Qader and Hill (34) observed hundred percent sulfur removal in the hydrocracking of a low temperature coal tar at 842^{o}F (450^{o}C), 887^{o}F (475^{o}C) and 932^{o}F (500^{o}C) in a batch autoclave reactor. Wan (46) and Sooter (43) in their theses work with raw anthracene oil observed an increase in desulfurization with an increase in temperature in the range 600-800^{o}F (316-427^{o}C) without any operational problems. They also reported an increase in desulfurization with an increase in space time (volume hourly basis) in the range 0.216-1.802 hours. However, the desulfurization increases markedly till one hour beyond which the rate of increase is relatively very slow. Johns, Jones and McMunn (13) in their pilot plant studies with FMC oil observed an increase in sulfur removal with an increase in space time in the range 1.3 to 5 hours (weight basis). In this laboratory unit, Others (31) have reported an increase in desulfurization for FMC oil, feedstock of the present thesis work, with an increase in space time in the range 0.5-3.14 hours (volume hourly basis). However, they reported increased flow resistance at 800°F (427°C) leading to forced shut down of the system. Chirakaparambil (5) in his thesis work in this laboratory unit with FMC oil and another coal-derived liquid, PAMCO composite oil, reported increased cracking tendency in the non-catalytic hydrotreatment operations. Sometimes he observed sulfur concentration in the product oils to be more than in the feedstock itself. He studied the two oils in the temperature range of 700-800°F (371-427°C) and space times of 1.8-3.14 hours (volume hourly basis). The increase in desulfurization with increase in space time seems logical because of the possibility of relatively more efficient liquid-catalyst contacting.

Pressure and Hydrogen Rate Effects

The nature of the feedstock seems to have a more pronounced effect on the choice of operating pressure than on the temperature in hydrodesulfurization operations. McKinley (20) in his review reported hydrogen pressures of 315-765 psig for the hydrodesulfurization of straight run gas oil and catalytic cycle oil in trickle bed reactors. Van Deemter (45) reported hydrodesulfurization of straight run gas oil at 735 psig in the first commercial unit employing a trickle bed reactor.

Residual oils contain relatively more asphaltenes, resins and organometallic compounds than the distillate or the straight run gas oil. These are hydrodesulfurized at relatively higher pressures.

McKinley and Stipanovich (21) reported pressures of the order of 800-3000 psig in the hydrodesulfurization of residual oils.

Wan (46) in his thesis work with raw anthracene oil observed no significant increase in desulfurization by increasing the pressure from 1000 to 2000 psig. Sooter (43) with the same feedstock confirmed that the effect of pressure beyond 1000 psig is less significant, however, desulfurization increases markedly with pressure below 1000 psig. Others (31) in this laboratory unit reported increased desulfurization for FMC oil with an increase in pressure in the range 500-1500 psig.

Scotti, et al. (42) in their pilot plant studies with a coal-derived liquid from the COED process reported hydrogenation at 1800-2400 psig with more than 96% sulfur removal. They observed no significant effect on desulfurization by changing the hydrogen purity from 97 to 80%.

Hydrogen partial pressure has been found to have a pronounced effect on desulfurization. Hydrogen is supplied in far excess amount than required for stoichiometric sulfur removal. This is done mainly to keep a high hydrogen partial pressure. Hoog (12) reported only a slight effect of hydrogen to oil feed ratio in the range of 250-1500 standard cubic feet/barrel (scf/bbl) for petroleum feedstocks. Wan (46) in his studies with raw anthracene oil at 800°F (427°C), 1000 psig and 0.901 hours space time observed no significant effect in the range 3980-39800 scf H_2/bbl oil. He also studied the effect at 700°F (371°F), 2000 psig and 0.901 hours and concluded insignificant effect of H_2 to oil ratio in the range 3980 to 39800 scf/bbl. Sooter (43) varied the ratio from 1500 to 20,000 scf H_2/bbl oil at 1000 psig, 650°F (343°C) and 1.5 hours space time and observed no significant effect of increasing the ratio beyond 1500.

The hydrogen requirement is closely related to the selectivity of the catalysts. Hence some of the pertinent literature will be reviewed next with respect to the catalysts.

Catalysts

The catalysts used for hydrodesulfurizing liquid feedstocks have been developed mostly for processing petroleum feedstocks. In the patent literature catalysts are sometimes referred to as those metals which belong to group VI and/or group VII of the periodic table. McKinley (20) in his review on hydrodesulfurization reported the use of vanadium, iron, chromium, cobalt, nickel, molybdenum, tungsten and platinum. These metals have been reported to be used either alone or in combinations. The most frequently used supported or unsupported combinations are Co-Mo, Ni-Mo, Ni-Co-Mo and Ni-W. The gamma alumina supported Co-Mo catalyst has been recognized by many as the most active and selective catalyst for hydrodesulfurization.

The supported catalysts have been observed to be more active and selective than the unsupported catalysts.

Catalyst Carriers

The present commercial practice is to use high surface area refractory materials such as alumina and silica as catalyst supports. The most commonly used supports are gamma alumina and gamma alumina stabilized with minor amount of silica. Among these two supports gamma alumina has been found to be more selective towards hydrodesulfurization. The silica stabilized support has been observed to have a relatively more hydrocracking activity than the gamma alumina support alone. Nahin and Huffman (25) reported the use of a synthetic gamma alumina support stabilized with approximately five percent silica. This support was observed to be more heat stable. The gamma alumina support in Co-Mo catalyst was observed to transform itself into alpha alumina form at temperatures as high as 925-950^{o}C (1697 to 1742^{o}F), resulting in the loss of activity. This loss in activity can be due to the crystal growth and hence loss in surface area. Grim and Berg (9) in their studies on hydrodesulfurization catalyst support materials reported that, supports having average pore diameter equal to or greater than 55 Å can contain silica even as a major component. They had varied the silica content from 0.24-74.7% in the Co-Mo-Alumina catalyst. They observed that at lower space time molecular sieves having an average pore diameter of 7-9 Å gave relatively less sulfur removal than the gamma alumina catalyst having an average pore diameter of 55-180 Å.

Thus catalysts with gamma alumina as support material have been observed to be more selective for the hydrodesulfurization of petroleum feedstocks.

Metals and Metallic Compositions Used in the Catalysts

Cobalt, nickel, molybdenum and tungsten are the most commonly used metals in the hydrodesulfurization catalysts. Cobalt and nickel act as promoters and molybdenum and tungsten act as precursors in these catalysts. These metals are present in the form of oxides in freshly prepared catalysts. These oxides in the presence of sulfur compounds are reduced to sulfides and the hydrodesulfurizing activity is attributed by many to these sulfides. Mitchell and Trifiro (23) in their studies on the effect of sulfiding on the structure of Co-Mo-Alumina catalysts have found the atomic ratios of Co, Mo and S to be 1:1.77:4.18 respectively in an industrially sulfided catalyst. They concluded that the sulfur content was less than that required for complete sulfiding, about 4.43 atoms sulfur per atom of cobalt.

The preferred industrial catalysts contain 2-4% Co as CoO and 8-15% Mo as MoO_3. Beuther, Flinn and McKinley (2) reported that commercial preparations consist of cobalt and molybdenum in atomic ratios of 0.1 : 1.0 to 1.0 : 1.0 and the maximum activity was observed for ratios around 0.3 : 1.0. In the case of Ni-Mo catalysts they observed maximum activity for an atomic ratio of about 0.6 : 1.0. The addition of cobalt or nickel to catalysts containing Co and Mo in atomic ratios of 0.2 : 1.0 to 0.5 : 1.0 was observed to affect insignificantly the activity of the catalyst. However for ratios less than 0.2 : 1.0, the addition of Ni to give an atomic ratio of 0.5 Ni : 1.0 Mo was observed to increase the activity of the catalyst significantly. Kawa, et al. (14) reported that in Co-Mo-Alumina catalysts, increasing the concentration of Mo beyond 14% had no significant effect in increasing the activity of the catalyst. They suggested that for concentrations more than 14%, the carrier surface can be assumed to be completely covered with a monolayer of MoS_2 and there exists a possibility of loss in catalyst activity.

The support properties also affect the activity of the catalyst to a great extent.

Catalyst Support Properties

Grim and Berg (9) reported that the properties of catalyst support have a more pronounced effect on the hydrodesulfurization activity than the amount of metal supported. In pre-pilot plant studies on hydrocracking (27) with supported catalysts, the support properties were observed to have a more pronounced effect on the initial high activity than the metallic compositions studied. The catalysts studied were Ni-Co-Mo (1.99 to 7.44 weight % Ni, 0.4-0.5 wt% Co and 7.8-10.93 wt% Mo), Ni-Mo (5.7 wt% Ni and 6.2-6.3 wt% Mo) and Co-Mo (2.3-2.6 wt% Co and 5.1-8.7 wt% Mo). In these catalysts the pore volume varied from 0.517-0.974 cc/gm, surface area from 200-300 M^2/gm and average pore size from 63 to 166 Å.

Beuther, Flinn and McKinley (2) reported that, as the porosity and hence the pore volume increases the amount of metal required increases. However, an increase in pore volume increased the activity to a certain extend beyond which it decreased. They observed that a catalyst having a pore volume of 0.45 cc/gm to be more active than that having a pore volume of 0.82 cc/gm.

Likins and Crynes (19) based on their review of the patent literature suggested a rather broad uniform pore size distribution within 50-250 Å, with some over 500 Å. Grim and Berg (9) observed that for supports having irregular pore size distribution the hydrodesulfurization increases with an increase in pore size.

In the research work at Oklahoma State University by Wan (46) and Sooter (43), four Co-Mo-Alumina catalysts were studied for hydrodesulfurizing raw anthracene oil. These catalysts had the same metallic composition but different support properties. They observed that at 1000 psig, 650°F (343°F) and liquid volume hourly space time of 0.3-1.5 hours, a decrease in the most frequent pore size from 33 to 25 Å resulted in slightly decreased hydrodesulfurization activity of the catalyst. Others (31) in this laboratory unit observed that for FMC oil, a catalyst having the most frequent pore radius of 33 Å to be better than a catalyst with 25 Å as the most frequent pore size.

Catalyst Deactivation

In the hydrodesulfurization of liquid feedstocks, carbonaceous and metallic depositions are the two main causes for the catalyst deactivation. Van Deemter (45) observed that the hydrodesulfurization activity of the catalyst decreases rapidly after processing 1.5×10^7 kg of gas oil. Schuit and Gates (39) in their review summarized from various sources that the deposition of solids in fixed-bed voids presents a major engineering problem. The depositions of organometallic compounds have a more severe effect on the catalyst activity than the carbonaceous deposits. These deposits block the pores of the catalyst, hence reduce the effective surface area, resulting in decreased activity.

Sooter (43) in his hydrodesulfurization studies with raw anthracene oil observed no appreciable loss in catalyst activity. The maximum period of operation in his studies was 200 hours. In studies with FMC oil and PAMCO composite oil, Others (31) observed significant loss in catalyst activity.

Literature Summary

The literature reviewed above can be summarized as follows:

1) There exists liquid distribution problems in narrow-bed reactors as well as large diameter commercial units. The tube diameter to particle diameter ratio (D_t/D_p) should be chosen as large as possible to obtain a good flow pattern, while not alleviating the negative effect of pressure drop on the processing conditions.

2) The liquid flow pattern can be approximated by plug flow. The mass transfer effects in the liquid phase can be considered to be negligible, except for low effectiveness factors. The decrease in catalyst size and/or increase in liquid velocity results in an increased holdup and hence more effective liquid-solid contact.

3) The processing conditions and the extent of desulfurization achieved depends to a great extent on the feedstock and the catalyst used.

4) The temperatures encountered in the hydrodesulfurization of all kinds of feedstocks (petroleum as well as coal-derived liquids) were in the range of 500-825^{o}F (260-441^{o}C). At higher temperatures increased cracking tendency was reported.

5) The choice of operating pressure is markedly effected by the nature of the feedstock. The operating pressure for distillate feedstocks were reported to be about 1000 psig, where as for residual oils 800-3000 psig were reported. In the case of raw anthracene oil pressure was observed to have a marked influence till 1000 psig, beyond which the effect of an increase in pressure was less significant.

6) Higher space times can result in increased liquid holdup and hence increased desulfurization due to more effective liquid-solid contacting.

7) An increase in hydrogen to oil feed ratio beyond 1500 scf/bbl was observed to have less significant effect on sulfur removal from petroleum as well as coal-derived liquid feedstocks. In one case, in which hydrogenation was the main objective, a decrease in hydrogen purity from 97-80% had no significant effect on percent sulfur removal from a coal-derived liquid.

8) Co-Mo-Alumina is the most favored catalyst for hydrodesulfurizing petroleum feedstocks. The pore size distribution seems to have a marked influence on the catalyst activity for hydrodesulfurizing petroleum feedstocks. Very little is known about the hydrodesulfurization of coal-derived liquids. Catalysts containing both micro and macro pores can exhibit better activity for the hydrodesulfurization of coal-derived liquids. This can be due to the more complex nature of coal-derived liquids than the petroleum feedstocks.

9) Carbonaceous and metallic depositions can block the pores of the catalyst, resulting in decreased catalyst activity. These can also deposit in the catalyst bed voids resulting in an increased resistance to flow and hence leading to a forced shut down of the system.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental system using a trickle flow reactor was designed to fulfill the following requirements:

1) Hydroprocessing coal-derived liquid feedstocks. These can be very viscous at room temperature.

2) Oil and hydrogen should be on stream on a 24 hour basis with minimum interruptions.

3) Reactor should be capable of isothermal operation at temperatures up to +850°F (454°C). Large amounts of cracking and coke deposition on the catalyst can occur beyond this temperature.

4) Reactor heating system should be capable of providing a "flat" temperature profile in the reaction zone (catalyst bed).

5) System should be capable of operation at constant pressures up to 1800 psig. This is the maximum safe limit for most of the bombs and tubings available on the apparatus.

6) Preheating of the feedstock to moderate temepratures, 200 to 300°F (93-149°C), and feeding it to the reactor at a constant pressure up to 1800 psig should be possible.

7) No voids for undesirable liquid accumulation should be present in the system.

8) Sampling should be possible without disturbing the normal operation.

9) Reactor and other parts of the system should be easily replaceable.

10) Pressure, temperature and flow control should be automatic to the maximum possible extent.

11) Rupture release lines and a combustible gas detector should be installed and adequate safety precautions taken.

The experimental system used in this study is shown in Figure 3. The experimental system components are numbered as shown in Figure 4. As shown in Figures 3 and 4, hydrogen enters at the top of the reactor through valve v-2, and flows down through the packed bed. The coal-derived liquid preheated to 250 ± 10°F (121 ± 6°C) joins the hydrogen at the top of the reactor before entering the catalyst zone and flows concurrent with it. The gases and liquids are separated in the sample bombs 24 and 25. The gases leave the system through the exit valves v-6 and v-14. The lower sample bomb can be isolated from the rest of the system by closing valves v-3 and v-4. The gases present in the sample bomb 25 can be released through the valves v-5 and v-13 to depressurize the bomb. The liquids present can now be purged with an inert gas, entering through valves v-8 and v-7 and escaping through the valves v-5 and v-13. The liquid sample is collected at room conditions through valves v-7 and v-9 without disturbing the normal operation. The system (Reactor) pressure is monitered on a Heise gauge, 27. An iron-constantan thermocouple is used for the reactor temperature response which is read on a digital readout.

A detailed description of the numbered experimental system is given below. A complete listing of the equipment items with relevant information is given in Table III.

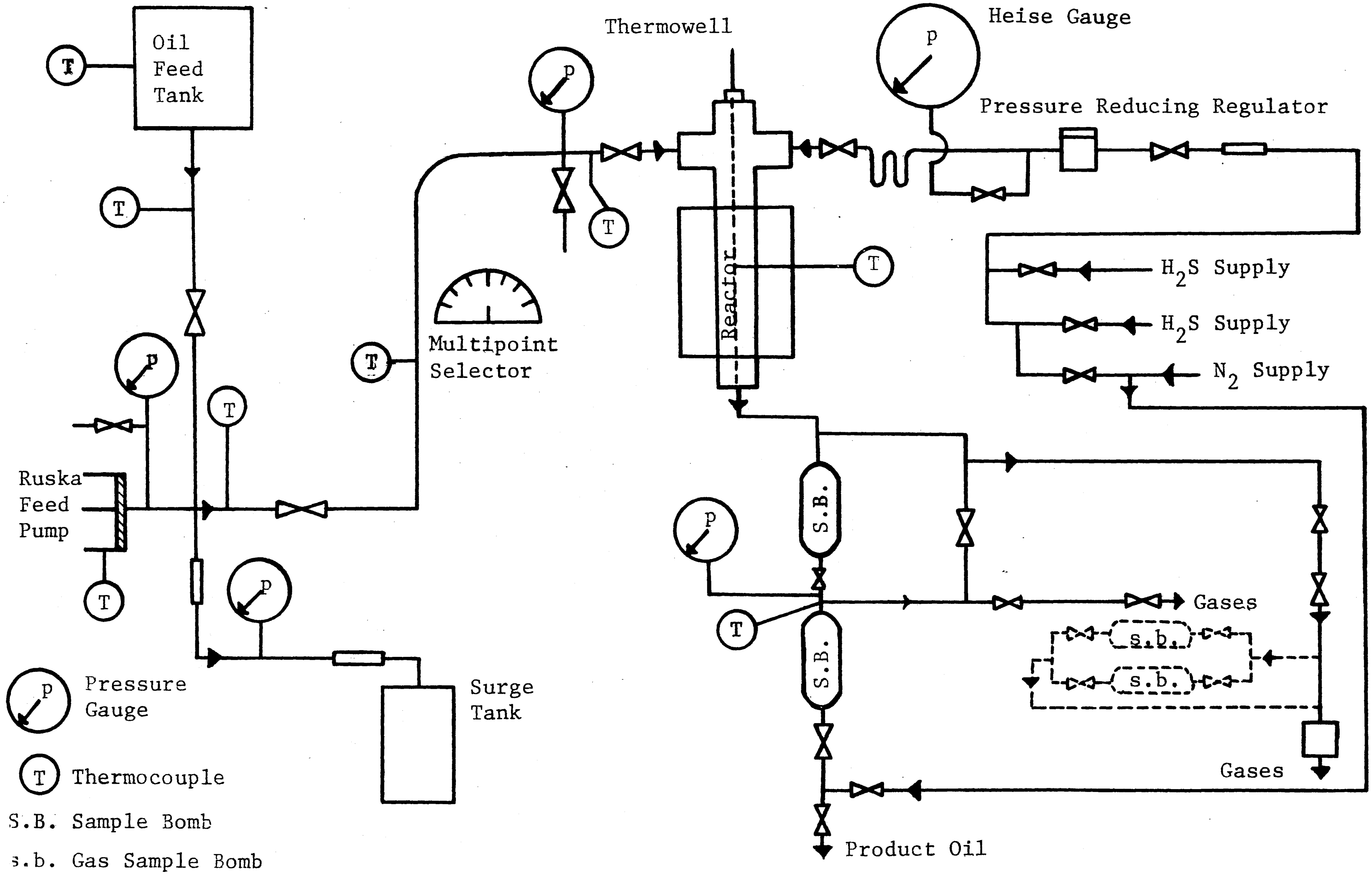

Figure 3. Experimental System

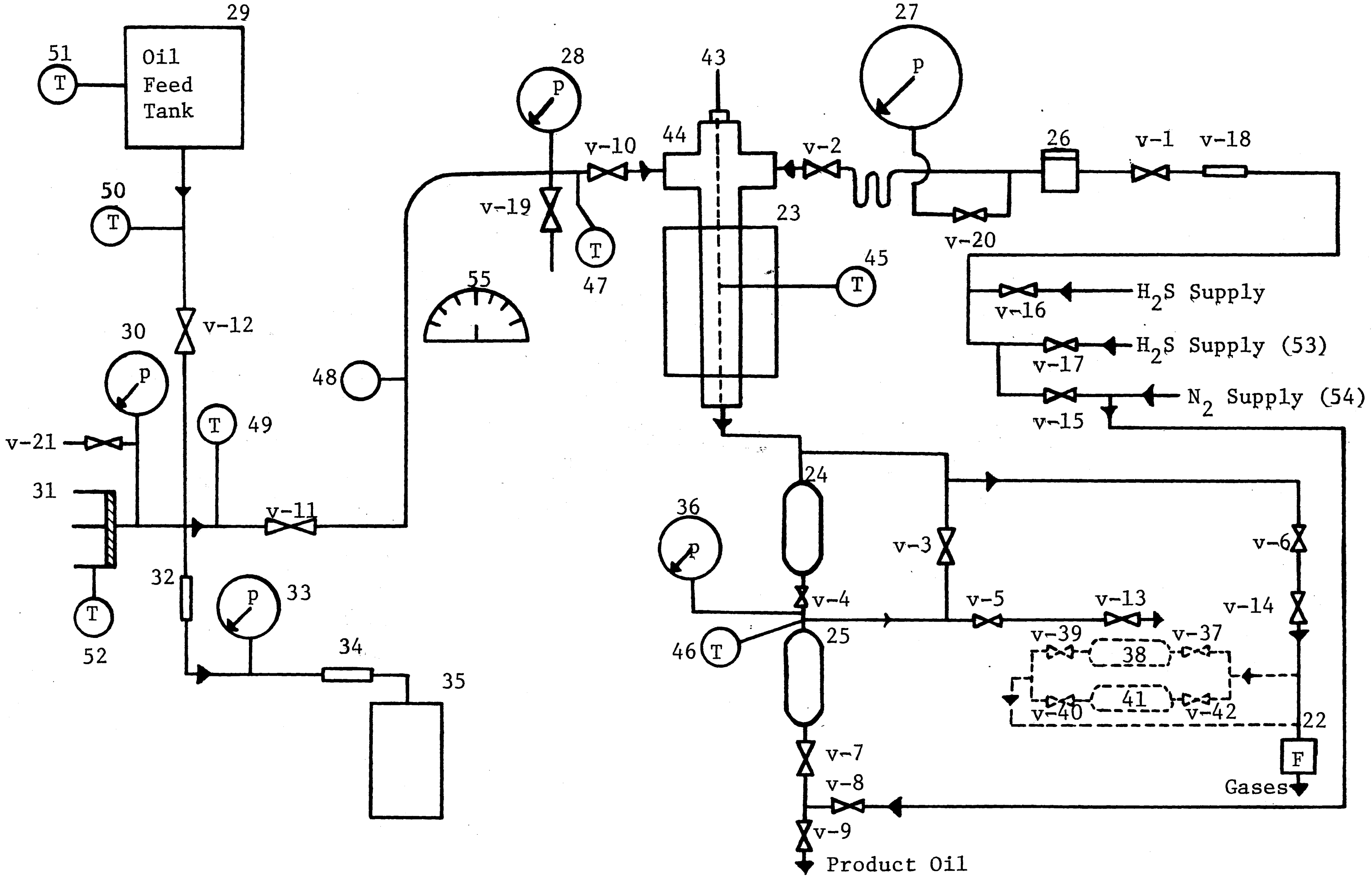

Figure 4. Numbered Experimental System

TABLE III

LIST OF EXPERIMENTAL EQUIPMENT ITEMS

Tubing	1/8-inch o.d., 316 stainless steel for carrying gas
Tubing	1/4-inch o.d., 316 stainless steel for carrying gas and liquid
Reactor, 23	1/2-inch o.d., 0.049 inch thickness, 316 stainless steel tubing
Thermowell, 44	1/8-inch o.d., 316 stainless steel tubing
Beaded heaters	115 volt, 1500 watts, 33 ft length, max. 2000^{o}F Marsh beaded heaters
Temperature controllers	Hewlett-Packard temperature programmer, 0-1832^{o}F Model 240M-25
Powerstats	Input 120 volts, output 0-140 volts, 10 amperes and 1.4 KVA, Superior electric type 116
Insulation material	Fiber glass, McMaster-Carr
Temperature indicator	Doric Scientific DS-300-T3, temperature range 0-1595^{o}F
Thermocouple, 45	Iron-constantan, 0.04 inch o.d., 304 stainless steel sheath, grounded sensor tip, 1/2-inch, Conax
Thermocouples, 46, 47,48,49,50,51 and 52	Iron-constantan, 0.04 inch o.d., 304 stainless steel sheath, bare sensor tip, 1/2-inch, Conax
Pressure gauge, 27	Heise-Bourdon tube gauge, max. 3000 psig
Pressure gauge, 28, 30,33 and 36	Crosby pressure gauge, max. 3000 psig
Sample bombs, 24 and 25	2300 cc, 1800 psig maximum, 304 stainless steel, Matheson Model #6-645-2320
Feed tank, 29	8.5 inch o.d., 7.5 inches height, stainless steel tank
Pump, 31	Ruska positive displacement pump, 500 cc barrel capacity, feed rates 2-240 cc/hr, 4000 psig max, Model #2242 BI

TABLE III (Continued)

Surge tank, 35	Five gallon can
Mity-Mite pressure regulator, 26	Model 94 (internally loaded), inlet pressure 5000 psi, outlet pressure 3000 psi maximum, operating temperature 0-165°F, 1/4-inch inlet and outlet connections
Back pressure regulators	Model #138416-1, Groove regulator company, 100-3000 psig at 200°F
Rupture disks, 32 and 34	1/4-inch, bursting pressure 1800 and 3000 psig at 72°F, Frangible Discs, Inc.
Heating tape	Briskeat flexible heating for lab use, 115 volts, 576 watts, one inch wide and 72 inches long
Gas sample bombs, 38 and 41	Stainless steel, 350 ml, Matheson
Powerstat fuses	8 amp, 125 volts, Little Fuse
Silver Goop	For temperatures up to 1500°F, Cramford Fitting Company
Valves, 1, 13 and 14	1/4-inch, 316 stainless steel micro metering valves, 3000 psi max., Whitey Model #22S4
Valves, 2,3,4,5, 7,15 and 16	1/4-inch, gate valves, 316 stainless steel, 3000 psi max., Whitey Model #IRS4
Valves, 6,8,9 and 21	1/4-inch gate valves, 316 stainless steel, Autoclave Engineers Model #6V-71U8
Valves, 10,11 and 19	1/4-inch gate valves, 316 stainless steel, Whitey Model #6VS4
Valve, 12	1/4-inch gate valve, 316 stainless steel, extended stem type, Autoclave Engineers Model #6V-71U8
Valve, 17	Quarter-turn valve, Whitey 43S4
Valve, 20	1/8-inch, needle valve, 11000 psi maximum, Autoclave Engineers Model #10V-2001
Glass Bottles (For liquid samples)	Matheson, Cat. #4321-20
Bottle Caps	Matheson, Cat. #4747-24

Reactor

The reactor is made up of half inch O.D. 316 stainless steel tubing, 24 inch long and fitted with half inch swagelok cross and union to the top and bottom of the reactor respectively. The half-inch to one-fourth inch reducing unions are used to connect the reactor to other parts of the system as shown in Figure 5.

A thermowell made up of 1/8 inch O.D. 316 stainless steel tubing with one end welded shut is secured at the top of the reactor by swagelok fittings. The closed end is at the bottom of the reactor and the 1/4 inch to 1/8 inch reducing union has to be drilled for easy sliding of the thermowell tubing.

The catalyst or inert material is held in place by wedging 50 mesh screens between the fittings and the top and bottom ends of the reactor.

An iron-constantan thermocouple with grounded tip sensor is used for measuring the temperature in the reactor. This thermocouple can be traversed up and down the well to obtain an entire temperature profile.

Reactor Heating System

Three specially designed, solid aluminum blocks with 1/2-inch diameter hole in the center for the reactor and grooved with 3/8-inch wide and 5/8-inch deep slots for beaded heaters are used to maintain the desired temperature profile. The blocks are of different lengths as shown in Figure 6. This is done to provide better heat distribution and temperature control. The blocks are split in the middle and hinged on one side for easy removal of the reactor.

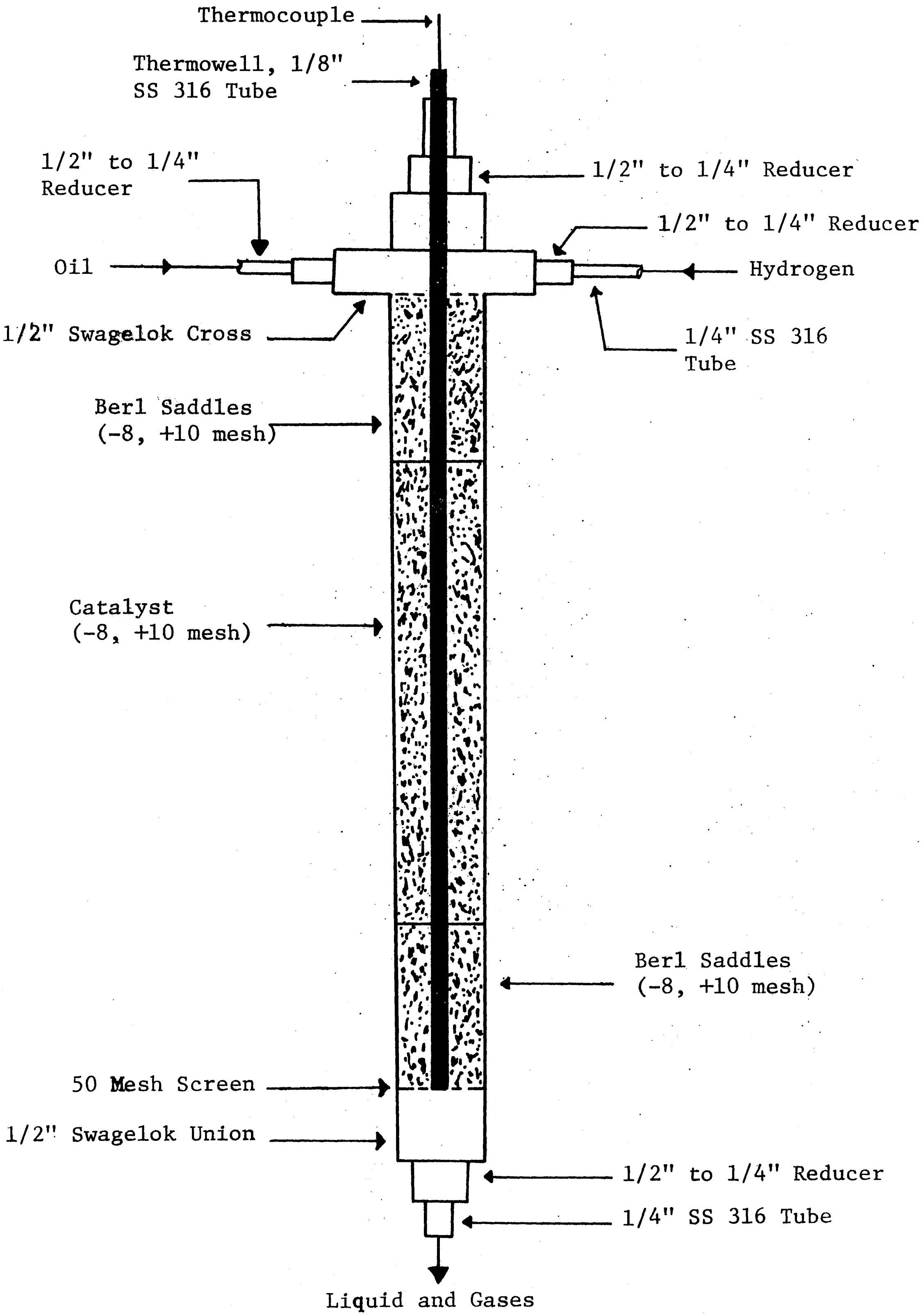

Figure 5. Reactor Configuration

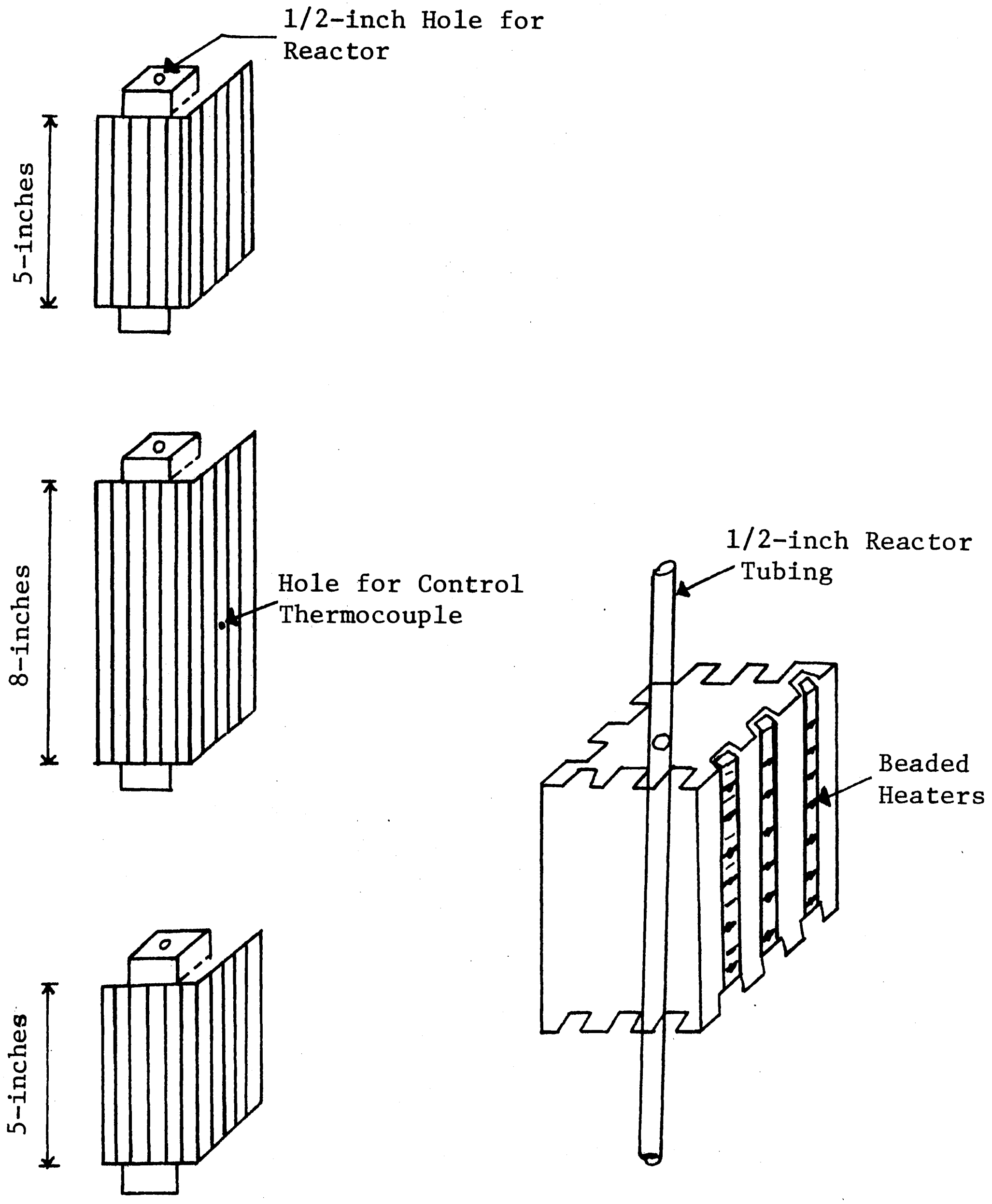

Figure 6. Reactor Heating Blocks

The top and bottom heaters are controlled by powerstats while the middle heater is controlled by a Hewlett-Packard 240 temperature programmer. The control thermocouple for the temperature programmer is placed in a small hole adjacent to the beaded heater. This hole is located about half-way down the middle heating block and is 19/16-inch deep. The top and bottom heaters are mainly used to counter end effect-heat losses. The control with powerstats is obtained by manual adjustment to achieve the desired temperature profile.

Felt fabric and fiber glass are used for making the insulation in the form of a rectangular box which is split in the middle. The entire heating blocks arrangement is surrounded by insulation. The insulation is held in place by metallic strips. Electrical connections for the heaters are made through the break in the insulation while carefully packing the break with fiber glass to avoid unnecessary heat losses.

Temperature Readout

The thermocouples in the oil feed line and the reactor are connected to a multipoint selector 55. This selector is a switching unit having the capability of accepting the outputs of up to nine thermocouples, selecting one of them and feeding the signal into a DS 300-T3, Doric scientific digital temperature readout. As mentioned previously, the reactor temperature is monitered by sliding the thermocouple along the thermowell and reading the response on the DS 300-T3 digital readout.

Pressure and Flow Control

The system pressure characterized by the pressure inside the reactor is monitered on a 0-3000 psig pressure gauge. This pressure gauge is located upstream from the reactor. The pressure control was accomplished with two back pressure regulators installed downstream from the reactor for the first four runs of the present study. However, these two were removed and a Mity-Mite pressure reducing regulator, 26, was installed upstream from the reactor for the remaining two runs. This latter arrangement is that shown in Figures 3 and 4. This change in pressure control was made to avoid the possible plugging of the downstream back pressure regulators. This plugging can affect the pressure control and may also lead to forced shut down of the system. The pressure upstream from the Mity-Mite is controlled by Matheson Model-8 pressure regulators connected to the hydrogen supply cylinders.

The gaseous flow control is maintained with two valves, v-16 and v-14, downstream from the reactor. The first valve, v-6, is an Autoclave vee tip type valve designed to take a major portion of the pressure drop. The second valve, v-14. is a Whitey needle valve designed for fine control of gas flow. The gas flow is monitered downstream from the control valves on a 0-25 ml bubble flow meter.

Oil and Hydrogen Feed Systems

The oil feed system consisted of a Ruska positive displacement pump, 31, and a stainless steel storage tank, 29. The feed storage tank, oil feed line to the reactor, and the pump cylinder are wrapped with flexible heating tapes and insulated with fiber glass to preheat the oil as it is fed to the reactor. The temperature is controlled manually by means of powerstats connected to the heating tapes. Six thermocouples, 47, 48, 49, 50, 51 and 52 along the oil line are connected to the multipoint selector, 55, for temperature measurement.

The feedstock is fed to the reactor by the Ruska positive displacement pump, 31, at a pre-set rate through its metered pumping device (36). The possible pressure build-up, while pumping liquids with a constant displacement type pump and the consequent damage in case of oil-lines becoming clogged, is avoided by installing rupture disks, 32 and 34. These rupture disks are installed close to the pump exit and a five gallon tank is connected to the system for collecting the break-through oil. A pressure gauge, 33, is connected in between the two rupture disks. The first disk, 32, ruptures at 2400 psi and the pressure is indicated on the pressure gauge, 33. The second disk ruptures at 3000 psi and the break-through oil is collected in the receiving can, 35. The pressure in the oil lines is monitered on three 0-3000 psi bourdon type pressure gauges 28, 30 and 36 as shown in Figure 4.

Hydrogen is fed to the reactor directly from the supply cylinder. A manifold is constructed to allow switching of hydrogen cylinders during the run. An excess flow valve, v-18, is installed upstream from the Mity-Mite pressure reducing regulator, 26, which could shut down the system in case of excess flow. A quarter-turn valve, v-17, is installed upstream to the excess flow valve, v-18, so as to achieve rapid manual cut-off of hydrogen supply to the system in case of emergency.

Sampling System

The sampling system is designed to provide continuous operation during the run with minimum interruptions. This consists of two stainless steel bombs, 24 and 25, each of 300 cc capacity and rated to 1800 psig. The first sample bomb, 24, was connected to the back pressure regulator during the first four runs and then to the reactor for the rest of the runs with a 1/4-inch stainless steel tubing as shown in Figure 7. A 1/2-inch to 1/4-inch swagelok reducer is drilled to allow the 1/4-inch tube to slip through, into the bomb while the seal on the tube is made by a swagelok fitting on the 1/4-inch tube. Vapor and liquid separates within the bomb and the liquid collects at the bottom. The second sample bomb, 25, is placed directly below the first, 24, while providing adequate valves and bypassing to insure smooth operation. A bourdon type pressure gauge, 36, monitors the pressure in the lower bomb. The bombs are wrapped with flexible heating tapes and insulated for easy removal of the liquid sample. A thermocouple, 46, connected to the multipoint selector monitors the temperature in the sampling system. A powerstat is connected to the heating tapes for temperature control.

Gas Detectors

A combustible gas detector, MSA model 501, is installed with two detector heads located over and near the reactor. The alarm is set to go off when the hydrogen concentration in the room reaches 50% of the lower explosive limit.

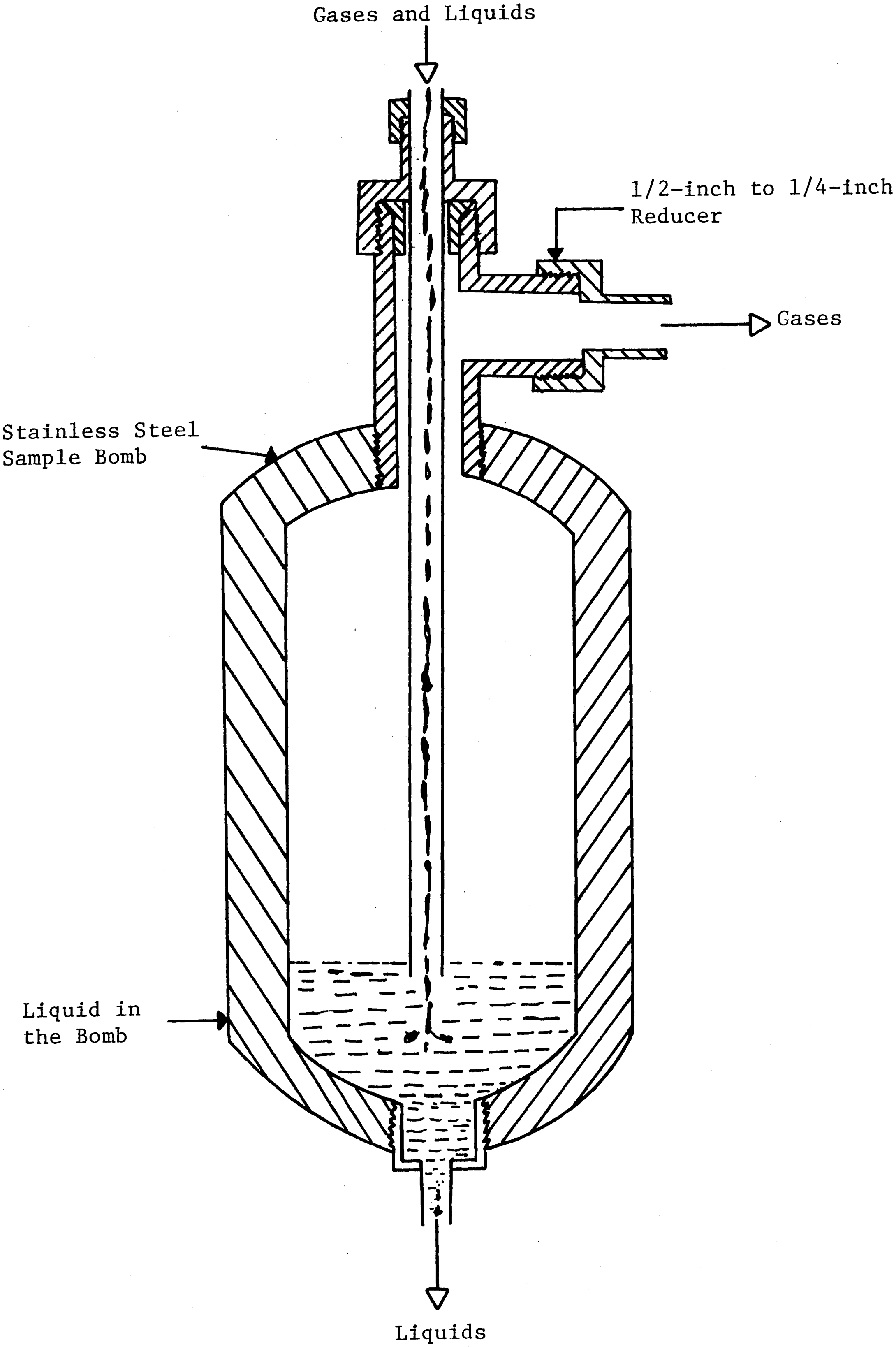

Figure 7. Sample Bomb

Inert Gas Purging Facility

The liquid porduct sample before collection from the second sample bomb is purged with an inert gas, nitrogen. This is done to remove NH_3 and H_2S dissolved in the liquid sample.

Nitrogen is supplied to the second sample bomb, 25, directly from the supply cylinder. Matheson model-8 pressure regulator is used to regulate the pressure at the nitrogen supply cylinder. Nitrogen enters the bomb, 25, through the valves, v-8 and v-7, and escapes to the hood through v-5 and v-13.

The nitrogen feed line to the bomb, 25, and the hydrogen feed line to the reactor are interconnected by a valve, v-15. This valve, v-15, is upstream from the excess flow valve, v-18, in the hydrogen feed line and valve, v-8, in the nitrogen feed line.

Gas Sampling

Gas sampling is not the objective of this study, however, provision has been made for doing so. The analysis of these samples is beyond the scope of the present study.

Two 350 cc stainless steel bombs, 38 and 41, have been connected in parallel, downstream from the control valves, v-6 and v-14. The gas sample can be collected in the bomb, 38, by closing the valves, v-40 and v-42, while keeping the valves, v-37 and v-39 open. After collecting the sample in bomb 38, valves v-37 and v-39 are closed and v-40 and v-42 are opened simultaneously. This time the sample will be collected in the bomb, 41, while bomb 38 is replaced.

Experimental Procedure

The experimental procedure consists of the seven basic steps of catalyst preparation and loading, catalyst activation, startup, normal operation, sampling, shut down, and sample analysis. These are described in detail in the following material.

Catalyst Preparation and Loading

The commercial 1/8-inch (0.32 cm) catalyst pellets are crushed to 8-10 mesh size. This is done to achieve an improved gas and liquid flow pattern as well as good liquid-catalyst contacting. The reactor is packed at both the ends with 8-10 mesh size crushed Berl saddles. The catalyst is packed in the middle of the reactor to minimize end effects. The reactor removed from the system is packed by pouring the material in the bottom and packing it from top down as follows:

1) Fifty mesh size screen is wedged between the top of the reactor and the 1/2 inch Swagelok cross.

2) The thermowell is held centrally in the reactor.

3) The 8-10 mesh size crushed Berl saddles are poured in the bottom of the reactor while tapping it vigorously for uniform packing around the thermowell. For every experimental run, the reactor is packed with fresh Berl saddles (8-10 mesh size) to a height of 5.125 inches (13.02 cm).

4) The 8-10 mesh size catalyst is then poured in the bottom of the reactor following the procedure described above. For every experimental run the reactor is packed with fresh catalyst to a height of 12.75 inches (32.39 cm).

5) Lastly, a fifty mesh screen is wedged between the bottom of the packed reactor tubing and the 1/2 inch Swagelok union.

Silver goop is used on all swagelok threads to facilitate their tightening and loosening and also to prevent seizing.

The packed reactor is then secured in the system by connecting the 1/2-inch swagelok cross at the top to the two feed lines by 1/2-inch to 1/4-inch reducers. The 1/2-inch swagelok union at the bottom of the reactor tubing is connected to the exit line by a 1/2-inch to 1/4-inch reducer. The system is pressure tested before installing the heating blocks. Each fitting and tubing in the entire system is checked for leaks by gradually pressurizing the system at room temperature with nitrogen gas. The system is tested at a maximum pressure of 1600 psig, 100 psi higher than the desired operating pressure. Snoop leak detector solution is used for detecting the leaks. A helium leak detector can be used for detecting stubborn leaks, but for the present study snoop leak detector has been found to be sufficient. The system is kept under pressure for about one hour. In case of any leaks, the system is depressurized and adequate measures taken for their rectification. If the pressure drop in about one hour is less than 10 psi, then the heating blocks are installed.

The beaded heaters in the heating blocks are properly positioned in the grooves. The heaters are connected to the controllers and insulated. A resistance of less than 10 ohms in the heater wires measured with a volt-ohm meter is taken as a sign of no short circuiting. The next step in the experimental procedure is the activation of catalyst.

Catalyst Activation

This consists of two steps, calcination and sulfiding as described below.

Calcination. The system is gradually heated to 800°F (427°C) and the temperature profile recorded every half hour. When the temperature is 800 ± 10°F (427 ± 6°C) in the catalyst zone, nitrogen is allowed to flow through the system at the rate of 3.1 cc/sec. The temperature is maintained at 800°F (427°C) for one hour and then allowed to fall to 450°F (232°C), with nitrogen flowing through the system. The temperature is then stabilized at 450°F (232°C) for 12 hours.

Sulfiding. The nitrogen supply to the system after 12 hours is cut-off, and a mixture of 5.14% H_2S in H_2 is passed through the system at 0-2 psig while maintaining the temperature at 450°F (232°C). Before sulfiding the Heise gauge is disconnected from the system by closing the valve, v-20. The H_2S-H_2 mixture is allowed to flow through the catalyst bed for 90 minutes at the rate of 3.1 cc/sec. The system is then flushed with pure hydrogen at 250 psig for about ten minutes, at a low flow rate of about 2 cc/sec. The temperature during flushing is maintained at 450°F (232°C).

During the catalyst activation all the gases flow through the valves, v-1 and v-2, into the reactor and through valves v-6 and v-14 to the hood. A summary of the valve positioning during the activation of catalyst is as given in Table IV.

Nalco Chemical Company (26) supplier of the catalysts has suggested catalyst presulfiding and calcination for obtaining better HDS activity. Brewer and Cheavens (4) and Kawa, et al. (14) also observed improved HDS activity on calcining and presulfiding the catalyst.

TABLE IV

SUMMARY OF VALVES POSITIONING DURING THE CATALYST ACTIVATION

Valve	Calcination Position	Sulfiding Position*
v-1	open	open
v-2	open	open
v-3	closed	closed
v-4	closed	closed
v-5	closed	closed
v-6	open	open
v-14	open	open
v-15	open	closed
v-16	closed	open
v-20	open	closed

* All valves, unless otherwise stated are kept closed.

Start Up Procedure

The Heise gauge is reconnected to the system and the reactor heated gradually with no gases flowing through it. The oil lines are heated to 250°F (121°C). The pump is filled with the coal-derived liquid following the procedure described later along with the sampling procedure. When the temperature inside the reactor is within 10°F (5.6°C) of the desired value, the system is pressurized with hydrogen to the experimental pressure, 1500 psig. The hydrogen flow rate is adjusted and the coal-derived liquid is then fed at 1500 psig, into the reactor at a pre-set rate. The maximum time lag between the hydrogen and oil flow into the reactor is not more than five minutes. The temperature is then stabilized at the desired value.

Normal Operation

The system is considered to be at normal operating conditions when the temperature and pressure have stabilized. A maximum deviation of $\pm$ 3^{o}F (1.7^{o}C) in the temperature and a maximum deviation of $\pm$ 20 psi in pressure is acceptable during normal operation. The temperature and pressure stabilized within one to two hours from the time both oil and hydrogen are on stream.

The temperature profile, pressure gauge reading, pump scale reading, temperature controller's setting and the flow rate of the gaseous products leaving the system are recorded every hour. The temperature profile is recorded every inch from above to below the catalyst zone.

Hydrogen is allowed to enter the reactor through valves v-1 and v-2 and flow down through the packed bed. Oil entering through valves v-11 and v-10 flows concurrent with hydrogen. The unreacted hydrogen and oil, together with the gaseous and liquid products flow down into the first sample bomb, 24. Here the gases and liquids are separated and the liquid flows down into the second sample bomb, 25, through the valve, v-4. The gases present in the bomb, 25, escape through the valve, v-3, and join the gases coming out of the first sample bomb, 24. These gases after flowing out through the control valves v-6 and v-14 are metered with a 0-25 cc bubble flow meter and then allowed to escape to the hood.

In some positions two valves back-to-back are used to ensure continuous operation in case of failure of any one of the valves. A summary of the valves position during the normal operation is as given in Table V.

TABLE V

VALVES POSITION SUMMARY DURING NORMAL OPERATION

Valve	Position	Valve	Position
v-1	open	v-12	closed
v-2	open	v-13	closed
v-3	open	v-14	open
v-4	open	v-15	closed
v-5	partially open	v-16	closed
v-6	open	v-17	open
v-7	closed	v-18	open
v-8	closed	v-19	closed
v-9	closed	v-20	open
v-10	closed	v-21	closed
v-11	open		

Sampling Procedure

The main objective is to collect a sample without disturbing the normal operation. The second sample bomb, 25, is isolated from the system by closing the valves, v-3 and v-4, and then depressurized by releasing the gases through the valve, v-13, to the hood. When the pressure in the bomb is completely released (pressure gauge, 36, reading zero), the liquid in the bomb is purged with nitrogen at 200 psig for 30 minute. This is done to strip-off the NH_3 and H_2S present in the liquid.

Nitrogen enters into the bomb, 25, through the valves, v-8 and v-7, and escapes to the hood along with the stripped gases to the hood through v-5 and v-13. After 30 minutes of purging, nitrogen supply to the bomb, 25, is cut-off and the bomb completely depressurized. The liquid sample is then collected in glass bottles by opening valves v-7 and v-9. After collecting the sample, valves v-7, v-9 and v-13 are closed.

The bomb is then repressurized to 1500 psig. Repressurization takes a short time, about 30 - 50 seconds. This can be done by supplying nitrogen to the bomb, 25. In case nitrogen at such high pressure is not available, hydrogen from the main supply can be used. This can be done by closing the valve, v-2, to cut-off the H_2 supply to the system and then opening valves v-15, v-8 and v-7. Immediately after repressurization, valves v-7, v-8 and v-15 are closed and v-2 opened to resume normal supply of hydrogen to the system. The bomb, 25, is reconnected to the system by opening valves v-3 and v-4, so that liquid products collected in the first bomb, 24, can drain into the lower bomb, 25.

The needed refilling of pump is planned at the time of collecting a sample. The oil storage tank is heated five to six hours prior to the refilling. The valve, v-10, is closed and the oil line depressurized completely by operating the pump manually in the reverse. The oil from the storage tank is then drawn into the pump's barrel by opening valve v-12, and operating the pump manually in the reverse. This refilling operation takes about 15-30 minutes. After refilling, valve v-12 is closed, oil line repressurized to 1500 psig and valve v-10 opened for oil to be on stream.

The capacity of the pump barrel is 500 cc. Liquid samples are collected every five or ten hours and the pump is to be refilled every 55 or 60 hours. A summary of the valve position during this step is as given in Table VI.

Shut Down Procedure

First hydrogen supply from the supply cylinder is cut-off and valve v-10 in the oil line is closed after switching off the pump. The system is then depressurized and purged with nitrogen at 250 psig for 30 minutes. The oil line is meanwhile depressurized. After purging with N_2, the liquid sample is collected and the heaters turned off.

The reactor is allowed to cool down to room temperature. The insulation is removed, heating blocks are taken out and the reactor disconnected from the system. The swagelok fittings are properly capped and the inerts and catalysts are removed from the reactor for further testing.

The used catalyst is heated in a muffle furnace at 500 to 600°C (932-1112°F), until no further loss in weight of the catalyst was observed on repeated heating.

Sample Analysis for Sulfur Concentration

The sulfur content of the feed and the product oil are determined by means of a Leco automatic sulfur analyzer. The Leco Bulletin (18)

TABLE VI

SUMMARY OF THE VALVE POSITIONS DURING SAMPLING OPERATION*

Valve	Position	Valve	Position
A) Purging with nitrogen:			
v-2	open	v-3	closed
v-4	closed	v-5	open
v-7	open	v-8	open
v-9	closed	v-13	open
v-15	closed		
B) Liquid sample collection:			
v-2	open	v-3	closed
v-4	closed	v-5	open
v-7	open	v-8	closed
v-9	open	v-13	open
v-15	closed		
C) Repressurizing the sample bomb, 25:			
v-2	closed	v-3	closed
v-4	closed	v-5	closed
v-7	open	v-8	open
v-9	closed	v-13	closed
v-15	open		
D) Pump, 31, refilling:			
v-10	closed	v-11	closed
v-12	open		

* Position of all valves unless otherwise stated above is as given in Table V.

describes the general procedure for analysis with this equipment. The procedure followed is that described by Wan (46), Sooter (43), and Chirakaparambil (5) in their theses.

The sulfur present in the sample is oxidized to SO_2 in the presence of an induction field in a combustion furnace. The SO_2 is then titrated with standard KIO_3 solution in an acidic solution containing iodide with starch as indicator. The phototube circuit operates a relay controlling the buret. The sulfur dioxide decolorizes the solution resulting in the addition of KIO_3 solution from the buret. The restoration of blue color results in closing of the buret control valve. The final end point is indicated when no more titrant (KIO_3 solution) is added.

The complete analytical system consists of a Model 521-500 induction furnace, Model 532-000 automatic titrator and an oxygen purifying train. The basic concept is based on the ASTM Combustion method E3065 (18), which specifies the titration of SO_2 obtained from the combustion of liquid feedstocks (petroleum) with KIO_3 solution.

The following solutions are required for analysis:

1) Starch solution - Two grams of arrow root starch is added to 50 cc of distilled water. This mixture is then added to 150 cc of boiling distilled water. The mixture is allowed to boil for one to two minutes and then allowed to cool down gradually to room temperature. Six grams of KI is added to the starch solution at room temperature and the solution stirred vigorously to dissolve all the KI. This solution is to be prepared daily and used fresh.

2) HCl solution - This solution is prepared by diluting 15 cc of concentrated HCl solution with distilled water to one liter and can be kept for a period of one month.

3) Potassium iodate solution - This solution is prepared by dissolving 0.444 grams of KIO_3 to prepare a one-liter solution in distilled water. The concentration of this solution can be varied to achieve the desired buret range. This solution can be kept for a period of one month.

4) Analytical procedure - The combustion tube, photocell, titrant vessel and the necessary apparatus are cleaned with distilled water and dried. The photocell alignment is then carried out. A resistance of 30,000-50,000 ohms measured with a volt-ohm meter across the photocell is considered acceptable for analysis.

The Leco induction furnace and the titrator are turned on and allowed to warm up for 30 minutes. The titrant receiver is filled with HCl solution to a pre-marked level. This level is maintained constant through out the analysis. This is done to use the same amount of HCl solution for each analysis. If the amount of HCl used varies, then the furnace factor described later also varies. After 30 minutes of warm-up period, oxygen is allowed to bubble through the HCl solution in the titrant receiver for 15 minutes. The trace heating wire wrapped around the glass tube connecting the induction furnace and the titrator is also turned on. The oxygen flow rate is adjusted to 1.2 liters per minute.

The sample to be analyzed is prepared following the order described below:

a) Add 0.282 ± 0.005 gm of MgO to a crucible supplied by Leco Corp.

b) Add 0.1 ± 0.005 gm of sample oil on the MgO layer, in the center of the crucible.

c) Add 0.282 ± 0.005 gm of MgO to cover the oil in the crucible.

d) Add 1.5 ± 0.005 gm of iron chips on the top of MgO layer.

e) Add 0.77 ± 0.005 gm of tin accelerator on top of the iron chips.

The crucible is then covered with a porous lid supplied by Leco Corporation. The sample is now considered to be ready for combustion.

5) End point determination - The bell shaped titration receiver is filled with HCl solution to the pre-marked level and 2 cc of starch solution is added to it. Oxygen is allowed to bubble through this mixture at the rate of 1.2 liters/min. The end point control switch is set at the extreme left position and the titrator double throw switch is turned on the "end point" position. The end point control knob is slowly turned clockwise till the addition of KIO_3 solution results in medium blue color. The end point control knob is set at this position and is not disturbed until the necessity to do so arrives. This blue color serves as the reference for the phototube relay circuit controlling the buret control valve.

6) Blank determination - The blank values are determined at the beginning and end of the analysis, with some in between. For this, the steps in the sample preparation, except the addition of the sample oil, are followed strictly in the sequence mentioned above. This blank reading takes care of the sulfur present in the crucible and other

chemicals used in the analysis. This reading is deducted from the buret reading obtained on analyzing a sample.

The titration vessel is filled with HCl solution to the pre-marked level and 2 cc of starch solution is added to it. Oxygen is allowed to bubble through the mixture at the rate of 1.2 liters/min. The end point is established by setting the titrator double throw switch on the "end point" position. No more addition of KIO_3 solution from the buret and a medium blue color of the solution in the titration receiver establishes the end point. The titrator double throw switch is now turned to the "neutral" position. The oxygen supply to the titration receiver is cut-off and the buret is filled with KIO_3 solution. About 0.7 grams of sodium azide (three scoops) are added to the mixture in the titration receiver. This is used to avoid the interference of nitrogen oxides and chlorine with the titration (15). The crucible with its contents is placed in the combustion tube and combusted in an atmosphere of pure oxygen. The titrator double throw switch is now turned to the "titrate" position. The unreacted oxygen together with the gaseous combustion products bubble through the titration receiver. The titration is assumed to be over when no more addition of KIO_3 takes place from the buret and the buret reading gives the blank value.

7) Sample analysis - The sample is prepared and combusted following the procedures described above.

8) Furnace factor - The reliability and accuracy of this method depends on the extent of oxidation of the sulfur present in the sample followed by its titration. To minimize the error due to incomplete combustion and titration, a furnace factor is determined by analyzing

a sample of known sulfur concentration. The calibration factor commonly referred to as furnace factor is calculated as follows:

$$\text{Furnace factor} = F = \frac{(\text{weight of the sample})\ (\%\text{S content})}{(\text{Buret reading} - \text{Blank reading})}$$

The reference oil is a coal-derived liquid supplied by the Pittsburg and Midway Coal Mining Co., and the sulfur concentration reported by the suppliers is used for calculating the furnace factor.

9) Chemistry of the analysis - The following reactions are supposed to be involved in the determination of end point:

$$KIO_3 + 5\ KI + 6\ HCl \longrightarrow 3\ I_2 + 6\ KCl + H_2O$$

$$I_2 + \text{Starch} \longrightarrow \text{Blue complex}$$

Substances with an oxidation potential much lower than the iodine-iodide system can be titrated with a standard iodine solution. These substances are oxidized by iodine and the following reactions are assumed to take place during the titration (15).

$$I_2 + 2\ e \rightleftharpoons 2\ I^-$$

$$4\ I^- + 4\ H^+ + O_2 \rightleftharpoons 2\ I_2 + 2\ H_2O$$

$$SO_2 + I_2 + 2\ H_2O \rightleftharpoons H_2SO_4 + 2\ HI$$

$$SO_3^{--} + I_2 + 2\ H_2O \rightleftharpoons SO_4^{--} + 2\ I^- + 2\ H^+$$

$$2\ NO_2^- + 2\ I^- + 4\ H^+ \rightleftharpoons 2\ NO + I_2 + 2\ H_2O$$

$$IO_3^- + 5\ I^- + 6\ H^+ \rightleftharpoons 3\ I_2 + 3\ H_2O$$

The interference of nitrogen oxides with the titration is avoided by the addition of sodium azide. The SO_2 formed during combustion decolorizes the solution, resulting in the addition of KIO_3 solution from the buret until the end point is reached. A sample calculation for sulfur concentration is as shown in Appendix A. A complete list of gases and chemicals used is given in Table VII.

Feedstock

The COED process developed by the FMC Corporation processed coal from the Colorado Bear mine to yield a coal-derived liquid. This coal-derived liquid was obtained through the Pittsburg and Midway Coal Mining Company and used as the feedstock in the present study. The properties of the coal-derived liquid reported by the suppliers are as given in Table VIII. This coal derived liquid is nearly a solid at room temperature, $77^{o}F$ ($25^{o}C$).

Catalysts

Two different Co-Mo-Alumina catalysts supplied by the Nalco Chemical Corporation were used in this study. The properties of the catalysts supplied by Nalco are given in Table IX. These catalysts differ only in pore size distribution and were analyzed for their surface area, pore volume and pore size distribution by an independent commercial laboratory, American Instrument Company.

The pore size distribution was obtained from mercury penetration data at 60,000 psi. Figure 8 is a plot of the cumulative pore volume against pore radius. Note that the plots for Nalcomo 474 and Sphericat Nalco 474 catalysts are nearly superimposed upon one another till a

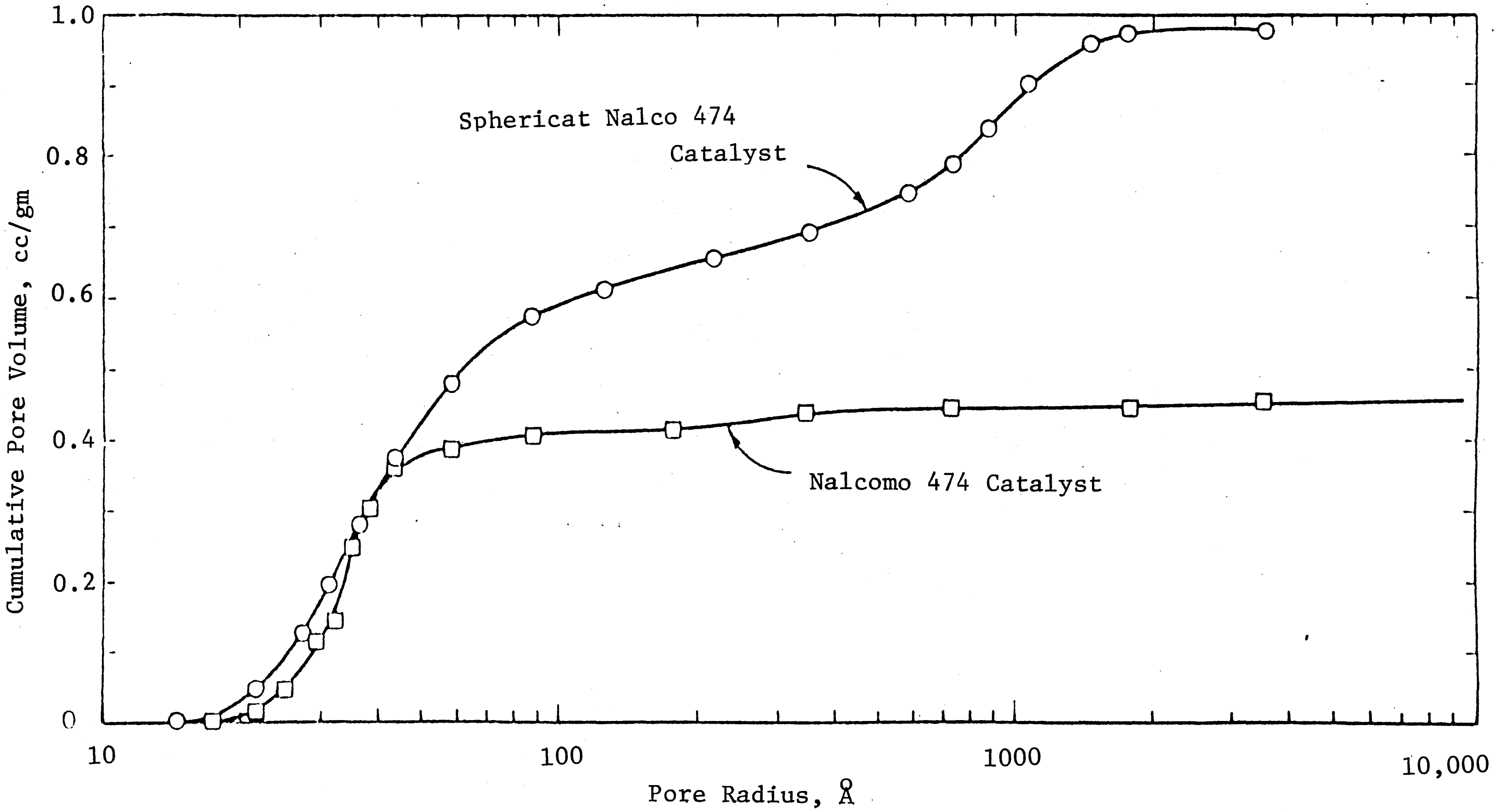

Figure 8. Dependence of Cumulative Pore Volume on Pore Radius

TABLE VII

LIST OF GASES AND CHEMICALS USED

Hydrogen	prepurified, 99.95%, 2200 psig (Air Products)
Nitrogen	purity, 99.997%, 3500 psig (Air Products)
Hydrogen sulfide	5.14% mixture in H_2, 2000 psig (Matheson)
Inert packing	6 mm, semi porcelain, Berl saddles (Fisher Scientific Company)
Chemicals used in analytical work:	
Oxygen	purity, 99.5%, 2100 psig (Sooner Supply)
Magnesium oxide powder	Analytical grade, Mallinckrodt Chemical Works
Potassium iodate	Analytical grade, Fisher Scientific Company
Potassium iodide	Analytical grade, Baker Chemical Company
Concentrated HCl solution	Fisher Scientific Company
Arrow root starch powder	Fisher Scientific Company
Sodium azide	Chemical purpose, Eastman Kodak Company
Iron chips	Leco Corporation, part #501-077
Tin accelerator	Leco Corporation, part #501-076
Crucible	Leco Corporation, part #528-036
Crucible porous lid	Leco Corporation, part #528-012

TABLE VIII

ANALYSIS OF THE FMC FEED OIL

Coal source	Colorado Bear mines
Moisture, wt%	0.20
Quinoline insoluble, wt% dry	0.20
Ultimate Analysis, wt% dry	
Carbon	83.05
Hydrogen	8.35
Nitrogen	1.13
Oxygen**	7.15
Sulfur	0.35
Ash	0.00
°API Gravity, 60°F/60°F	-4 to -5
Pour point, °F	118 (48°C)
Flash point, °F	350 (177°C)
Viscosity @ 210°F (99°C), SUS	1090

** Oxygen determined by difference

pore size of 45 Å, beyond which there is a significant difference in the cumulative pore volumes of the two catalysts. This cumulative pore volume data shows the dependence of cumulative pore volume on the pore size distribution. Nalcomo 474 catalyst has a pore volume of 0.463 cc/gm. Sphericat Nalco 474 catalyst has a pore volume of 0.981 cc/gm. For cylindrical pores a plot of dV/dlnr against "r" gives an idea of the pore size distribution in the catalyst, where "V" is the cumulative pore volume and "r" is the pore radius. This plot is shown in Figure 9. Note that Nalcomo 474 catalyst has a rather narrow pore size distribution at 33 Å compared to Sphericat Nalco 474 catalyst with modes at 30 Å for micropores and 860 Å for macropores. The presence of macropores is expected to be an advantage in processing heavier petroleum feedstocks as discussed earlier. The catalyst properties are as given in Table IX.

Co-Mo-Alumina combination is the most favored in the catalysts for hydrodesulfurizing petroleum feedstocks. As discussed under literature review in this thesis, the atomic ratios around 0.2 Co : 1.0 Mo to 0.5 Co : 1.0 Mo has been observed to have maximum activity and selectivity in hydrodesulfurizing petroleum feedstocks. The two catalysts, Nalcomo 474 and Sphericat Nalco 474 contain 3.5 wt% CoO and 12.5 wt% MoO_3. This corresponds to an atomic ratio of 0.54 Co : 1.0 Mo.

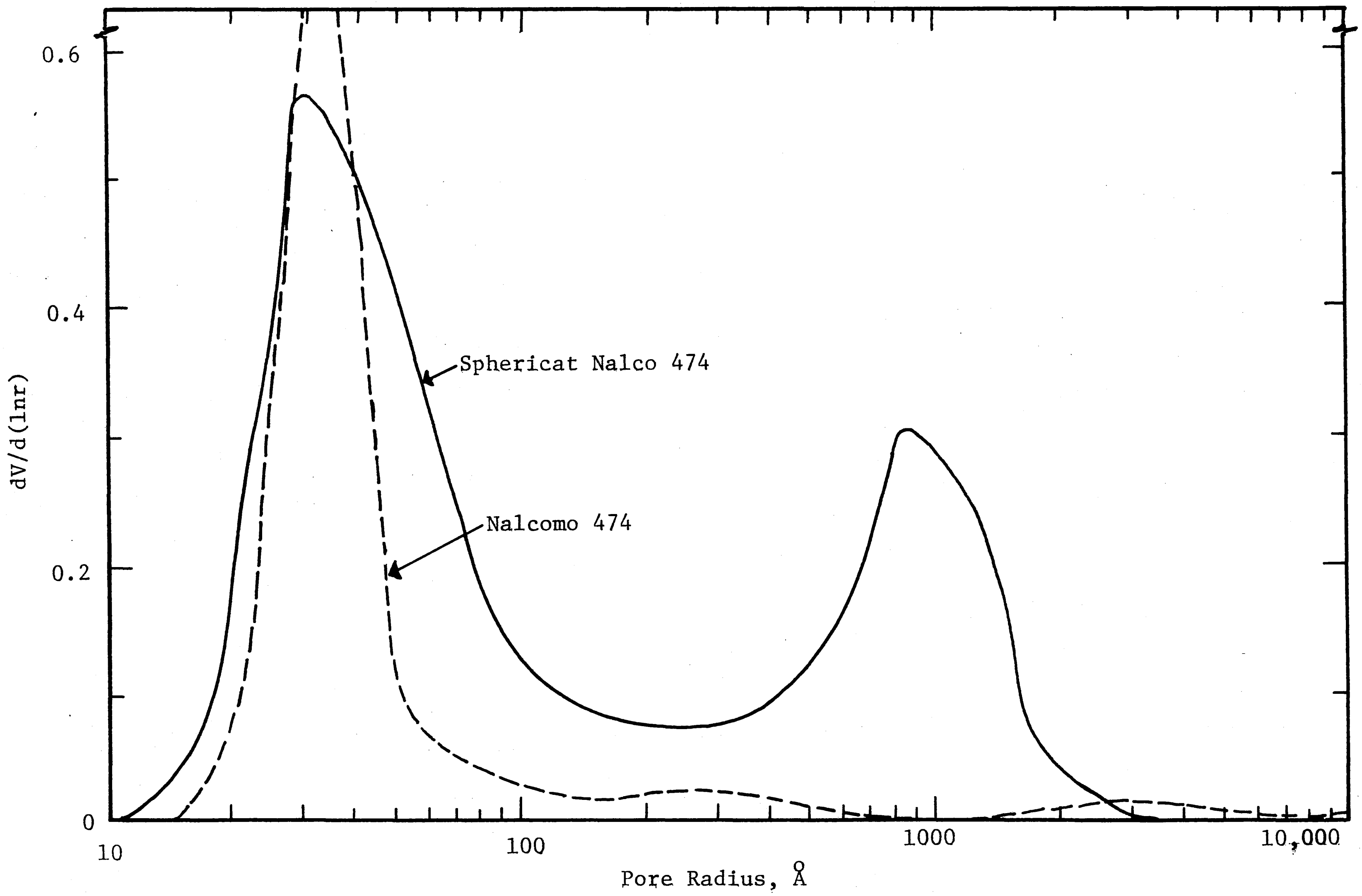

Figure 9. Catalysts Pore Size Distribution

TABLE IX

CATALYST PROPERTIES*

	Nalcomo 474	Sphericat Nalco 474
Chemical Analysis, wt%, Dry Basis		
MoO_3	12.5	12.5
CoO	3.5	3.5
Na_2O	0.08	0.08
Fe	0.03	0.03
SiO_2	1.5	1.5
Alumina	82.39	82.39
Physical Properties		
Surface area, M^2/gm	270 (240)**	270 (286)**
Pore volume, cc/gm	0.51 (0.46)**	0.65 (0.98)**
Most Frequent Pore Radius, Å	33**	30** Micropores 860** Micropores

* Nalco Chemical Company data

** Measured by American Instrument Company

CHAPTER IV

EXPERIMENTAL RESULTS

The experiments were designed to assess the short term deactivation of catalysts in the hydrodesulfurization (HDS) of coal-derived liquids. Two commercial catalysts, Nalcomo 474 and Sphericat Nalco 474 were tested in this study using FMC oil. Earlier in this laboratory unit, Nalcomo 474 and Nalco 474-B catalysts were used by Others (31) to study the effect of temperature, pressure and space time on the HDS of FMC oil.

Experimental Runs were conducted in a trickle bed reactor packed with -8, +10 mesh size catalyst particles. The catalyst bed height in these Runs was maintained constant at 12.75 inches (32.39 cm). The primary objective of this chapter is to identify the effect of temperature and total hours of operation on the observed sulfur removal activity of the two catalysts from the experimental results. The total hours of operation in this study were counted from the time oil was on stream. The product oils were analyzed using the Leco sulfur analyzer mentioned in the preceeding chapter. The results are reported in the form of weight percent sulfur (wt% S) in the oil. The sulfur content in the product oil can be taken as a measure of the observed activity of the catalyst. Complete details of the results are given in Table XV to XX in Appendix D.

Effect of Temperature and Total Hours of Operation for Nalcomo 474 Catalyst

To obtain a comparison with earlier studies (29) on this feedstock, Run SC-F was conducted at 700°F (371°C), 1500 psig 7500 Scf H_2/bbl FMC oil and a volume hourly space time of 2.99 hours. The sulfur concentration observed in the product oil after only 10 hours of operation was 0.045 wt% as shown in Figure 10. The sulfur level in the product oil decreased during the next 30 hours and then remained stable at about 0.02 wt%. The catalyst maintained its activity to give this sulfur level of 0.02 wt% during the next 120 hours of operation. A comparison of these results with those obtained earlier (29) will be given in the following chapter.

In the earlier studies (28) increased resistance to flow through the reactor was observed at 800°F (427°C). To study the effect of total hours of operation on the activity of the catalyst at 800°F (427°C) Run SC-C was conducted. After only five hours of operation more than 94% sulfur removal was achieved, as shown in Table XVII. During the 100 hours of total operation, the catalyst maintained its activity to give more than 94% sulfur removal. Since in the over all program sulfur concentrations of the order of 0.05 to 0.1 wt% are considered to be satisfactory and the lower limit of the Leco sulfur analyzer is 0.02 wt%, no attempt was made to determine the specific sulfur concentrations below this lower limit. For some product oil samples, volume titrated was observed to be less than the blank reading. This indicates the serious limitation of the Leco sulfur determinator to analyze for sulfur concentrations less than 0.020 wt% in the product oil. In the

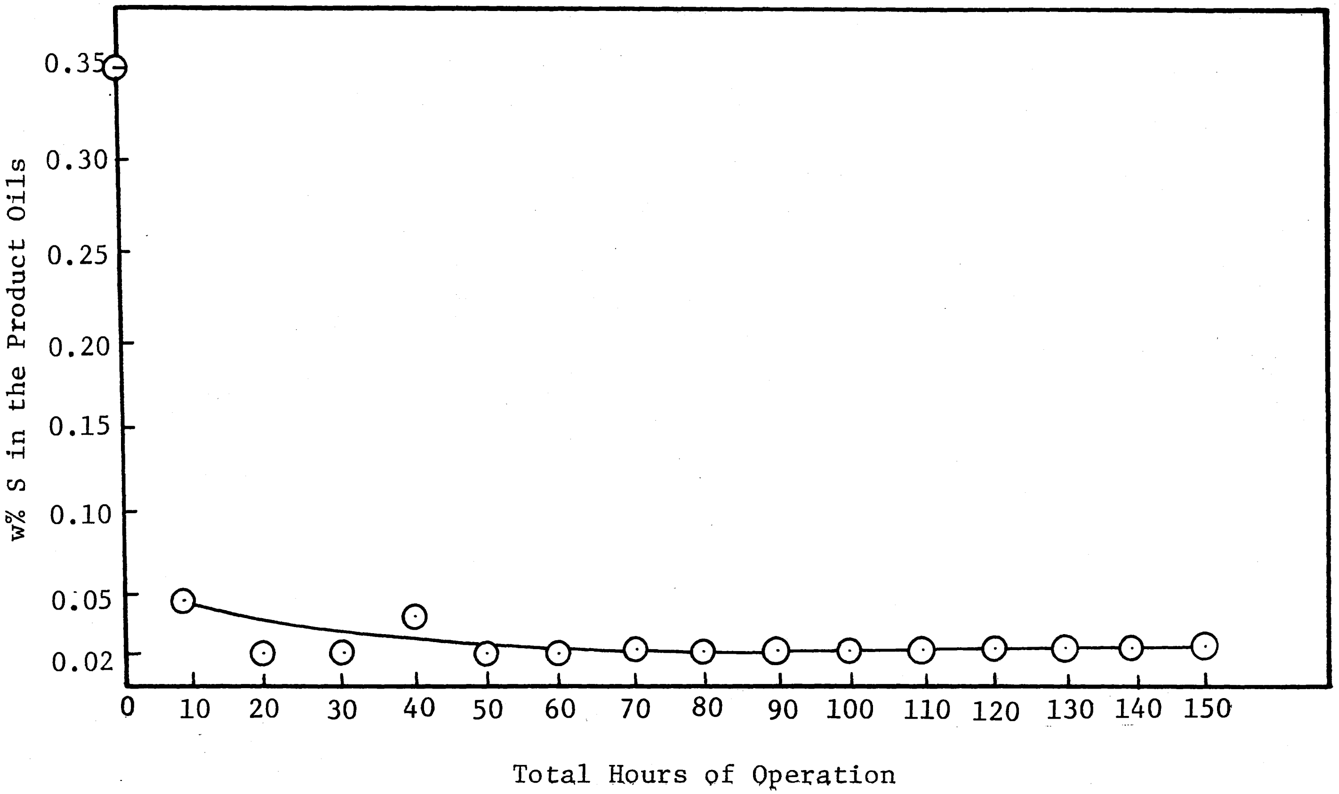

Figure 10. Effect of Total Hours of Operation on Nalcomo 474 Catalyst HDS Activity at 700°F (371°C)

entire 100 hours of operation, sulfur levels below 0.02 wt% (below the lower limit) corresponding to more than 94% desulfurization were observed.

Effect of Temperature and Total Hours of Operation for Sphericat Nalco 474 Catalyst

The Run SC-E was conducted using Sphericat Nalco 474 Catalyst at 700°F (371°C) to obtain a comparison with Nalcomo 474 Catalyst under similar conditions as in Run SC-F. The observed sulfur concentrations were as shown in Figure 11. The percent sulfur removal obtained after only 10 hours of operation was 94% (0.02 wt% S). The catalyst maintained its activity during the next entire 140 hours of operation to give 94% sulfur removal. An interesting point with this catalyst when compared to Nalcomo 474 catalyst was the low sulfur concentration in the product oils (0.02 wt%) during the first 30 hours of operation.

To obtain a comparison with the results of SC-E run, under identical operational conditions but slightly different catalyst presulfiding procedure, Run SC-A was conducted. In this Run, SC-A, presulfiding was carried out by passing pure H_2 and pure H_2S. H_2S in the hydrogen mixture was crudely estimated to be one to six percent while the actual value was very close to the lower limit for most of the time. This estimation was based on the mixing of flow streams by the adjustment of flow control valves. The results were as shown in Figure 12. The observed sulfur concentration in the product oil after only 10 hours of operation was 0.163 wt%. In the case of Run SC-E, the corresponding concentration was 0.02%. After 40 hours of operation the sulfur level in the product oil was observed to be 0.068 wt%, as shown in

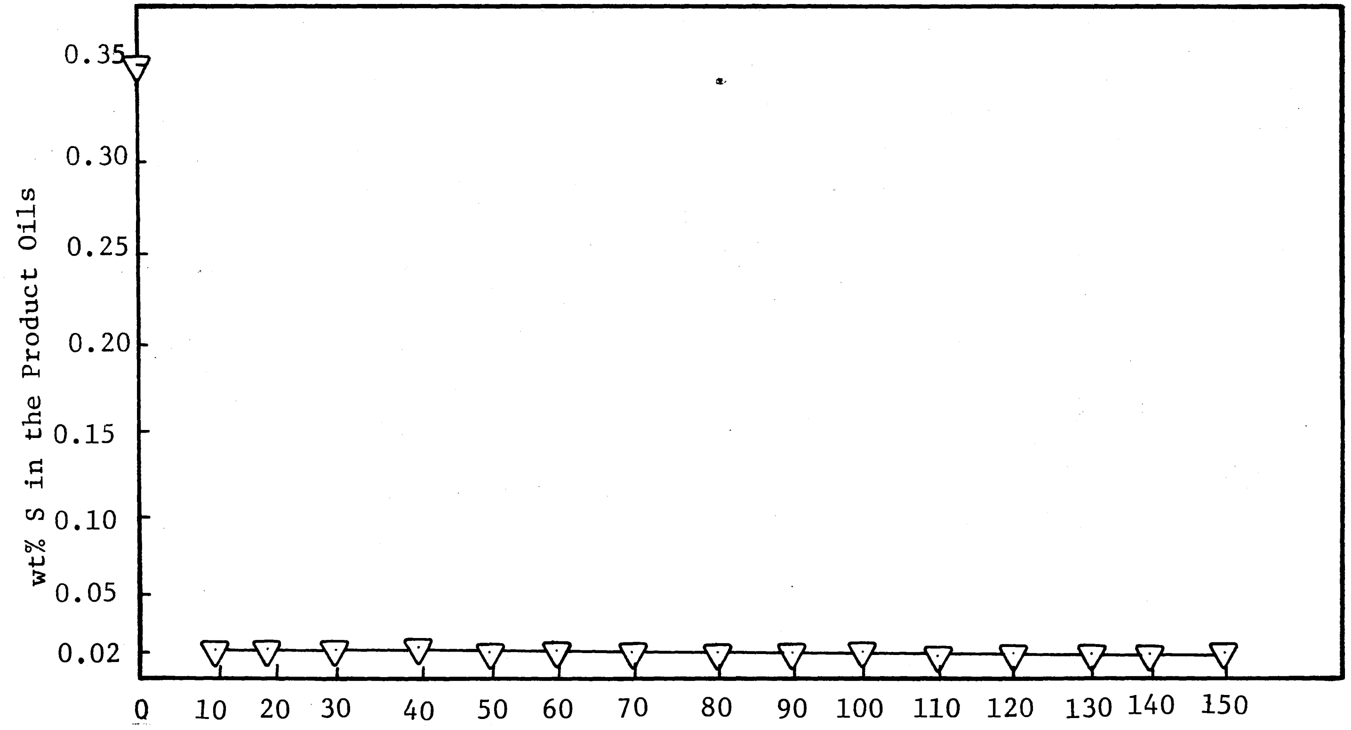

Figure 11. Effect of Total Hours of Operation on Sphericat Nalco 474 HDS Activity at 700°F (371°C)

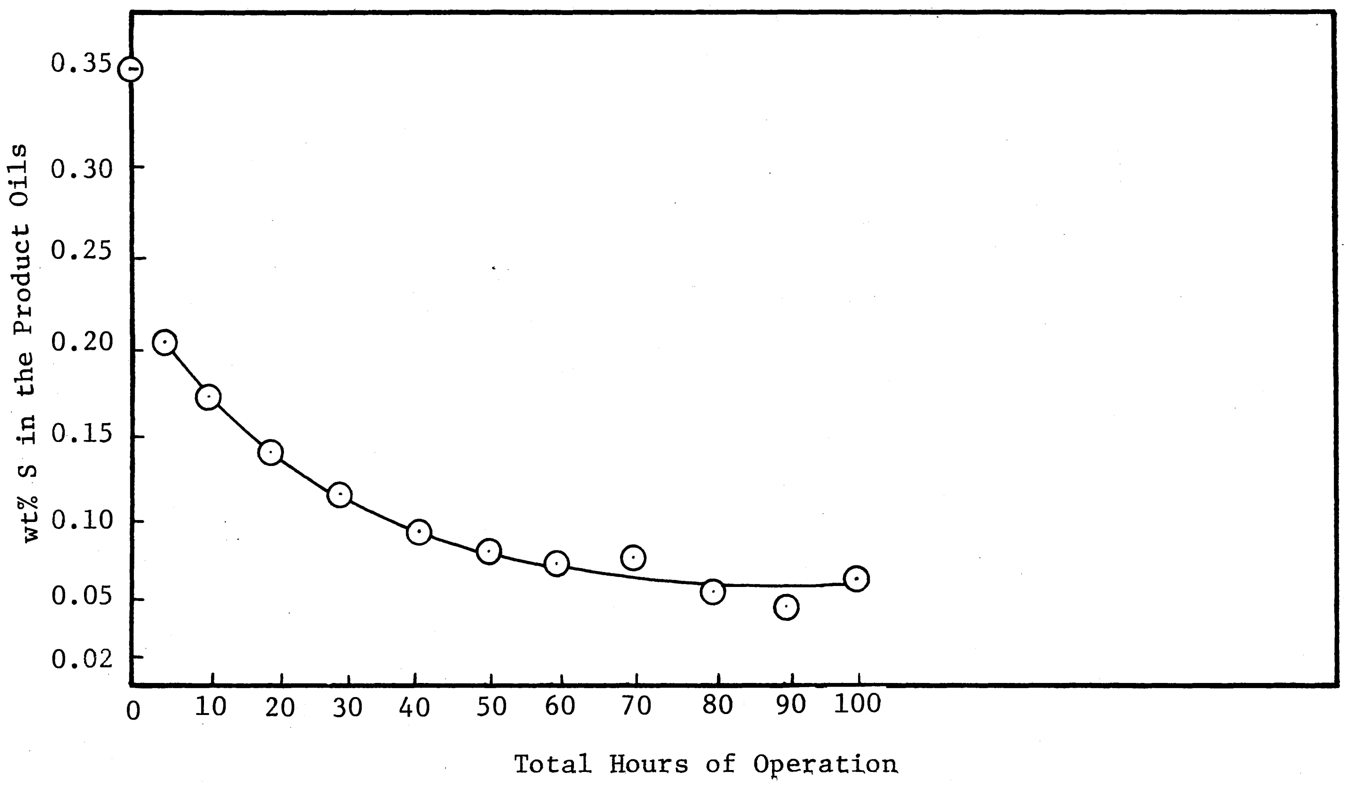

Figure 12. Effect of Total Hours of Operation on Sphericat Nalco 474 Catalyst HDS Activity at 700°F (371°C)

Figure 12. The catalyst maintained its activity to give sulfur concentrations of about 0.064 wt% in the product oils during the next sixty hours of operation. However, in the entire 150 hours of operation in Run SC-E the sulfur concentrations were 0.02 wt% in the product oil.

Sphericat Nalco 474 catalyst has bimodal pore size distribution. Because of the presence of both micro and macro pores in this catalyst, it is expected to have an advantage over the Nalcomo 474 catalyst having only micro pores. Run SC-B was conducted using Sphericat Nalco 474 catalyst to obtain a comparison with Nalcomo 474 catalyst in Run SC-C, under identical operational conditions. The results of this run are summarized in Table XVI. The observed sulfur concentration in the product oil after only five hours of operation was below the lower limit of the Leco analyzer. This was also observed in Run SC-C as shown in Table XVII. The catalyst maintained its activity during the entire 200 hours of operation to give sulfur concentrations below 0.02 wt%. These low sulfur concentrations in the product oils do not enable one to justify the advantage of the presence of macro pores in the catalyst.

The experience with similar studies (28) in this laboratory unit suggested a strong possibility of increased flow resistance across the catalyst bed, leading to forced shut down at higher temperatures. They thought that this would happen due to increased coking at higher temperatures of the order of 800+°F (427+°C). To establish an upper temperature limit on operation in this program and to assess their assumption, Run SC-D was conducted at 850°F (454°C). The results of this run were as summarized in Table XVIII. As expected, sulfur concentrations well below 0.02 wt% were observed during the entire 145 hours of operation. In fact, the sulfur level after only five hours of operation was well below 0.02 wt% in the product oil. This corresponds to more than 94% desulfurization. At no time during the entire 145 hours of operation were there any indication of increased flow resistance across the catalyst bed.

In fact, in all of the experimental runs of the present study, no major operational problems were encountered. No significant pressure drop increase or increased flow resistance were observed. However in Run SC-D, after 130 hours of operation, some pressure fluctuations of the order of 10-90 psi were observed. But these fluctuations were short lived and did not affect the operation during the next 15 hours. The maximum pressure fluctuation observed during the last five hours before voluntary shut down was 15 psi. In this study a pressure variation of ± 20 psi was considered to be satisfactory. However, there exist a possibility of increased flow resistance at this temperature because of the increased coking. This hinderance to flow is possible across the reactor and/or any where downstream from the reactor across the fine control valves and pressure regulators.

Carbon Build-up on the Catalyst

After voluntary shut down and the disengagement of the reactor, catalysts were removed easily. There was no sign of plugging or increased resistance to flow in the catalyst bed. Since coking and carbonization were suspected causes of reactor plugging or increased flow resistance across it, the catalyst was heated to determine the extent of carbon build-up during the operation. The catalyst after use within the reactor were heated to burn off the carbonaceous deposits on it. Little or no variation in the catalyst weight after heating at at least one higher temperature than the previous heating temperature was considered satisfactory in the calculation of percent loss in weight of the catalyst. The results were as summarized in Table X. There was 13% loss in weight of the fresh (unused) Sphericat Nalco 474 catalyst compared to 11% of fresh Nalcomo 474 catalyst. There seems to be no difference in the percent loss in weight of Sphericat Nalco 474 catalyst in the two runs, SC-B at 800°F (427°C) for 200 hours and SC-E at 700°F (371°C) for 150 hours of operation (36 wt%). The loss in weight of Nalcomo 474 catalyst after 100 hours of operation in Run SC-C was 33% compared to 29% in the Run SC-F.

TABLE X

PERCENT LOSS IN WEIGHT OF USED/FRESH CATALYSTS

	Sphericat Nalco 474					Nalcomo 474		
Run Series	Fresh	SC-A	SC-B	SC-D	SC-E	Fresh	SC-C	SC-F
Operational Temperature °F	-	700	800	850	700	-	800	700
Total Hours of Operation	-	100	200	145	150	-	100	150
% Loss in Catalyst wt.	13	33	36	53	36	11	33	29

All the results given in this chapter will be discussed in the next chapter.

CHAPTER V

DISCUSSION

The present study is a part of a research program at the School of Chemical Engineering, Oklahoma State University. This program concentrates on the development of catalysts for hetero-atom removal from the coal-derived liquids. At the present stage of this program sulfur concentrations of the order of 0.05-0.1 wt% in the product oils are considered to be satisfactory (7). Correct evaluation of the present study requires a careful consideration of the objectives of the overall research program.

In heterocatalytic reactions the rate of reaction is a measure of the activity of the catalyst and in the case of hydrodesulfurization (HDS) reactions the sulfur concentration in the product oils can be taken as a measure of the catalyst activity. In operations with fixed catalyst bed the activity of the catalyst is also a function of time. The loss in catalyst activity with time can be mainly due to the metallic and carbonaceous depositions on it. The active life of the catalyst can be defined as the period during which the desired conversion with minimum undesirable side reactions can be obtained. This period is an important parameter in determining the commercial feasibility of the catalyst and hence the process. Some of the other factors that can affect the catalyst active life are sintering caused by exposure of the catalyst to extreme conditions of temperature and pressure, catalyst pore mouth blockage by solid depositions and catalyst bed plugging. One of the objectives of this thesis work was to study the short-term deactivation of the catalyst for sulfur removal from FMC oil, a coal-derived liquid.

The success and usefulness of any research work depends on the reproducibility of its results. These can be affected by the variations in the maintenance of operational conditions and the performance of the trickle bed reactor used.

In fixed bed reactors, the exothermic reactions can result in hot spots that can deactivate the catalyst and temperature control can become a major operational problem for large diameter units. In the present study a maximum deviation of ± $2^{o}F$ ($1^{o}C$) from the desired value was observed in the temperature profile across the catalyst bed. The temperature was read on a Doric digital temperature indicator using iron-constantan thermocouple. A typical temperature profile across the catalyst bed under steady state conditions during an experimental run was as shown in Figure 13. Sooter (43) in his thesis work on a similar unit had measured the temperatures in the radial center of the reactor and at corresponding points on the reactor outer tube wall through a hole drilled in the massive aluminum heating blocks. Using the same thermocouple for both measurements, he observed a maximum radial ΔT of $3.1^{o}F$ ($1.7^{o}C$) at $750^{o}F$ ($399^{o}C$). Since the temperatures measured are at the tube walls, the ΔT across the catalyst bed will be smaller than $3.1^{o}F$ ($1.7^{o}C$).

As discussed in Chapter III of this thesis, the increase in pressure beyond 1000 psig has a negligible effect on the sulfur removal from petroleum as well as coal-derived liquid feedstocks. In

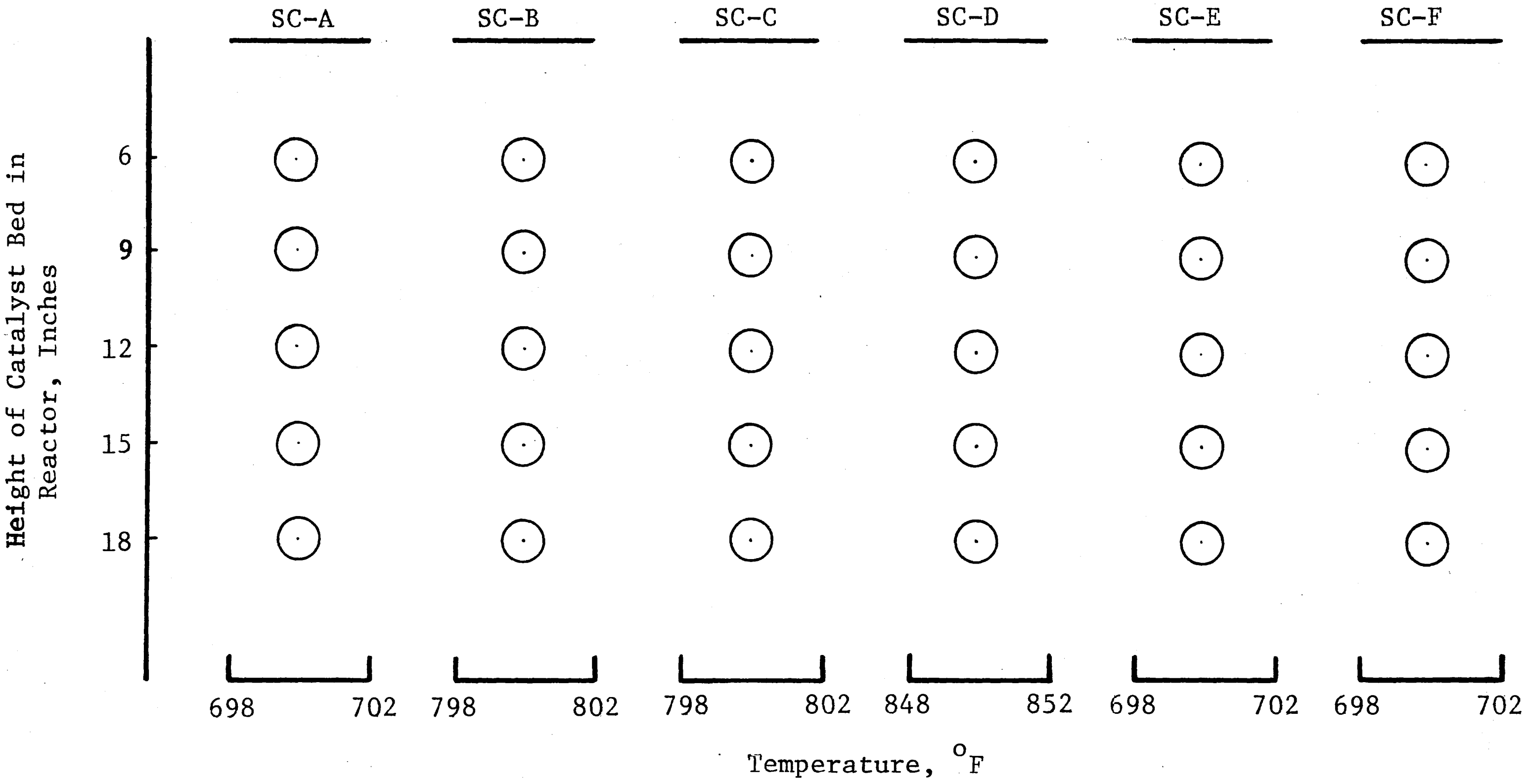

Figure 13. Temperature Profile Under Steady State Conditions Across the Catalyst Bed

the present study a maximum variation of 20 psi in the operating pressure was observed. This corresponds to a deviation of 1.3% from the desired value of 1500 psig.

Wan (46) and Sooter (43) in their theses work with raw anthracene oil observed that an increase in liquid volume hourly space time beyond one hour increases the desulfurization very slightly. The space time can be affected by variations in catalyst loading, catalyst bed height and liquid flow rate. The space time in this study was defined as the ratio of the reactor volume based on the catalyst bed height to the liquid volumetric flow rate. In some literature, space time is defined as the ratio of the weight of the catalyst to the liquid mass flow rate, hence the importance of considering variations in catalyst loading. Variations in catalyst bed density (wt. of catalyst used/volume of the reactor based on the catalyst bed height) can be taken as a measure of that in catalyst loading. In the four runs with Sphericat Nalco 474 catalyst, the bed density was 0.5, 0.56, 0.51 and 0.51 gm/cc. In the case of the two experimental runs with Nalcomo 474 catalyst the bed density was constant at 0.72 gm/cc. This indicates little or no variation in catalyst bed density. In the two Runs, SC-A and SC-E, conducted under identical operational conditions, the bed density was 0.5 and 0.51 gm/cc respectively. Hence, one can conclude that the catalyst loading was consistent within this study.

In all the runs of this study, catalyst bed height was maintained constant at 12.75 inches (32.39 cm) within ± 0.125 in. (0.32 cm). This can cause a maximum of one percent error in the calculation of space time. This much error has negligible effect on the desulfurization at a space time of 2.99 hours used in this study.

A positive displacement pump was used for feeding the FMC oil to the reactor. This pump can feed at a pre-set constant rate with little or no variations in liquid flow rate due to line voltage fluctuations. Hence, variations in liquid flow rate were either absent or were negligible in this study.

Wan (46) and Sooter (43) in their HDS work with raw anthracene oil observed no significant effect of increase in H_2/oil feed ratio in the range 3980 to 20,000 scf/bbl. In the present thesis work this ratio was maintained in the range 6525 to 9075 and the desired value was 7500 scf H_2/bbl FMC oil. Thus variations in this ratio were insignificant to affect the results.

Hence, for the reproducibility of the results of this thesis work variations in temperature, pressure, space time, catalyst loading and H_2/oil feed ratio should be within the appropriate range mentioned above.

Performance of Trickle Bed Reactor

The performance of trickle bed reactor can be another limiting factor in this study. Some of the important factors to be considered are the flow distribution, liquid holdup and the backmixing effects. These factors are important because of the different magnitudes of the reactor sizes and the flow rates involved in the laboratory and the commercial units.

Consideration of the tube diameter to particle diameter ratio (D_t/D_p), liquid flux, and gas flux can give an insight to the flow distribution effects. In this study the D_t/D_p ratio was 5.8. Schwartz suggested this ratio to be more than 30 for co-current gas-liquid operations, while Schiesser (38) reported significant radial variations in velocity profile for D_t/D_p as large as 16. Since this study was not designed to study the effect of this ratio, no conclusion can be drawn on this aspect.

Sooter (43) in his desulfurization studies on a similar reactor used a D_t/D_p ratio of 5.8 and varied the liquid flux in the range 4.84-9.69 gallons/hr. ft^2. No significant effects on desulfurization were observed by him. The liquid flux used in this study was 2.65 gallons/hr. ft^2. This suggests that the effect of flow distribution in the present study may be of less importance.

Wan (46) and Sooter (43) in their theses work on a similar unit using a D_t/D_p ratio of 5.8 observed no significant effect of H_2/oil feed ratio in the range 3980-20,000 scf/bbl. The ratio in this study was 7500 scf H_2/bbl FMC oil. Considering the similarities of the present study with that of Wan (46) and Sooter (43), the flow distribution effects in this study seem to be less significant.

The backmixing effects can be evaluated by considering the Mears criteria (22). This criteria requires the calculation of liquid Peclet number Pe_L, and hence the liquid diffusion coefficient D_L. This criteria assumes an axial dispersion model for the backmixing effects. Considering the complexity of the liquids encountered in HDS studies this model is a powerful tool for the evaluation of backmixing effects. However, the assumptions made in calculating D_L may be seriously questionable. Hochman and Effron (11) in their studies with nitrogen-methanol system in co-current gas-liquid operation in a packed bed correlated the liquid Reynolds number Re_L and Pe_L in graphical form. However, for the present study the viscosity of FMC oil at 210°F (99°C) was determined to be 1090 SUS (2.6 gm/cm/sec) and the liquid Reynolds number based on this viscosity is outside the range of the plot given by Hochman (11). Mears (22) had suggested h/D_p equal to 350 for first order reactions and this ratio in the present study was 148. Most of the other studies (37, 41) on trickle bed reactors also conclude that the backmixing effects are of less importance. Hence, there exists a strong possibility for the absence of significant backmixing effects and the operation approaching very nearly plug flow.

In the case of negligible backmixing effects Paraskos, Frayer and Shah (32) suggested the use of the following model for evaluating the liquid holdup effects in trickle bed reactors.

$$\ln \frac{C_{A_i}}{C_{A_o}} = \frac{k' \, (h)^b}{(\mathrm{LHSV})^{1-b}} \quad \text{where } k' \text{ and } b \text{ are constants.}$$

The constant "b" lies between 0 and 1 in this model. This constant can be evaluated by comparing the results obtained under similar operational conditions but with different catalyst bed heights and/or different liquid hourly space velocities (LHSV). The catalyst bed height used in this study was 12.75 inches (32.39 cm). Others have reported studies (28) in this laboratory unit with a 10 inch (25.4 cm) catalyst bed under comparable conditions for the FMC oil. The calculation of the constant "b" for the two studies at 700°F (371°C), 1500 psig revealed a value of 1.62 as shown in Appendix B. Since "b" lies between 0 and 1 in the original model, the liquid holdup effects seems to be negligible in the present study.

Summarizing the above discussion one can conclude that the flow distribution, liquid holdup and backmixing effects in the present thesis work seem to be less important. However, Ross (35) reported that these effects could be of different magnitude under similar operational conditions in narrow bed reactors and in large diameter commercial units.

Analytical Precision

Sooter (43) in his thesis work on the HDS of raw anthracene oil observed that the precision of analytical results was seriously affected below 0.02 wt% S in the oil. A comparison of the results of the present study with that obtained by Sooter (43) for known sulfur concentrations is as shown in Table XI. The results are consistent within Sooter's observations.

The low precision at/or below 0.02 wt% S in the oil is not a limitation in the evaluation of a particular catalyst within the scope of the program at this stage. As mentioned earlier, the acceptable sulfur concentrations in the product oils are 0.05-0.1 wt%. These low concentrations, 0.02 wt% and below are highly appreciable and the catalyst is assumed to be active until the sulfur level in the product oil increases beyond 0.05-0.1 wt%. Hence the analytical technique is not a major limiting factor within the scope of the program. But the low sulfur concentrations, 0.02 wt% and below, do not allow a distinction between the two catalysts, Sphericat Nalco 474 and Nalcomo 474 used in this study.

TABLE XI

PRECISION OF THE ANALYTICAL TECHNIQUE

Sample	Present Study			Sooter's Work (43)		
	Observed			Known wt% S	Observed	
	wt% S	Deviation	% Deviation		Deviation	% Deviation
Feed oil						
SC-A #2	0.162	±0.004	2.47	0.20	±0.00838	4.0
#3	0.109	±0.003	2.75	0.15	±0.00525	3.5
#7	0.084	±0.005	5.95	0.10	±0.00581	5.8
#8	0.068	±0.003	4.41	0.08	±0.00692	8.6
#16	0.053	±0.003	5.66	0.06	±0.00491	8.2
#18	0.045	±0.005	11.11	0.04	±0.00379	9.5
SC-F #4	0.03	±0.007	23.33	0.02	±0.00400	20.0

In the case of heterocatalytic reactions the ability of a catalyst to maintain its activity is of prime importance. For a given feedstock the observed desulfurization activity of a catalyst during an operation can be a function of one or more of the following factors:

1) Catalyst pretreatment

2) Hydrotreating conditions

Isolation of the effect of these individual factors on the catalyst activity may be difficult. An attempt will be made to obtain an understanding of the relative importance of these factors.

Catalyst Presulfiding Effects

Catalyst pretreatment consists of two steps, calcination and sulfiding. Most of the people in industry attribute the HDS activity of a catalyst to its sulfiding. MoS_2 is considered to be the active constituent in the catalyst. In the HDS of petroleum feedstocks, catalyst presulfiding was observed (4) to increase the activity and hence the catalyst active life.

A comparison of the results of Runs SC-A and SC-E conducted under identical operational conditions suggest that the extent of presulfiding can also affect the catalyst activity. No guidance can be obtained from the literature on the extent of necessary presulfiding required in hydrotreating coal-derived liquids. The metallic oxides present in the catalyst are observed to be reduced to their respective sulfides in the presence of sulfur compounds. The amount of H_2S required for the complete sulfiding of Co to Co_9S_8 and Mo to MoS_2 can be taken as a measure of the necessary required catalyst presulfiding. This may or may not be a representative approximation; however, this can give an insight to the understanding of the presulfiding effect.

The amount of H_2S supplied during catalyst presulfiding and the actual amount required for the complete sulfiding of Co to Co_9S_8, and Mo to MoS_2 were as given in Table XII. The calculations are given in Appendix C.

TABLE XII

H_2S SUPPLIED FOR CATALYST PRESULFIDING

	Sphericat Nalco 474				Nalcomo 474	
Run Series	SC-A	SC-B	SC-D	SC-E	SC-C	SC-F
Catalyst weight, gms	12.00	13.36	12.19	12.20	17.28	17.29
H_2S supplied, gms	0.24-1.41	1.21	1.21	1.21	1.21	1.21
H_2S required, gms*	0.899	1.001	0.913	0.914	1.294	1.295

* For complete sulfiding of the metals present in the catalyst.

The inconsistency between the results of Run SC-A and SC-E as shown in Figure 14 can be attributed to the extent of catalyst presulfiding effects. As mentioned above, the amount of H_2S supplied for catalyst presulfiding in Run SC-A was 0.24-1.41 gms and the possible stoichiometric requirement was 0.899 gms. In Run SC-E conducted under identical operational conditions of temperature, pressure, space time and H_2/oil ratio as in Run SC-A, the amount of H_2S supplied was 1.21 gms compared to a requirement of 0.914 gms. After only 10 hours of operation the sulfur concentration in the product oil in Run SC-A was 0.163 wt% compared to a relatively very low value of 0.02 wt% in Run SC-E at the same time. The sulfur concentration in the product oils leveled off at about 0.06 wt% after 40 hours of operation for

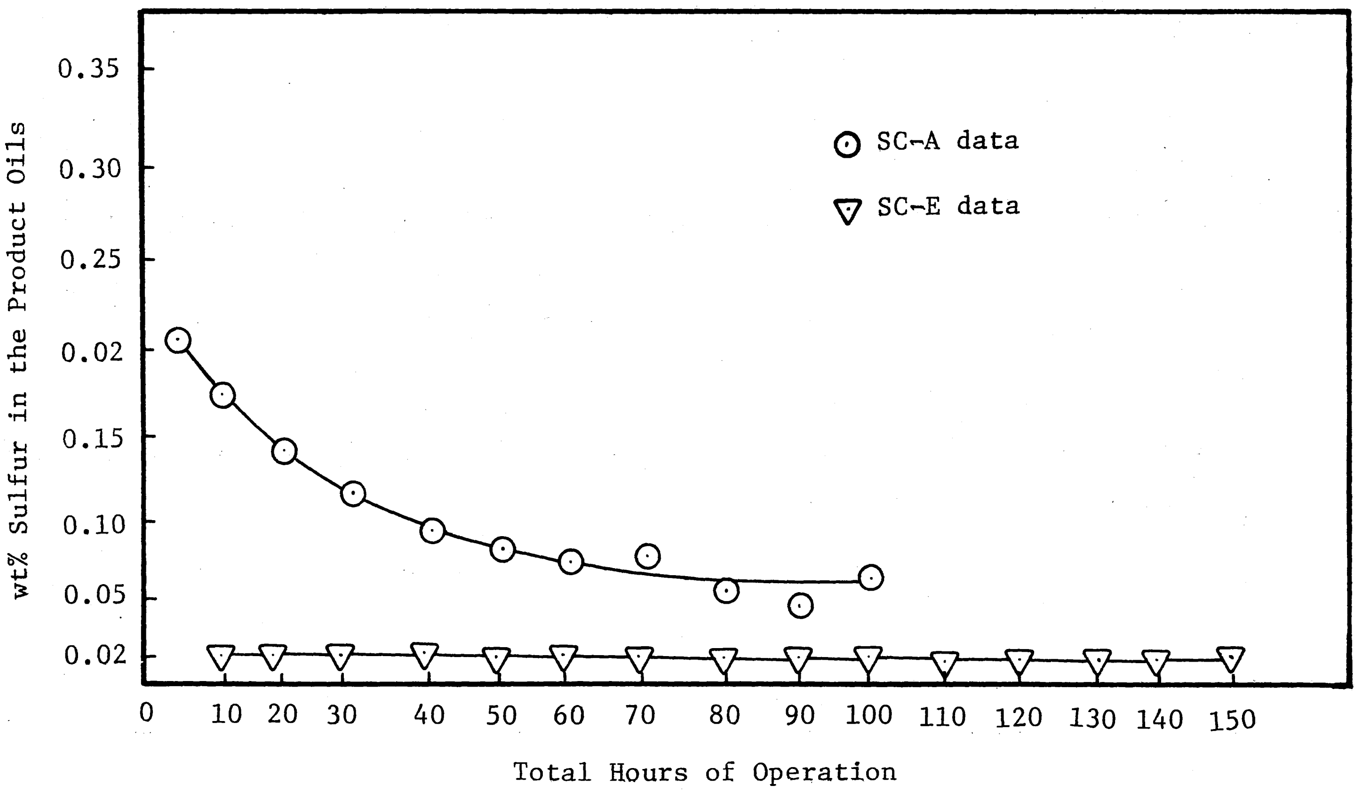

Figure 14. Comparison of SC-A and SC-E Results for Presulfiding Effects

SC-A, whereas SC-E products were much lower at 0.02 wt% during this period.

Assuming the product oils in SC-A contained an average sulfur concentration of 0.1 wt% during the first 40 hours and all the sulfur removed from the oil was used for sulfiding, the amount of H_2S supplied would be 1-2.17 gms. However, the catalyst maintained its activity during the next sixty hours of operation to give about 0.06 wt% S in the product oils. In the case of SC-E, the catalyst maintained its activity to give 0.02 wt% S in the product oil even at the end of 150 hours of operation.

This same feedstock, FMC oil, was studied by others (30) in this laboratory unit using Nalcomo 474 catalyst. They had presulfided the catalyst with 5% H_2S in H_2 mixture flowing at the rate of 0.5 cc/sec for 90 minutes. This corresponds to an amount of only 0.19 gms of H_2S supplied compared to the requirement of 0.82 gms for their catalyst loading. In Run FT-H of the earlier work (30), the operation was started at 1500 psig, 800°F (427°C) and a space time of 1.57 hours. After 18 hours of operation the space time was changed to 3.14 hours. If an assumption of 0.05 wt% S in the product oil is made based on their results, then the total amount of H_2S supplied would be 0.99 gms compared to a requirement of 0.82 gms. The results of the Run FT-H of the earlier work (30) and the Run SC-C of the present study for identical operational conditions can be compared as shown in Table XIII. After 20 hours of operation in FT-H, the sulfur concentration in the product oil was 0.049 wt%, which dropped to 0.029 wt% after five more hours of operation. However, the first 16 hours of operation was conducted at lower space times of 1.57 and 0.752 hours. The corresponding Run SC-C of the present study gave sulfur concentration in the product oils below 0.02 wt% throughout the 100 hours of operation. In the case of Run FT-H of the earlier work, a change in operating pressure to 1000 psig resulted in increased flow resistance leading to forced shut down of the system after only 50 hours of operation. Similarly, in Run FT-G (29) at 700°F (371°C) the sulfur level was 0.057 after 76 hours compared to 0.02 wt% in Run SC-F of the present study under the same operational conditions.

TABLE XIII

COMPARISON OF FT-H (30) AND SC-C RUNS (WT% S) AT 800°F (427°C)

Total hours of operation	FT-H		SC-C	
	wt% S	% S removal	wt% S	% S removal
20	0.049	86	X	XX
25	0.029	92	X	XX

X sulfur concentration below 0.02 wt%
XX sulfur removal more than 94%

The above discussion can be summarized by concluding that the observed low activity of the catalyst for sulfur removal from FMC oil under identical operational conditions can be explained at least partly by considering the extent of catalyst presulfiding.

Effect of the Total Hours of Operation for the Two Catalysts

The two catalysts used in this study, Nalcomo 474 and Sphericat Nalco 474 have different pore properties as given in Table VIII. Nalcomo 474 and Sphericat Nalco 474 catalysts have unimodal and bimodal pore size distribution respectively. The presence of micro and macro pores in the catalyst have been observed to be an advantage in the hydrotreatment of heavier petroleum feedstocks (9). These macropores are believed to accommodate the solid depositions, while serving as active sites for molecules bigger than the micropores. The complex nature of coal and hence the coal-derived liquids suggest the need for macropores in the catalyst. One of the objectives of the overall research program is to obtain a distinction, if any, between catalysts having unimodal and bimodal pore size distribution, for maintaining their activity to produce sulfur concentrations of the order of 0.05-0.1 wt% in the product oils.

A comparison can be obtained between Sphericat Nalco 474 catalyst in Run SC-E and Nalcomo 474 catalyst in Run SC-F with respect to the sulfur concentration in the product oils as shown in Figure 15. In Run SC-F, using Nalcomo 474 catalyst, 0.045 wt% S was observed in the product oil at ten hours of operation. The corresponding sulfur concentration at 10 hours of operation in Run SC-E was 0.02 wt%. After 30 hours of operation, Nalcomo 474 catalyst also gave 0.02 wt% S in the product oil. The catalyst, Nalcomo 474 then maintained its activity to give product oils containing 0.02 wt% S during the next 120 hours of operation. The Sphericat Nalco 474 catalyst maintained its activity during the entire 150 hours of operation to give 0.02

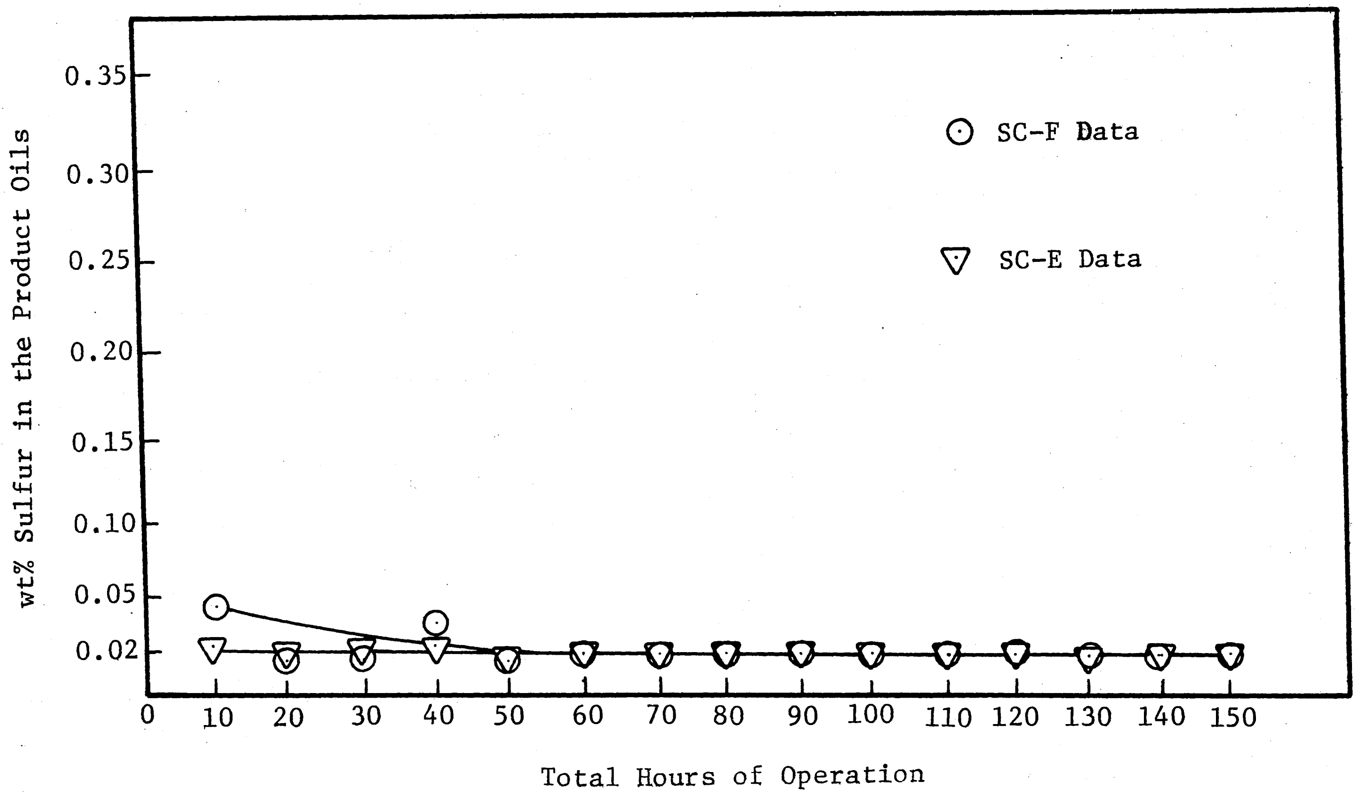

Figure 15. Comparison of Sphericat Nalco 474 Catalyst and Nalcomo 474 Catalyst in SC-E and SC-F Respectively at 700°F (371°C)

wt% S in the product oil. One can conclude from this comparison that the two catalysts can maintain their activity to produce oils containing 0.02 wt% S under the operational conditions encountered in these two runs. At least 150 hours of operation can be expected from these two catalysts for obtaining 0.02 wt% S in the product oil. However, more than 150 hours of operation is possible for obtaining sulfur concentration in the product oils beyond 0.05-0.1 wt%.

At higher temperatures, +800°F (427°F), there exists a possibility of increased cracking resulting in increased carbon depositions within the pores of the catalyst and also within the catalyst bed. These deposits can result in increased flow restrictions to the fluids within the catalyst bed and can lead to prematured shut down. This was observed in an earlier study (30) with FMC oil, feedstock of this thesis work, at 800°F (427°C) after only 50 hours of total operation. As mentioned in the previous chapter, two Runs of the present study SC-B with Sphericat Nalco 474 and SC-C with Nalcomo 474 catalyst were conducted at 800°F (427°C). The observed sulfur concentration in the product oils were as given in Table XVI and XVII. Objectives of the overall research program should be considered in assessing the importance of these two Runs, SC-B and SC-C. Since sulfur concentrations of the order of 0.05-0.1 wt% are considered to be satisfactory, analysis of the product oil at levels below 0.02 wt% are not within the scope of the program. The most interesting observation was that the two catalysts maintained their activity during the entire 200 hours of operation in SC-B and 100 hours of operation in SC-C, to give sulfur concentration below 0.02 wt%. Considering the low sulfur levels, analyses of which are beyond the scope of the overall program, Run SC-C was terminated after only 100 hours of operation. However, Run SC-B was continued for a total of 200 hours to assess the possible effect of increased flow restrictions on the operation. No significant flow restrictions were observed and the catalyst maintained its activity to give sulfur concentration below 0.02 wt% in the product oil even at the end of 200 hours.

Based on the above discussion, one can conclude that the Sphericat Nalco 474 catalyst can maintain its activity for more than 200 hours to give satisfactory sulfur levels of the order of 0.05-0.1 wt%, under the operational conditions encountered in Run SC-B. Similarly, more than 100 hours of operation can be expected from Nalcomo 474 catalyst to give 0.05-0.1 wt% S in the product oils under the operational conditions of Run SC-C. A distinction cannot be obtained between the two catalysts, Sphericat Nalco 474 with bimodal pore size distribution and Nalcomo 474 with unimodal pore size distribution, because of the low sulfur concentration observed in the product oils. However, a distinction can be obtained at lower space times because of the expected relatively higher sulfur concentrations in the product oils.

One of the main objectives of Run SC-D was to establish an upper temperature limit of 850°F (454°C) on the HDS operation in the overall program. As expected, concentrations well below 0.02 wt% S in the product oils were observed during the entire 145 hours of operation. No significant flow restrictions were observed during the operation at this rather high temperature. However, some pressure fluctuations of the order of 10-90 psi were observed after a total operation of 130 hours. The maximum pressure fluctuation observed during the last five hours of operation was 15 psi. Since a variation of 20 psi was considered satisfactory in this study, these fluctuations may not be due to increased flow restrictions in the reactor itself. This can happen also due to an increased flow restriction in the system, downstream from the reactor such as in flow control valves. The solid depositions within the reactor can result in prematured shut down at pressures lower than 1500 psig and at lower space times as observed in the earlier work (30) at 1000 psig.

Carbon Build-up on the Catalyst

The amount of carbonaceous material deposited on the catalyst can be taken as an indication of the potential for increased flow restrictions within the catalyst bed. As mentioned in the previous chapter, the catalysts were removed from the disengaged reactor after voluntary shut down and were heated in oxygen to burn off carbon. Little or no variations in catalyst weight on repeated heating were taken as a measure of the complete burn off of carbon deposited on the used catalysts. An effective loss in weight can be defined as the difference in weight loss of the used and fresh catalyst. These are summarized in Table XIV. An increase in catalyst weight due to the complete sulfiding of the Co and Mo species present in it is calculated to be 2.1% as shown in Appendix C. The feedstock initially had no ash in it as shown in Table VIII. Hence, the carbonaceous material deposited on the catalyst can be calculated as shown in Table XIV.

Molecules bigger than the micro pores can enter the macro pores present in a catalyst and take part in the cracking reactions. This may result in increased carbon depositions on the catalyst. However, this distinction cannot be made between the two catalysts used in this study. In the two Runs, SC-E using Sphericat Nalco 474 and SC-F using Nalcomo 474 catalysts at 700°F (371°C), the percent carbonaceous material deposited on the catalyst was observed to be 21.3 and 15.9 respectively. But in Run SC-B using Sphericat Nalco 474 and SC-C using Nalcomo 474 catalysts at 800°F (427°C), the carbonaceous deposits were 20.8 and 19.6% respectively. Most of the carbonaceous material seems to deposit during the first 100 hours of operation. The higher value of 38% obtained at 850°F (454°C) in Run SC-D is probably due to increased cracking at this rather high temperature level. At higher temperatures, relatively higher carbonaceous depositions due to cracking are not unusual.

TABLE XIV

EFFECTIVE LOSS IN WEIGHT OF USED CATALYSTS

Run Series	SC-A	SC-E	SC-B	SC-D	SC-C	SC-F
Temperature °F	700	700	800	850	800	700
Total Hours of Operation	100	150	200	145	100	150
Effective Loss in Weight, %=A	19.6	23.4	22.9	40.1	21.7	18.0
Increase in Catalyst Weight Due to Sulfiding, %=B	2.1	2.1	2.1	2.1	2.1	2.1
Carbonaceous Material Deposited, %*	17.5	21.3	20.8	38.0	19.6	15.0

* By difference in A and B

Beuther and Schmid (3) reported that in the case of heavier petroleum feedstocks, 10-20 wt% carbonaceous deposits were observed during the 16 days of operation. Most of these depositions were observed during the first 12 hours of operation. The relatively low H/C atom ratio in coal-derived liquids may result in relatively higher carbonaceous depositions than observed with petroleum feedstocks. Hence, these carbon accumulation results obtained in this study can be considered as reasonable.

An attempt can be made with the help of these results to obtain a plausible explanation for increased flow restrictions within the catalyst bed. Since these were observed in earlier studies (28), these should also be considered.

In the earlier studies (28), the reactor was packed with Nalcomo 474 catalyst to a height of 10 inches (25.4 cm) and the bed density was 0.72 gm/cc. In the present study the catalyst bed height was 12.75 inches (32.39 cm) and the bed density was 0.72 gm/cc. If the density of the catalyst based on alumina can be taken as one gm/cc and that of carbonaceous materials based on carbon to be also one gm/cc then, the volume of the voids present in the fresh catalyst bed can be calculated. If an assumption is made that, an equivalent amount of carbon deposited on the catalyst is also deposited within the catalyst bed voids then the decrease in bed porosity can be calculated. This decrease in bed voidage can result in increased flow restrictions within the catalyst bed. The present study was conducted at 1500 psig and no significant flow restrictions were observed even at a rather high temperature of 850°F (454°C). In the earlier work (28) at 800°F (427°C), lowering the pressure from 1500 psig to 1000 psig during the operation resulted very rapidly in prematured shut down of the run due to increased flow restrictions. This was also observed after only 30 hours of operation in another run of the earlier work (28) when the operation was started at 500 psig and 800°F (427°C). Operations at 700°F (371°C) were carried out smoothly in both the studies without any sign of increased flow restrictions within the catalyst bed or elsewhere in the system. This suggests that for operations at +800°F (427°C), the most suitable operating pressure is 1500 psig.

The experience with petroleum feedstocks (3) indicated relatively more rapid bed plugging at lower space times, of the order of one hours, than at higher space times, about two hours. At lower space times, the probability for the formation of lighter molecular fragments due to cracking and their escape along with the gaseous products is comparatively low. At higher space times the probability for the formation and escape of the lighter molecular fragments is comparatively more than at lower space times. This aspect can also be considered in obtaining a plausible explanation for the observed bed plugging in the earlier work (28).

A major difference in the two studies was the start up procedure. In the earlier work (28) oil and hydrogen were allowed to be on stream immediately after presulfiding the catalyst. The temperature was then increased gradually to the desired value. In the present study the catalyst bed was first heated gradually to within 10°F (6°C) of the desired value and then oil and hydrogen were allowed to be on stream. In the case of starting at higher temperatures and higher space times, the cracking products can escape with the gases leaving the system. If the operation is started at lower pressures and lower space times, the chances for the escape of relatively heavier cracked products can be less. These heavier products can further under go condensation and polymerization reactions. Accumulation of these condensation and polymerization products along with the carbonaceous material in the bed voids can result in increased pressure drop and/or increased restrictions to the flow of fluids.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions can be drawn based on the results of this study.

1) The experimental system used in this study was highly satisfactory to fulfill the over all objectives of the program to obtain 0.05-0.1 wt% S in the product oils. In fact, lower sulfur concentrations of the order of 0.02 wt% and below were obtained with satisfactory maintenance of operational conditions.

2) Successful operation was conducted using Sphericat Nalco 474 catalyst for 145 hours at 1500 psig, 2.99 hours (liquid volume hourly space time), 7500 standard cubic feet Hydrogen per barrel of FMC oil and at a rather high temperature of $850^{o}F$ ($454^{o}C$).

3) Sphericat Nalco 474 and Nalcomo 474 catalysts maintained their activity at $800^{o}F$ ($427^{o}C$) and under the operational conditions of this study to give more than 94% sulfur removal from FMC oil. In fact, 94% sulfur removal was observed only after five hours of operation and even at the end of 200 hours for Sphericat Nalco 474 catalyst and 100 hours for Nalcomo 474 catalyst.

4) Even at a temperature as low as $700^{o}F$ ($371^{o}C$) the two catalysts Sphericat Nalco 474 and Nalcomo 474 maintained their activity to give 94% sulfur removal during the 150 hours of operation.

5) Under the operational conditions of this study, the presence of macropores in the bidispersed Sphericat Nalco 474 catalyst provided no advantage over the Nalcomo 474 catalyst having only unimodal pore size distribution. This advantage of the presence of macropores in a catalyst can become obvious at less severe operating conditions of temperature, pressure and space time.

6) The extent of catalyst presulfiding seems to have an effect on the desulfurization activity of the catalyst. Relatively less amount of H_2S (presulfiding agent) supplied during the catalyst presulfiding resulted in slightly decreased activity of the Co-Mo-Alumina catalyst.

7) At 850°F (427°C), the increased tendency for cracking and carbonization can lead to increased carbon build-up within the catalyst bed as well as on the catalyst itself.

8) Most of the carbon build-up on the catalyst seems to take place during the first 100 hours of operation.

9) Operational problems can be encountered due to the blocking of the catalyst bed itself and/or the narrow orifices present in the controllers downstream from the reactor because of the carbonaceous deposits at higher temperatures.

Recommendations

The following recommendations are made on the basis of the results of the present study.

1) Catalysts with different metallic combinations and compositions should be studied for the hydrodesulfurization of coal derived liquids and a comparison should be obtained between them.

2) Coal-derived liquids obtained from different sources should be processed so as to become capable of tailoring catalyst for their hydrodesulfurization.

3) Experimental runs should be conducted at less severe operational conditions of temperature, pressure and space time to observe the possible advantage of the bimodal pore size distribution in a catalyst.

4) Experimental runs should be conducted for more than 2000 hours to assess the catalyst active life for hetero-atom removal.

5) Distillation tests should be carried out to assess the simultaneous hydrocracking activity of the catalyst.

6) A comparison should be obtained on the effectiveness of the catalyst presulfiding agent by using other compounds like CS_2 instead of H_2S.

7) The effect of the concentration of H_2S in the feed gas on the desulfurization activity of the catalyst should be studied. This can be done by recycling the gases coming out of the reactor while controlling its H_2S concentration. These gases contain more than 90% hydrogen, some hydrogen sulfide and the rest lighter hydrocarbons with some water vapor.

8) Experiments should be conducted to assess the affect of metallic impurities present in the feedstock on the activity of the catalyst. This can be done by processing feedstocks encountered in industrial practice or by introducing metallic impurities in a feedstock like raw anthracene oil or FMC oil.

9) Experiments should be designed to study the effect of start up procedures on the catalyst activity in the long run (about 2000 hours). This can be done by starting an experiment at lower temperature

and/or pressure and then increasing them to the desired operational level. A fixed combination of pressure, temperature and space time should be studied during a particular run. These procedures of start up should be compared with those starting at the desired operational levels of temperature, pressure and space time.

10) Additional tests should be conducted on the carbonaceous and metallic depositions, if any, on the catalyst.

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APPENDIX A

SAMPLE CALCULATIONS FOR SULFUR ANALYSIS

A furnace factor "F" was calculated to account for the possible error due to incomplete combustion of the sample. A sample of known sulfur concentration was analyzed to determine this furnace factor. The calculations were as shown below:

$$\text{Furnace factor, "F"} = \frac{(\text{Sample wt})\text{x}(\text{Known wt\% S})}{(\text{Volume titrated - Blank})}$$

This furnace factor can be used for calculating the sulfur concentration in an oil sample as follows:

$$\text{wt\% S} = (\text{F})\frac{(\text{Volume titrated - Blank})}{(\text{Sample weight})}$$

For example:

F = 0.164

Sample weight = 0.02749 gms

Blank = 0.034

Volume titrated = 0.093

wt% S = 0.352

APPENDIX B

LIQUID HOLD EFFECTS IN TRICKLE BED REACTORS

The use of the following inequality in the case of negligible backmixing effects has been suggested by Paraskos, Frayer and Shah (32) for negligible liquid hold up effects:

$$\ln \frac{C_{A_i}}{C_{A_o}} = \frac{k' \, (h)^b}{(\mathrm{LHSV})^{1-b}} \quad \text{where } k' \text{ and } b \text{ are constants.}$$

In the present study the catalyst bed height, "h" was 12.75 inches while in a previous study (28) in this laboratory unit the catalyst bed height for hydrodesulfurizing FMC oil under comparable operational conditions was 10 inches. The liquid volume hourly space time in the present study was 2.99 hours compared to 3.14 hours in the previous study (28). Therefore

$$\frac{(\ln C_{A_i}/C_{A_o})_1}{(\ln C_{A_i}/C_{A_o})_2} = \frac{k'_1 \, (h_1)^b/(\mathrm{LHSV})_1^{1-b}}{k'_2 \, (h_2)^b/(\mathrm{LHSV})_2^{1-b}} \qquad (1)$$

For the present study:	For the previous study (28):
C_{A_i} = 0.35 wt% S	0.35 wt% S
C_{A_o} = 0.02 wt% S @ 800°F, 1500 psig	0.039 wt% S @ 800°F, 1500 psig
h = 12.75 inches	10.00 inches
LHSV = 1/(2.99 hours)	1/(3.14 hours)

Since temperature and pressure for both the studies are the same and there is only a slight difference in space time hence "k'" a function of temperature, pressure and space time can be considered constant. Substituting the values of the various factors in equation (1) we get:

$$b = 1.62$$

In the original model "b" lies between "0 and 1" for negligible liquid hold up effects.

APPENDIX C

SULFIDING OF Co AND Mo SPECIES PRESENT IN THE CATALYST

Cobalt and molybdenum species present in the catalyst can be assumed to be completely sulfided. Mitchell (23) reported that in an industrially sulfided Co-Mo-Alumina catalyst the atomic ratios were 1.0 Co : 1.77 Mo : 4.18 S. However, the actual requirement for complete sulfiding of the Co and Mo species present in the catalyst was such as to give 1.0 Co : 4.43 S. Hence, the effect of the approximation of complete sulfiding made in this study can be negligible on the conclusions drawn.

The two catalysts used in this study, Nalcomo 474 and Sphericat Nalco 474, contained the same amount of Co and Mo species in them. Cobalt was present in the form of CoO to the extent of 3.5 wt% of the catalyst compared to 12.5 wt% of MoO_3.

Co, Atoms	0.0467	S, Atoms required for forming Co_9S_8	$\cong$	0.0467
Mo, Atoms	0.0868	S, Atoms required for forming MoS_2		2(0.0868)
		S, Total Atoms required		0.2203

CoO	3.5	Co_9S_8	≅	4.25
MoO_3	12.5	MoS_2		13.89
Alumina	84.0	Alumina		84.00
Total weight of Catalyst	100.0			102.14

Therefore increase in catalyst weight due to sulfiding was 2.14 wt%.

Sulfur required in the form of H_2S for complete sulfiding of Co and Mo species present in the catalyst was as follows:

H_2S required = (S atoms required for complete sulfiding) (34)

where the molecular weight of H_2S is 34.

H_2S required = (0.2203)(34) = 7.49 grams of H_2S per 100 grams of catalyst

H_2S supplied during presulfiding = (0.0514 cc H_2S per cc of H_2S-H_2 Mixture)x (25 cc/8 sec)x(90 x 60 sec)x($273^oK/298^oK$)x (1 gm-mole/22,400 cc)x(34 gm/gm-mole) = 1.21 gms H_2S

APPENDIX D

EXPERIMENTAL DATA

Experimental data were taken at 1500 psig, 2.99 liquid volume hourly space time and 7500 scf H_2/bbl FMC oil for temperatures of 700^{o}F (371^{o}C), 800^{o}F (427^{o}C) and 850^{o}F (454^{o}C) using Sphericat Nalco 474 catalyst and for 700^{o}F (371^{o}C) and 800^{o}F (427^{o}C) using Nalcomo 474 catalyst. The product oils were analyzed for sulfur concentration using a Leco automatic sulfur analyzer. Complete details of the data and the results are given in the following tables.

TABLE XV

EXPERIMENTAL DATA USING SPHERICAT NALCO 474 CATLYST IN RUN SC-A

Sample Number	Temperature °F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#1	700	1510	2.99	6919	5	0.210	40
#2	700	1505	2.99	7500	10	0.163	53
#3	700	1500	2.99	8188	15	0.109	69
#4	700	1503	2.99	8932	20	0.119	66
#5	700	1512	2.99	7777	25	0.120	66
#6	700	1507	2.99	7656	30	0.108	69
#7	700	1510	2.99	7860	35	0.084	76
#8	700	1502	2.99	7597	40	0.068	81
#9	700	1515	2.99	8878	45	0.065	81
#10	700	1505	2.99	7443	50	0.070	80
#11	700	1501	2.99	7314	55	0.075	79
#12	700	1502	2.99	7798	60	0.066	81
#13	700	1510	2.99	8421	65	0.063	82
#14	700	1511	2.99	7696	70	0.069	80
#15	700	1504	2.99	7369	75	0.063	82
#16	700	1502	2.99	8543	80	0.053	85
#17	700	1514	2.99	8120	85	0.057	84
#18	700	1495	2.99	7923	90	0.045	87
#19	700	1509	2.99	7538	95	0.057	84
#20	700	1516	2.99	6839	100	0.064	82

TABLE XVI

EXPERIMENTAL DATA USING SPHERICAT NALCO 474 CATALYST IN RUN SC-B

Sample Number	Temperature °F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#1	800	1500	2.99	6807	5	x	xx
#2	800	1504	2.99	6985	10	x	xx
#3	800	1506	2.99	8256	15	x	xx
#4	800	1512	2.99	8165	20	x	xx
#5	800	1502	2.99	7387	25	x	xx
#6	800	1504	2.99	7777	30	x	xx
#7	800	1514	2.99	8233	35	x	xx
#8	800	1512	2.99	7716	40	x	xx
#9	800	1507	2.99	8120	45	x	xx
#10	800	1508	2.99	7636	50	x	xx
#11	800	1503	2.99	6760	55	x	xx
#12	800	1507	2.99	8279	60	x	xx
#13	800	1517	2.99	8188	65	x	xx
#14	800	1508	2.99	6699	70	x	xx
#15	800	1503	2.99	8303	75	x	xx
#16	800	1503	2.99	7577	80	x	xx
#17	800	1498	2.99	7350	85	x	xx
#18	800	1520	2.99	9357	90	x	xx
#19	800	1514	2.99	7332	95	x	xx
#20	800	1505	2.99	7332	100	x	xx
#21	800	1505	2.99	7242	105	x	xx
#22	800	1508	2.99	8264	110	x	xx
#23	800	1506	2.99	8010	115	x	xx

TABLE XVI (Continued)

Sample Number	Temperature ^{o}F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#24	800	1511	2.99	6669	120	x	xx
#25	800	1508	2.99	8932	125	x	xx
#26	800	1504	2.99	7860	130	x	xx
#27	800	1502	2.99	7676	135	x	xx
#28	800	1512	2.99	7443	140	x	xx
#29	800	1506	2.99	7369	145	x	xx
#30	800	1504	2.99	7332	150	x	xx
#31	800	1506	2.99	7207	155	x	xx
#32	800	1508	2.99	7314	160	x	xx
#33	800	1500	2.99	7068	165	x	xx
#34	800	1510	2.99	6714	170	x	xx
#35	800	1506	2.99	7068	175	x	xx
#36	800	1500	2.99	7945	180	x	xx
#37	800	1508	2.99	8188	185	x	xx
#38	800	1510	2.99	7406	190	x	xx
#39	800	1502	2.99	6729	195	x	xx
#40	800	1508	2.99	7332	200	x	xx

x = wt% S below 0.02
xx = Sulfur Removal more than 94%

TABLE XVII

EXPERIMENTAL DATA USING NALCOMO 474 CATALYST IN RUN SC-C

Sample Number	Temperature ^oF	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#1	800	1494	2.99	7777	5	x	xx
#2	800	1502	2.99	6952	10	x	xx
#3	800	1505	2.99	7597	15	x	xx
#4	800	1505	2.99	7350	20	x	xx
#5	800	1517	2.99	7650	25	x	xx
#6	800	1511	2.99	6594	30	x	xx
#7	800	1505	2.99	8031	35	x	xx
#8	800	1504	2.99	8593	40	x	xx
#9	800	1500	2.99	7462	45	x	xx
#10	800	1500	2.99	7443	50	x	xx
#11	800	1509	2.99	7154	55	x	xx
#12	800	1503	2.99	8303	60	x	xx
#13	800	1505	2.99	7902	65	x	xx
#14	800	1507	2.99	7198	70	x	xx
#15	800	1504	2.99	7902	75	x	xx
#16	800	1508	2.99	7406	80	x	xx
#17	800	1503	2.99	7035	85	x	xx
#18	800	1507	2.99	6784	90	x	xx
#19	800	1506	2.99	7696	95	x	xx
#20	800	1503	2.99	9328	100	x	xx

x = wt% S below 0.02

xx = Sulfur Removal more than 94%

TABLE XVIII

EXPERIMENTAL DATA USING SPHERICAT NALCO 474 CATALYST IN RUN SC-D

Sample Number	Temperature °F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#1	850	1501	2.99	7251	5	x	xx
#2	850	1505	2.99	6669	10	x	xx
#3	850	1504	2.99	8010	15	x	xx
#4	850	1506	2.99	7500	20	x	xx
#5	850	1501	2.99	6714	25	x	xx
#6	850	1497	2.99	8606	30	x	xx
#7	850	1504	2.99	8421	35	x	xx
#8	850	1507	2.99	7757	40	x	xx
#9	850	1511	2.99	7415	45	x	xx
#10	850	1505	2.99	6855	50	x	xx
#11	850	1504	2.99	7120	55	x	xx
#12	850	1509	2.99	7102	60	x	xx
#13	850	1508	2.99	7120	65	x	xx
#14	850	1507	2.99	7120	70	x	xx
#15	850	1513	2.99	7892	75	x	xx
#16	850	1494	2.99	7839	80	x	xx
#17	850	1500	2.99	9825	85	x	xx
#18	850	1509	2.99	9585	90	x	xx
#19	850	1502	2.99	7434	95	x	xx
#20	850	1507	2.99	7051	100	x	xx
#21	850	1495	2.99	7966	105	x	xx
#22	850	1499	2.99	9041	110	x	xx
#23	850	1515	2.99	7902	115	x	xx

TABLE XVIII (Continued)

Sample Number	Temperature °F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#24	850	1509	2.99	7443	120	x	xx
#25	850	1510	2.99	6968	125	x	xx
#26	850	1505	2.99	8772	130	x	xx
#27	850	1507	2.99	8350	135	x	xx
#28	850	1515	2.99	7860	140	x	xx
#29	850	1524	2.99	8932	145	x	xx

x = wt% S below 0.02
xx = Sulfur Removal more than 94%

TABLE XIX

EXPERIMENTAL DATA USING SPHERICAT NALCO 474 CATALYST IN RUN SC-E

Sample Number	Temperature °F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#1	700	1506	2.99	6792	10	0.02	94
#2	700	1509	2.99	7865	20	0.02	94
#3	700	1503	2.99	8026	30	0.02	94
#4	700	1507	2.99	8233	40	0.02	94
#5	700	1506	2.99	8727	50	0.02	94
#6	700	1506	2.99	6839	60	0.02	94
#7	700	1508	2.99	8309	70	0.02	94
#8	700	1507	2.99	7269	80	0.02	94
#9	700	1506	2.99	7163	90	0.02	94
#10	700	1510	2.99	8338	100	0.02	94
#11	700	1507	2.99	8669	110	0.02	94
#12	700	1505	2.99	7060	120	0.02	94
#13	700	1502	2.99	6976	130	0.02	94
#14	700	1506	2.99	7854	140	0.02	94
#15	700	1506	2.99	7854	140	0.02	94

TABLE XX

EXPERIMENTAL DATA USING NALCOMO 474 CATALYST IN RUN SC-F

Sample Number	Temperature °F	Pressure psig	Space Time Hours	H_2/Oil Ratio scf/bbl	Total Hours of Operation	wt% S in Product Oils	% Sulfur Removal from FMC Oil
#1	700	1507	2.99	8733	10	0.045	87
#2	700	1506	2.99	8421	20	0.02	94
#3	700	1509	2.99	7966	30	0.02	94
#4	700	1510	2.99	6118	40	0.031	91
#5	700	1509	2.99	7757	50	0.02	94
#6	700	1510	2.99	7839	60	0.02	94
#7	700	1510	2.99	7548	70	0.02	94
#8	700	1504	2.99	7818	80	0.02	94
#9	700	1506	2.99	9211	90	0.02	94
#10	700	1503	2.99	8891	100	0.02	94
#11	700	1507	2.99	8494	110	0.02	94
#12	700	1507	2.99	8669	120	0.02	94
#13	700	1508	2.99	9083	130	0.02	94
#14	700	1511	2.99	8531	140	0.02	94
#15	700	1500	2.99	8733	150	0.02	94

2

VITA

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Master of Science

Thesis: AN INVESTIGATION OF THE ACTIVITY OF TWO COBALT-MOLYBDENUM-ALUMINA CATALYSTS FOR HYDRODESULFURIZATION OF FMC OIL, A COAL-DERIVED LIQUID

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