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**CATALYSTS FOR HYDROCRACKING AND REFINING HEAVY OILS AND TARS
PART 3: THE EFFECT OF PRESULPHIDING CONDITIONS ON CATALYST
PERFORMANCE**

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Catalysts for Hydrocracking and Refining Heavy
Oils and Tars, Part 3: The Effect of
Presulphiding Conditions on Catalyst Performance

by

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ABSTRACT

Catalysts used in commercial hydrorefining reactors are often presulphided with CS_2 or some other sulphur compound prior to the introduction of the hydrocarbon feedstock. The presulphiding process converts the catalyst from its oxidized form to a sulphided form. Increased catalyst life and catalyst activity have frequently been obtained by presulphiding. Virtually all industrial experience with presulphiding has been obtained with top feed trickle bed reactors, usually with a naphtha or gas oil feedstock which is in the vapour phase under reaction conditions. In contrast studies at the Energy Research Laboratories have been performed with bottom feed liquid phase reactors and higher boiling feedstocks such as bitumens or heavy gas oils. In order to determine whether or not similar beneficial effects occur with the reaction systems used at the Energy Research Laboratories, a series of presulphiding experiments was performed. It was found that the sulphur content of the catalyst could vary from 2 to 4 wt % depending upon the presulphiding conditions used. After the catalyst had been in contact with the reaction mixture, its sulphur content approached the value required for all of the nickel and molybdenum in the catalyst to exist as Ni_3S_2 and MoS_2 . The properties of the liquid hydrocarbon product and the wt % coke in the catalyst were found to be approximately the same regardless of the presulphiding conditions used. Presulphiding with the feedstock produced essentially the same results as presulphiding with other materials such as CS_2 and H_2S . The high sulphur content in the feedstock and the liquid phase operation of the reactor probably combined to produce the favourable results obtained when the feedstock was used for presulphiding.

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LIST OF FIGURES

	<u>Page</u>
ABSTRACT	i
RESUME	ii
INTRODUCTION	1
EXPERIMENTAL	2
Equipment and Procedures for Reaction Studies	4
Materials	4
Presulphiding Procedures	6
Analytical Techniques	6
RESULTS AND DISCUSSION	11
The Effect of CS ₂ Presulphiding on Gas Oil Hydrorefining	11
The Effect of CS ₂ Presulphiding Conditions on Catalyst Sulphur Content	19
The Effect of the Reaction Mixture on Catalyst Sulphur Content	19
Coke and Distillable Oil Accumulated by the Catalyst	22
The Effect of Presulphiding with Materials Other than CS ₂	26
CONCLUSIONS	29
REFERENCES	30

LIST OF FIGURES

Figure No.

1	The Correction Curve for Sulphur Analyses by the Eschka Method	10
2	The Effect of the Catalyst Sulphur Content after Presulphiding on Liquid Product Properties	12
3	The Effect of the Catalyst Sulphur Content after Presulphiding on Hydrocracking	14
4	The Effect of the Catalyst Sulphur Content after Presulphiding on its Sulphur Content after Reaction	21
5	The Effect of the Catalyst Sulphur Content after Presulphiding on Coke Deposition	24

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
1	Hydrorefining Reaction Conditions	3
2	Properties of the Feedstock	5
3	Comparison of Reaction Results Obtained Using Three Different Batches of Identical Catalyst	5
4	Carbon Disulphide Presulphiding Conditions	7
5	Summary of the Distillation Analyses and the Sulphur Contents of the Distillate Fractions of the Feedstock and of the Products Obtained at 400°C	15
6	Catalyst Composition and Liquid Product Properties Obtained at Various Presulphiding Conditions	20
7	Catalyst Coke Content	25
8	Changes in Hydrocarbon Product Properties Caused by H ₂ S Presulphiding	28
9	Changes in Catalyst Sulphur and Coke Content Caused by H ₂ S Presulphiding	28

INTRODUCTION

A number of investigations (1, 2) designed to determine the effect of catalyst composition and of catalyst preparation methods on the hydrocracking and refining of heavy tars and oils have been performed at the Energy Research Laboratories. This report is the third in this series. It describes the changes in catalyst performance caused by varying the conditions used to presulphide the catalyst. Catalyst presulphiding is known to produce higher catalyst activity and longer catalyst life in many cases (3). Recent results obtained by Aoshima and Wise (4) for the hydrodesulphurization of n-butyl mercaptan indicate that there may be a relationship between coke formation on the catalyst and catalyst sulphur content.

Both metals deposition and coke formation contribute to the catalyst fouling which occurs when heavy oils such as Athabasca bitumen are hydrocracked (5). The metals cause a relatively slow but permanent decline in catalytic activity. In contrast the decrease in catalyst activity due to coke formation is extremely rapid. For example the weight percent sulphur in the liquid product has been found to double within 50 hours. It has been shown (5) that the loss in activity was predominantly caused by coke formation. This illustrates the tremendous impact of coke on the life and activity of hydrocracking catalysts. Any techniques which minimize the formation of coke on the catalyst, such as presulphiding, could produce a vast improvement in catalyst life.

The effects of presulphiding obtained with the reactor configuration used at the Energy Research Laboratories may be different than those reported in the literature for trickle bed reactors (3). It has been shown (6, 7) that, for heavy residual oils, it is advantageous to have the mixture of hydrogen and hydrocarbon feed enter the bottom of the reactor rather than the top, as is the case in trickle bed reactors. In the bottom feed configuration any low boiling material will pass through the reactor relatively quickly because it is in the vapour phase. In contrast the high boiling hydrocarbon in the liquid phase will have a much longer residence time and therefore a greater likelihood of being hydrocracked. Liquid phase material tends to have a shorter residence time in trickle bed reactors than in bottom feed reactors. Also, the problems sometimes encountered with liquid distribution in trickle bed reactors, do not exist

in bottom feed reactors. The bottom feed reactor configuration used at the Energy Research Laboratories is sufficiently attractive that it is now being studied in other laboratories (8) and also for other systems (9).

The objective of this study was to identify optimum presulphiding conditions for a catalyst used in a bottom feed reactor configuration. As a result, all of the experiments were performed on the same catalyst formulation. Furimsky and Amberg (10) recently showed that hydrodesulphurization catalysts having only slightly different cobalt to molybdenum ratios are presulphided to different extents, even when the same presulphiding conditions were used. In order to simplify the investigation, all experiments were performed using catalyst pellets having the same composition. The variables studied were temperature, partial pressure, total pressure, and type of presulphiding compound.

EXPERIMENTAL

Several different experimental measurements were made in order to determine the effectiveness of a particular set of presulphiding conditions. After catalyst presulphiding, hydrorefining reaction studies were performed using heavy gas oil. The catalyst activity was evaluated in terms of the quality (wt % S and wt % N) of the hydrorefined liquid produced by each presulphided batch of catalyst. The amount of coke deposited on the catalyst during the hydrorefining reactions was taken as a relative indication of catalyst life. Attempts were made to relate the amount of coke formation to the sulphur content of the catalyst and to the catalyst presulphiding conditions.

Each experiment in the investigation consisted of a sequence of operations:

- A. The oxide form of the catalyst was presulphided inside the hydrocracking reactor.
- B. After presulphiding the catalyst was removed from the reactor and its sulphur content measured.
- C. Another batch of oxide catalyst was presulphided repeating the experimental conditions used in step A.

- D. A heavy gas oil derived from Athabasca bitumen was hydrocracked and hydrodesulphurized in the presence of the presulphided catalyst. In most cases two experiments, one at 400°C (673 K) and the other at 450°C (723 K) were performed. In a few cases a series of four consecutive experiments were performed at reaction temperatures of 400°C (673 K), 420°C (693 K), 400°C (673 K) and 380°C (653 K). The other operating conditions are shown in Table 1.
- E. The samples of oil obtained during gas oil hydrodesulphurization were analyzed. Specific gravity, sulphur and nitrogen measurements as well as fractional distillations were performed.
- F. The catalyst removed from the reactor after gas oil hydrodesulphurization was analyzed for sulphur and coke.

Details of each of the above steps are outlined below. The equipment used for the presulphiding and for the reaction experiments, the procedures followed in performing the experiments, the methods used to analyze the liquid oil samples and the solid catalyst samples, and the materials used, are also described below.

TABLE 1

Hydrorefining Reaction Conditions

Pressure	2000 psig (13.9 M Pa)
Gas Oil Flowrate	200 ml/hr (55.6 ml/ks)
H ₂ Flowrate	5000 cf/bbl (0.0572 l/sec at STP)
Liquid Volumetric Space Velocity	2.0 hr ⁻¹ (0.56 ks ⁻¹)
Temperature	as specified

Equipment and Procedures for Reaction Studies

The experimental equipment used for presulphiding and for gas oil hydrorefining reaction studies has been described in detail previously (11). Therefore, only a brief description will be given here. The high pressure reactor had an inside diameter of one inch (25.4 mm) and an internal length of 12 inches (0.305 m). The bottom 3 inches (76.2 mm) and the top inch (25.4 mm) of the reactor were filled with porcelain berl saddles. The other 8 inches (0.2032 m) of the reactor were filled with 100 ml of catalyst particles. For the presulphiding experiments the reactants consisted of a mixture of either carbon disulphide dissolved in toluene and hydrogen or hydrogen sulphide and hydrogen. The reactants consisted of gas oil and hydrogen for the hydrorefining reaction studies. The reactants entered the bottom of the reactor and flowed up through the bed of catalyst particles. The reaction products flowed from the top of the reactor into one of two receiver vessels where the vapour and liquid were separated. One of the receiver vessels was used during startup, shutdown, and other periods of transient operation. The second receiver vessel was used during the steady state sampling period.

Materials

Several different materials were used in this study. The gas oil consisted of the 650-975^oF (345-525^oC) portion of the liquid product obtained by thermally hydrocracking Athabasca bitumen in the Energy Research Laboratories pilot plant. Its properties are shown in Table 2. The hydrogen was made by the electrolysis of water and had a purity of 99.9 wt %. The carbon disulphide was the purified grade obtained from Fisher Scientific (C-183). The hydrogen sulphide was obtained from the Matheson Company and was stated to have a purity of 99.5 percent. The catalyst was prepared using the same procedure described previously (2). In the oxide form it contained 2.1 wt % NiO and 5.4 wt % MoO₃ supported on γ -alumina. It was necessary to make three different batches of catalyst to ensure that there would be an adequate amount for the entire series of experiments. Reaction results for each of the three batches, shown in Table 3, were similar. Therefore, the three batches of catalyst powder were mixed together. Catalyst pellets formed from the mixture were used in all of the presulphiding experiments described here.

TABLE 2

Properties of the Feedstock

Boiling Range	650-975 ^o F (345-525 ^o C)
Specific Gravity 60/60 ^o F ...	0.987
Conradson Carbon Residue ..	0.97 wt %
Sulphur	3.64 wt %
Nitrogen	0.38 wt %
Vanadium	<1 ppm
Kinematic Viscosity	108.8 cSt at 100 ^o F

TABLE 3

Comparison of Reaction Products Obtained Using
Three Different Batches of Identical Catalyst

Catalyst No.	Reaction at 400 ^o C			Reaction at 450 ^o C		
	Spec. Grav. 60/60 ^o F	Sulphur (wt. %)	Nitrogen (wt %)	Spec. Grav. 60/60 ^o F	Sulphur (wt %)	Nitrogen (wt %)
MB 165	0.940	0.78	0.246	0.907	0.12	0.112
MB 212	0.942	0.91	0.272	0.909	0.15	0.136
MB 211	0.942	0.81	0.234	0.908	0.15	0.125

Presulphiding Procedures

Carbon disulphide presulphiding experiments were performed using the conditions shown in Table 4. The same procedure was followed in each experiment. The reaction system was pressurized with hydrogen and the reactor temperature raised to 150°C (323 K). At this temperature the flowrates of both the hydrogen and the carbon disulphide-toluene solution, shown in Table 4, were established. The temperature was subsequently raised to the desired value, maintained for 1½ hours, and finally decreased to ambient. The flow of hydrogen and of carbon disulphide-toluene solution were stopped when the reactor had cooled to 150°C (323 K).

A different procedure was followed when a mixture of hydrogen and hydrogen sulphide was used to presulphide the catalyst. Presulphiding was performed at a temperature of 400°C (673 K), a pressure of 1 atm (0.101 MPa) with a hydrogen flowrate of 5 cu ft/hr (39.4 ml/sec at STP). Both hydrogen and hydrogen sulphide flowed through separate water bubblers prior to mixing. The number of bubbles passing through each bubbler per unit time was controlled in order to maintain approximately 15 volume percent hydrogen sulphide in the mixture. While the H₂-H₂S mixture was flowing, the reactor temperature was raised from ambient to 400°C (673 K) in approximately 3 hours (10.8 ks), maintained at 400°C for 1 hour (3.6 ks), and cooled to 250°C (523 K). At 250°C the flow of H₂S was stopped, but the H₂ flow was continued for an additional 15 minutes (0.9 ks).

The third substance used for catalyst presulphiding was the gas oil described previously. The presulphiding temperature was 400°C (673 K), and the other presulphiding conditions were the same as those shown for hydrorefining in Table 1. The operational procedure was identical to that used for the hydrorefining reaction studies.

Analytical Techniques

Several of the techniques used to analyze the hydrocarbon liquids have been described in detail previously (1, 2). The specific gravity of the liquid products was measured with a hand hydrometer. The sulphur content was determined using an X-Ray fluorescence technique (12) and the nitrogen content was measured using a hydrogenation micro-coulometric apparatus (13).

TABLE 4

Carbon Disulphide Presulphiding Conditions

Run No.	Temperature		Total Pressure		H ₂ Flowrate		CS ₂ Solution* Flowrate		Moles CS ₂ hr ⁻¹	Partial Press. CS ₂	
	(°C)	(°K)	(psi)	(M Pa)	(cu ft/hr)	(ml/sec)	(ml/hr)	(ml/ks)	Moles H ₂ hr ⁻¹ x 10 ²	(psi)	(k Pa)
16	400	673	2015	13.9	7.27	57.2	gas oil used		-	-	
7B	400	673	25	0.172	6.27	49.3	483.3	134.3	5.40	0.820	5.65
13B	400	673	25	0.172	1.23	9.7	490.7	136.3	27.9	1.610	11.1
19B	400	673	765	5.27	6.61	52.0	488.7	135.8	5.19	24.48	168.8
11B	400	673	2015	13.9	6.53	51.4	496.7	138.0	5.33	65.7	453.0
9B	200	473	25	0.172	6.63	52.2	493.3	137.0	5.23	0.805	5.55
21B	300	573	25	0.172	6.11	48.1	505.3	140.4	5.80	0.858	5.92

*The CS₂ was dissolved in toluene to give a solution of 0.818 mole CS₂ per litre.

Distillation analyses were obtained using a modification of the US Bureau of Mines Hempel Distillation Procedure (14). When the distillation analyses of feed and product samples were compared, the change in the amount of material boiling at a particular temperature was apparent. This was used as an indication of the amount of hydrocracking or molecular weight reduction that had occurred.

The following procedure adapted from earlier work (7) was used to measure the amount of distillable hydrocarbon and non-distillable char (coke) which remained on the catalyst after the hydrocracking experiments. Stainless steel screen (100 mesh U.S. Standard Sieve Series) was used to construct three boxes, four inches (10.2 cm) in length, which would fit side by side in the tube reactor. The bottom of the reactor was filled with six inches of porcelain berl saddles. Above were placed the screen boxes, each containing a weighed sample of about eight grams of catalyst pellets. Hydrogen was passed over the catalyst pellets at a rate of 3.6 cu ft/hr (28.3 ml/sec at STP) as the temperature was raised over a period of about two hours to 530°C (803 K). The hydrogen flow was then stopped and the reactor allowed to cool to approximately 150°C in the presence of H₂. At this point nitrogen was passed through the reactor while the catalyst particles were being removed. By preventing air from contacting the catalyst, weight changes due to oxidation or adsorption of water vapour were minimized. The catalyst was allowed to cool to room temperature in a desiccator before being weighed. The change in weight was ascribed to the amount of distillable oil removed from the catalyst. The catalyst was then left overnight in a muffle furnace at 600°C (873 K). After the sample was removed from the furnace, it was allowed to cool to room temperature in a desiccator before finally being weighed. This second weight change was ascribed to char (coke) being burned from the catalyst. Each of the weight changes was expressed as a percent of the final catalyst weight (oil and char free).

An ultimate analysis for carbon and hydrogen (15) was used as a second measure of the coke content of the catalysts. The weighed sample was burned in a closed system and the products of combustion were collected in an absorption train. After correcting the reported H content for the hydrogen contained in the moisture in the catalyst, the hydrogen and carbon values were added to provide an indication of the amount of coke on the catalyst.

The sulphur content of the catalyst was measured using the Eschka method (16, 17). The sample, in the form of fine powder, was completely surrounded by Eschka mixture (2 parts by weight MgO and one part Na_2CO_3). It was then heated to 800°C (1073 K). The presence of the Eschka mixture caused the sulphur in the catalyst to be converted to sulphate rather than gaseous sulphur dioxide. The solids were dissolved in water, barium chloride was added, and a barium sulphate precipitate was formed. The weight percent sulphur in the catalyst was calculated from the weight of the barium sulphate precipitate.

Other cations, such as Al^{+3} and Na^{+2} , are known to form sulphates which co-precipitate with the barium sulphate (17). An attempt to quantitatively measure the extent of co-precipitation was made, since the catalyst being studied had a large Al^{+3} content. Amounts of elemental sulphur varying from 0 to 5 weight percent were added to samples of the powdered catalyst in its initial oxide form. The amount of sulphur in these samples as measured by the Eschka method has been compared with the known amount of elemental sulphur in the samples in Figure 1. Results obtained by adding $\text{NiSO}_4 \cdot \text{H}_2\text{O}$ to the powdered catalyst instead of elemental sulphur fell on the same curve. However, different results were obtained when NaSO_3 was added to the catalyst powder. This was probably caused by the co-precipitation of the sodium ions.

When a presulphided catalyst which had not contacted the gas oil was exposed to air while being removed hot from the reactor, an odour attributed to SO_2 was readily apparent. Presumably the formation of SO_2 occurred when oxygen in the air reacted with molybdenum and nickel sulphides to form the corresponding oxides. De Beer has reported the same phenomenon for presulphided Co-Mo-Al catalysts (18).

In order to obtain a correct analysis of sulphur in the catalyst, all of the sulphur had to remain in the solid phase until the catalyst had been combined with the Eschka mixture. Therefore, precautions were taken to minimize the exposure of the presulphided catalyst to air. As soon as the reactor was removed from the reaction system, a flow of nitrogen was established through the catalyst bed. This procedure helped to remove hydrogen sulphide, carbon disulphide, toluene and any reaction products. While the nitrogen continued to flow, the reactor was opened and a sample of catalyst pellets was taken from a position approximately 4 inches (0.1 m) below the top of the reactor.

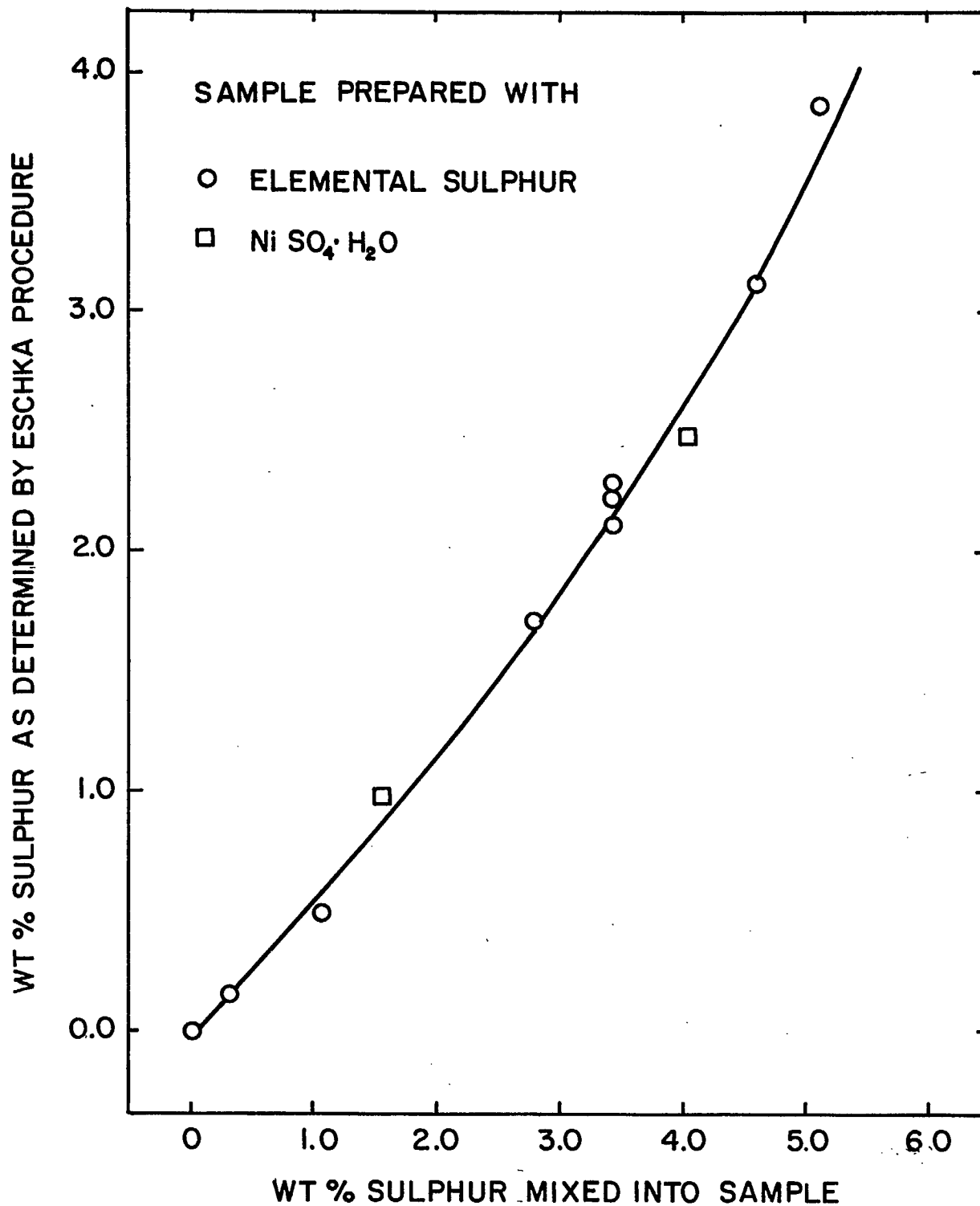


Figure 1. The Correction Curve for Sulphur Analyses by the Eschka Method

The catalyst pellets were immediately placed under acetone and ground to form a fine powder. The wetted powder was placed in a crucible containing a previously weighed amount of Eschka mixture and stirred. A second preweighed amount of Eschka mixture was then placed on top of the solids in the crucible. The crucible was left open to the atmosphere for 15 hours (54 ks), so that ample time would be available for the acetone to evaporate. Tests were performed to determine the weight loss from the solids due to acetone evaporation as a function of time. It was found that approximately 99 percent of the weight loss occurred in the first 3 hours (10.8 ks). Therefore, the 15 hour period allowed for acetone evaporation was considered more than adequate. Following the 15 hour evaporation period, the crucible was weighed to determine the weight of catalyst sample added to the Eschka mixture. The sulphur analysis was then performed using the Eschka procedure described above.

The catalyst pellets which had been in the presence of the gas oil plus hydrogen reaction mixture contained a considerable amount of liquid hydrocarbon when they were removed from the reactor. This oil film tended to prevent oxygen in the air from reacting with the metal sulphides to form SO_2 . Two different methods were used to remove the hydrocarbon from the catalyst, prior to sulphur analysis. In the first method the catalyst pellets were ground to form a fine powder, subjected to benzene extraction in a Soxhlet apparatus for approximately 5 hours (18 ks), washed with acetone and finally analyzed using the Eschka procedure. In the second method the catalyst pellets were heated up to 530°C in a stream of flowing hydrogen, ground to a fine powder and analyzed for sulphur using the Eschka procedure.

RESULTS AND DISCUSSION

The Effect of CS_2 Presulphiding on Gas Oil Hydrorefining

By varying the conditions used to presulphide the catalyst with CS_2 it was possible to obtain a number of catalysts having a range of sulphur contents. Despite this variation in sulphur all of the catalysts produced gas oil products having essentially the same properties. In Figure 2, specific gravity, wt % sulphur removed and wt % nitrogen removed are shown as functions of catalyst sulphur content after presulphiding. A set of essentially horizontal lines was obtained. However, the two lines corresponding to sulphur

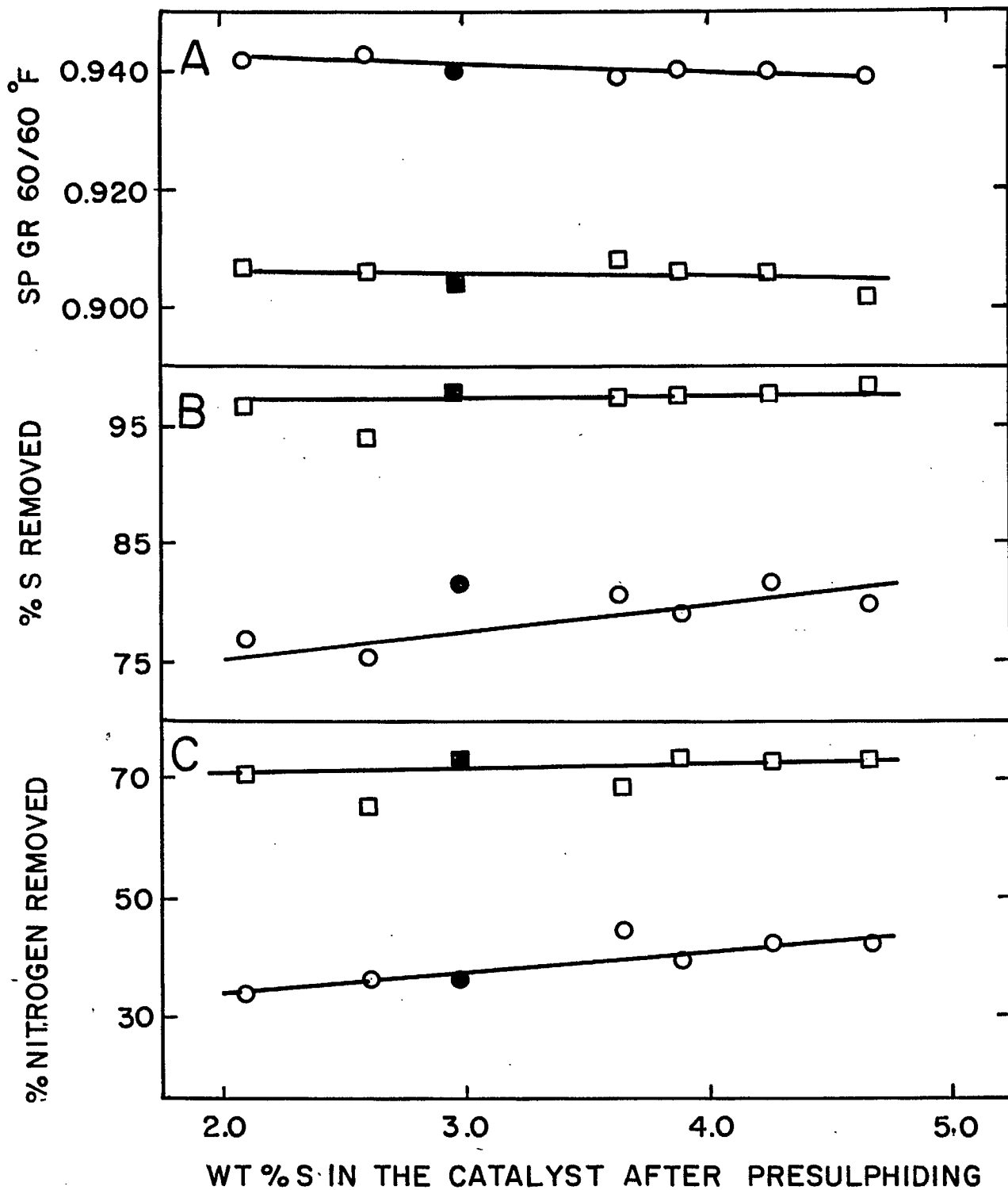


Figure 2. The Effect of the Catalyst Sulphur Content after Presulphiding on Liquid Product Properties. Reaction results obtained at 400°C and 450°C are represented by circles and squares respectively. The solid and open data points represent presulphiding with gas oil and carbon disulphide respectively.

and nitrogen removal at 400°C have a slight positive slope which indicates a small trend toward increased sulphur and nitrogen removal with increase in catalyst sulphur content after presulphiding. This trend is definitely not apparent in the properties of the products of the 450°C reactions.

The extent of hydrocracking can be evaluated by determining the change in boiling point of the liquid product. In practice this is measured as an increase or decrease in the amount of hydrocarbon material which boils within a particular temperature range. Hydrocracking would be expected to cause an increase in the fraction of low boiling distillate and a decrease in the fraction of high boiling distillate. The changes in the amount of distillate within several different boiling ranges are shown in Figure 3 and in Table 5. Similar results were obtained for each of the catalysts studied. This shows that the sulphur content of the catalyst after presulphiding did not have an appreciable effect on hydrocracking.

There are at least two explanations for the fact that variations in the sulphur content of the catalysts after presulphiding were not clearly reflected in the product properties. The first is simply that sulphur may not play any important part in the reaction mechanisms. This is rather unlikely since it is contrary to the experience reflected in established refining practice (3) and to many reports in the scientific literature (4, 18, 19, 20). The second explanation is that sulphur does play an important role but that under reaction conditions the sulphur content of all the catalysts becomes the same. Presumably the steady state sulphur content of the catalyst would be determined by an equilibrium with the sulphur in the surrounding reaction mixture. The steady state sulphur content of the catalyst may not have been established during the first experiment with gas oil at 400°C. Evidence for this is provided by the data in Figures 2B and 2C. The extents of both sulphur and nitrogen removal tend to increase slightly as the amount of sulphur in the catalyst after presulphiding increases. The experiments at 450°C were always performed after the experiment at 400°C. Therefore, the catalyst would have been in contact with the reaction mixture for a longer time and at a higher temperature. Both of these effects would tend to bring the catalyst to its steady state sulphur level. The horizontal lines in Figures 2B and 2C obtained at 450°C suggest that the steady state sulphur level in the catalysts had been established in all these experiments.

CHANGES IN AMOUNTS OF DISTILLATE IN DIFFERENT BOILING RANGES (ie HYDROCRACKING)

WT % PRODUCT IN BOILING RANGE - WT % FEED BOILING RANGE (SULPHUR FREE BASIS)

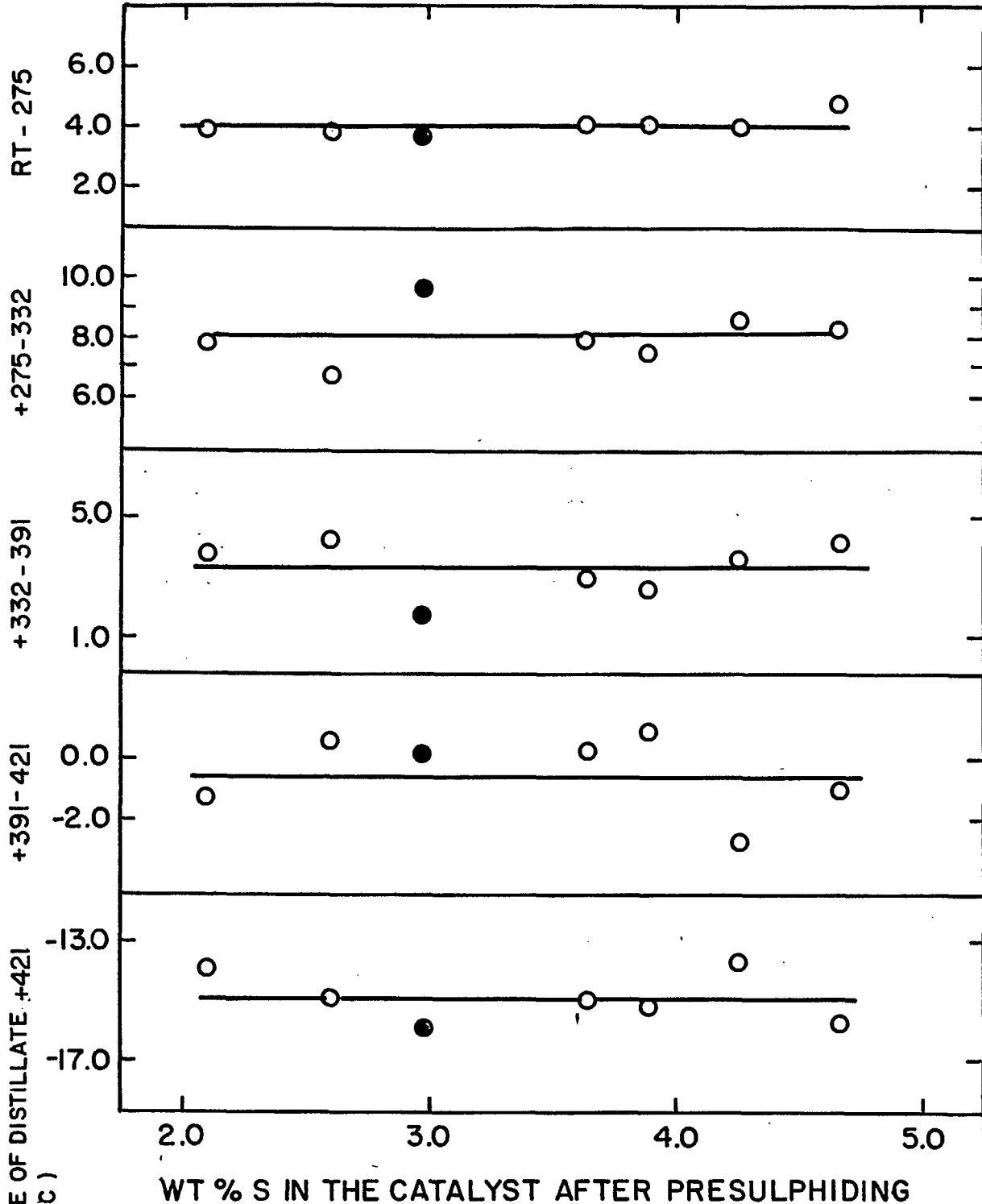


Figure 3. The Effect of the Catalyst Sulphur Content after Presulphiding on Hydrocracking.

TABLE 5

SUMMARY
of the Distillation Analyses and the Sulphur Contents
of the Distillate Fractions of the Feedstock and of the Products
obtained at 400°C.

Boiling Range of Fraction Equip temp at one atm (°C) (°F)		Amount (wt % of feed on S-free basis)	Wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)	Amount (wt % of feed on S-free basis)	wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)
Product Number		Feed Stock				SCP 7			
IBP-200	IBP-392	-	-	-	-	1.24	1.24	0.647	-
200-250	392-482	0.18	-	-	-	1.39	1.21	0.766	-
250-275	482-527	0.54	-	0.660	2.05	1.99	1.45	0.810	0.09
275-332	527-630	2.71	-	0.835	2.65	10.52	7.81	0.897	0.42
332-361	630-682	14.47	-	0.926	2.92	15.50	1.03	0.916	0.63
361-391	682-736	12.59	-	0.941	3.01	15.36	2.77	0.921	0.87
391-421	736-790	19.55	-	0.967	3.24	18.27	-1.28	0.946	1.01
+421	+790	49.96	-	-	3.95	35.92	-14.04	-	1.13

TABLE 5 (cont'd)

Boiling Range of Fraction Equiv temp at one atm (°C) (°F)		Amount (wt % of feed on S-free basis)	Wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)	Amount (wt % of feed on S-free basis)	wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)
Product Number		SCP 9				SCP 11			
IBP-200	IBP-392	0.95	0.95	0.630	0.05	1.10	1.10	0.652	0.01
200-250	392-482	1.34	1.16	0.691	-	1.50	1.32	0.703	-
250-275	482-527	2.21	1.67	0.815	0.14	2.14	1.60	0.827	0.09
275-332	527-630	9.43	6.72	0.901	0.40	10.23	7.52	0.901	0.33
332-361	630-682	17.46	2.99	0.920	0.60	16.39	1.92	0.924	0.53
361-391	682-736	13.82	1.23	0.924	0.80	13.32	0.73	0.933	0.71
391-421	736-790	20.16	0.61	0.943	0.97	20.42	0.87	0.946	0.97
+421	+790	34.98	-14.98	-	1.18	34.71	-15.25	-	1.18

TABLE 5 (cont'd)

Boiling Range of Fraction Equiv temp at one atm (°C) (°F)		Amount (wt % of feed on S-free basis)	Wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)	Amount (wt % of feed on S-free basis)	wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)
SCP 13					SCP 17				
IBP-200	IBP-392	1.64	1.64	0.691	0.03	0.80	0.80	-	0.10
200-250	392-482	1.58	1.40	0.695	-	1.46	1.28	0.682	-
250-275	482-527	2.28	1.74	0.807	0.09	2.10	1.56	0.823	0.09
275-332	527-630	10.98	8.27	0.907	0.33	12.36	9.65	0.905	0.31
332-361	630-682	16.96	2.49	0.913	0.54	16.43	1.96	0.917	0.43
361-391	682-736	14.28	1.69	0.926	0.76	12.38	-0.21	0.924	0.65
391-421	736-790	18.49	-1.06	0.939	0.91	19.66	0.11	0.954	0.73
+421	+790	34.20	-15.76	-	0.98	34.01	-15.95	-	0.95

TABLE 5 (cont'd)

Boiling Range of Fraction Equiv temp at one atm (°C) (°F)		Amount (wt % of feed on S-free basis)	Wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)	Amount (wt % of feed on S-free basis)	wt % of Product -wt % of feed (on S-free basis)	Specific Gravity 60°/60° F	Sulphur (wt %)
IBP-200	IBP-392	1.24	SCP 19 1.24	0.656	<0.04	1.06	1.06	SCP 21 -	<0.04
200-250	392-482	1.81	1.63	0.712	<0.04	1.66	1.48	0.694	<0.04
250-275	482-527	1.61	1.07	0.802	<0.04	2.05	1.51	0.816	<0.04
275-332	527-630	11.25	8.54	0.905	0.27	10.60	7.89	0.908	0.29
332-361	630-682	16.75	2.28	0.918	0.43	16.99	2.52	0.922	0.44
361-391	682-736	13.94	1.35	0.929	0.70	13.06	0.47	0.931	0.68
391-421	736-790	16.77	-2.78	0.944	0.73	19.88	0.33	0.944	0.81
+421	+790	36.26	-13.70	-	1.04	34.97	-14.99	-	1.06

The Effect of CS₂ Presulphiding Conditions on Catalyst Sulphur Content

A cursory examination of the effects of presulphiding conditions on catalyst sulphur content after presulphiding was performed. The variations in temperature, total pressure and CS₂ mole fraction are shown in Table 4. The seven experiments performed were insufficient to accurately establish the effects of the above three variables. However, within certain ranges the data show that the weight percent sulphur in the presulphided catalyst tends to increase with temperature, total pressure and CS₂ mole fraction. The large variations in presulphiding conditions listed in Table 4 produced only small changes in properties of the hydrocarbon product, as was shown in Figures 2 and 3. Therefore, no attempt was made to define the effects of presulphiding conditions more accurately.

The Effect of the Reaction Mixture on Catalyst Sulphur Content

Two different methods were used to measure the sulphur content of the catalysts after they had been used to hydrorefine the gas oil. The results are listed in Table 6. When the adhering hydrocarbon oil was removed from the catalyst by benzene extraction in a Soxhlet apparatus, sulphur results varying from 3.1 to 4.8 weight percent were obtained. In contrast, when the adhering oil was removed from the catalyst by placing it in a stream of flowing hydrogen at 530°C much less scatter was observed. The catalyst sulphur content measured by the second method is shown in Figure 4 as a function of the catalyst sulphur content after presulphiding.

Although the results for wt % sulphur in the catalyst after reaction, obtained by the benzene extraction procedure, contain considerable scatter, they are generally greater than the wt % sulphur in the catalyst after presulphiding and before reaction. This suggests that the presence of sulphur compounds in the reaction mixture can alter the amount of sulphur incorporated into the solid catalyst. The scatter in the "after reaction" sulphur results may be partially caused by the benzene extraction. It is possible that the benzene may have removed some of the sulphur in the solid while the hydrocarbon oil was being extracted.

TABLE 6

Catalyst Composition and Liquid Product Properties Obtained at Various Presulphiding Conditions

Run No., 400°C, 450°C	Presulphiding Conditions			Solid Analysis					Liquid Product Analysis					
	Temp. (°C)	Total Pressure (psi)	Partial Pressure CS ₂ (psi)	Wt % Sulphur			Wt % Coke	Distill- able Oil Wt %	Reaction at 400°C			Reaction at 450°C		
				After Presulphiding	After Reaction				Spec. Grav. 60°/60°F	Sulphur (wt %)	Nitrogen (ppm)	Spec. Grav. 60°/60°F	Sulphur (wt %)	Nitrogen ppm
					Hydrocarbon Removed by									
17,18	400	2015	Gas oil used	2.97	Benzene Extraction	H ₂ -Temp Treatment	3.53	40.3	0.940	0.68	2,450	0.904	0.07	1,110
23,24	400	15	H ₂ S used	2.58	3.12	3.78	2.16	45.1	0.943	0.92	2,700	0.911	0.23	1,300
7,8	400	25	0.820	2.09	4.02	2.78	2.88	37.5	0.942	0.86	2,590	0.907	0.12	1,220
13,14	400	25	1.610	4.66	4.10	2.45	3.47	40.2	0.939	0.75	2,340	0.902	0.06	1,110
19,20	400	765	24-48	4.25	3.50	2.94	3.58	47.0	0.940	0.69	2,300	0.906	0.09	1,100
11,12	400	2015	65-7	3.88	4.48	3.09	3.13	40.2	0.940	0.78	2,410	0.906	0.11	1,140
9,10	200	25	0.805	2.60	4.81	3.00	3.46	39.3	0.943	0.93	2,490	0.906	0.11	1,080
21,22	300	25	0.858	3.63	3.08	3.02	3.63	34.5	0.939	0.72	2,200	0.908	0.10	1,230

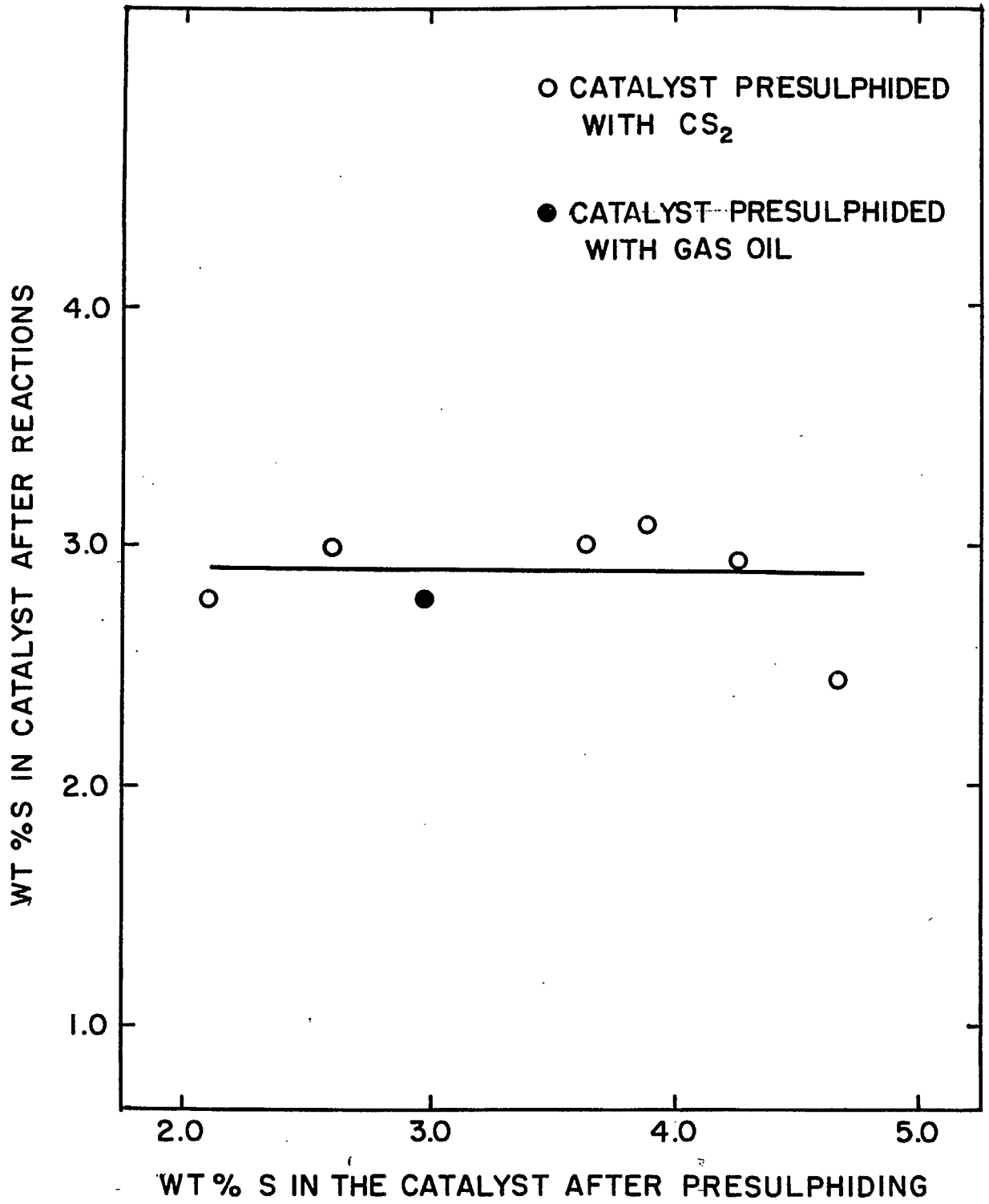


Figure 4. The Effect of the Catalyst Sulphur Content after Pre-sulphiding on its Sulphur Content After Reaction.

The catalyst sulphur content after reaction, when measured by the hydrogen treatment method, was considerably lower than when measured by benzene extraction. It was also lower than the catalyst sulphur content after presulphiding. Therefore, there appeared to be two types of sulphur in the catalyst: a loosely bound sulphur which is removed by hydrogen treatment and a more firmly bound sulphur which is not. The loosely bound sulphur could be either adsorbed sulphur species such as H_2S or sulphur atoms incorporated into the vacancies in the solid.

The more firmly bound sulphur is probably part of chemical compounds formed with molybdenum and nickel. Brewer and Cheavens (21) have stated that during catalyst sulphiding MoO_3 is converted to MoS_2 and NiO is converted to Ni_3S_2 . De Beer's data (18) also suggest that chemical transformations similar to this occur. The catalyst used in this study would have a sulphur content of 2.97 weight percent if all of the molybdenum and nickel in the catalyst were converted to MoS_2 and Ni_3S_2 respectively. The results shown in Figure 4 are reasonably close to the 2.97 weight percent stoichiometric value.

The possibility that sulphided catalysts may contain more than one form of sulphur has been suggested by other workers. Massoth (20) proposed that two types of sulphur exist in Mo-Al catalyst. He used the term "exchanged sulphur" to describe sulphur atoms which had replaced oxygen atoms in the oxidized form of the catalyst. Sulphur atoms which were added to the solid without replacing oxygen atoms were referred to as incorporated sulphur. Kalechits (22) proposed that three types of sulphur are present in WS_2 catalysts used to hydrogenate benzene. They were stoichiometric sulphur which was associated with the tungsten, mobile sulphur which was mechanically entrained molecular sulphur, and chemisorbed sulphur which was responsible for the catalyst's acidic properties.

Coke and Distillable Oil Accumulated by the Catalyst

As described in the experimental section, the amount of distillable oil was defined as the weight loss from the catalyst after it had been exposed to a flowing stream of hydrogen at $530^{\circ}C$. The results are expressed as a percentage of the catalyst weight, on an oil and coke free basis, in Table 6. The weight percent of distillable oil amounted to about 40 percent of the catalyst weight. No particular relationship between distillable oil and any other variable was apparent.

The coke content of the catalyst was measured by two methods. Results of the combustion method are shown in Figure 5. In general the catalysts contained about 3.5 weight percent coke. It must be noted that a weight change of 1.5 percent was due to the conversion of molybdenum and nickel sulphides to their respective oxides. The measured catalyst weight losses were corrected by this amount before they were plotted in Figure 5. No corrections were made for other chemical changes which may have occurred during combustion of the coke.

The weight percent carbon and weight percent hydrogen were measured by the ultimate analysis procedure (15). The sum of these two quantities was considered as another indication of the amount of coke on the catalyst. These results are listed in Table 7. The coke content of the catalyst varied roughly from 4.0 to 4.5 weight percent when determined by ultimate analysis, which is somewhat higher than the 3.5 weight percent obtained by the combustion method. The combustion temperature was different in the two methods, 600°C in the combustion method and 900°C in the ultimate analysis procedure. However, it is doubtful that the lower temperature used in the combustion method was responsible for incomplete removal of coke. After the combustion method had been completed the colour of the catalyst particles had changed from black to their original colour. Even when the pellets were crushed, no visual indication of carbonaceous material was apparent. Finally, it is possible that some of the coke on the catalyst may have been hydrogenated and volatilized in the presence of hydrogen at 530°C. If this occurred, the amount of coke determined by both methods would be low.

The hydrogen/carbon ratios determined by ultimate analyses were higher than expected. Paraffin, aromatic, and condensed aromatic hydrocarbons typically have hydrogen/carbon ratios close to 2, 1 and less than one, respectively. It was anticipated that coke would have a hydrogen/carbon ratio of one or less. The values reported in Table 7 are generally above 2. Some difficulties were encountered in accurately measuring values of the moisture content of the samples. Any water chemisorbed on the catalyst which was desorbed at higher temperatures would tend to produce high values for hydrogen/carbon ratios.

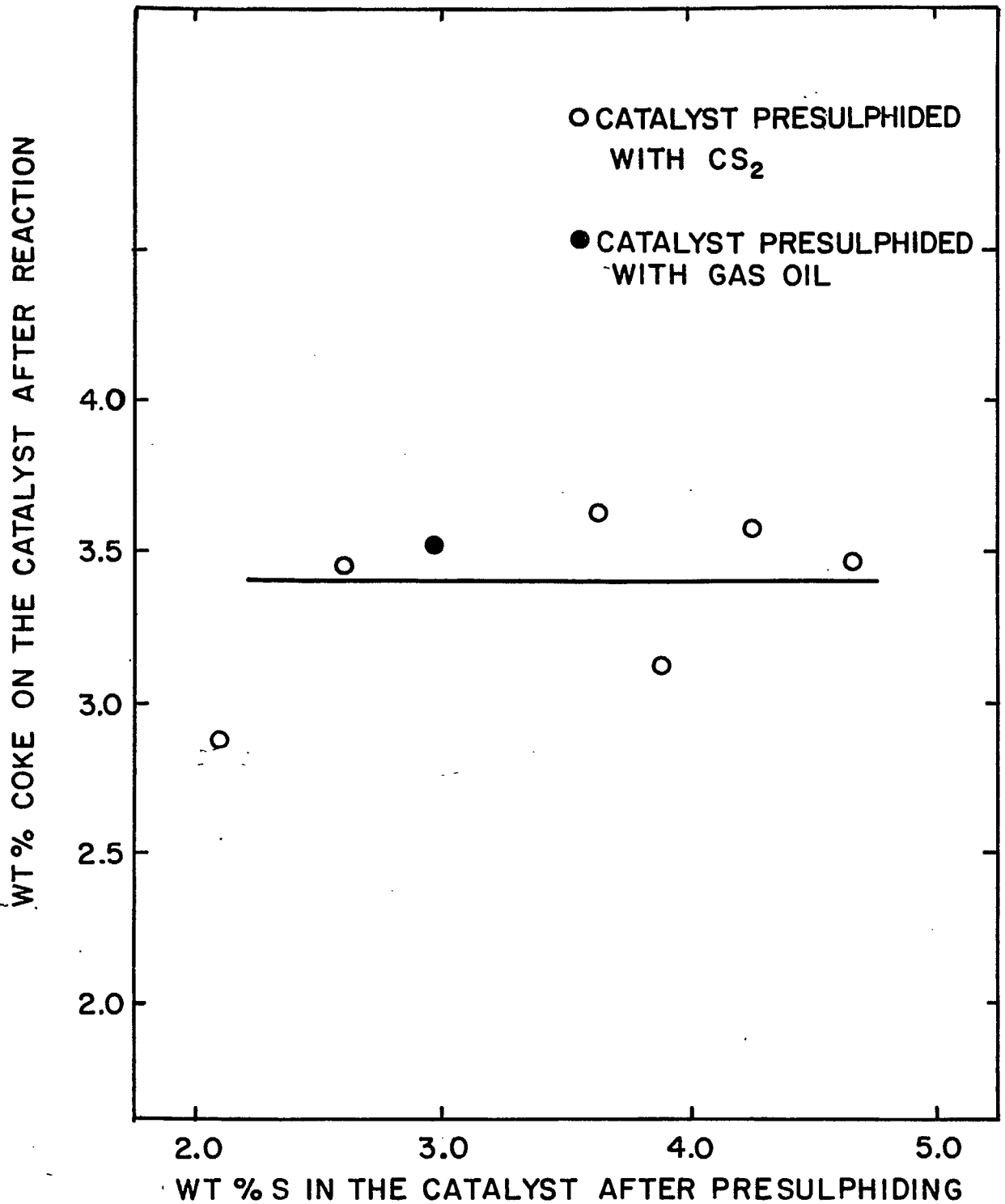


Figure 5. The Effect of the Catalyst Sulphur Content after Presulphiding on Coke Deposition.

TABLE 7

Catalyst Coke Content

Run No.	Wt % Coke (Combustion Method)	Ultimate Analysis			
		Wt % Carbon	Wt % Hydrogen corrected for moisture	H/C atom/atom	Wt % Coke (C+H)
7, 8	2.88	4.53	0.55	1.46	5.08
9, 10	3.46	3.78	0.64	2.03	4.42
11, 12	3.13	3.26	0.66	2.43	3.92
13, 14	3.47	3.33	0.69	2.49	4.02
17, 18	3.53	3.59	0.82	2.74	4.41
19, 20	3.58	3.11	0.77	2.97	3.88
21, 22	3.63	3.41	0.60	2.11	4.01

Presumably conditions which cause less coke formation on the catalyst will also cause longer catalyst life. Aoshima and Wise (4) performed hydrodesulphurization studies with an MoS_2 catalyst in which they varied the catalyst sulphur content. They associated the formation of a carbonaceous residue in the catalyst with a low catalyst sulphur content. The data in Figure 5 and Table 7 show that approximately the same extent of coke formation was observed at all CS_2 presulphiding conditions. In other words, the catalyst sulphur content after presulphiding did not influence the amount of coke. This can be explained by the catalyst sulphur content changing when the catalyst was exposed to the reaction mixture. As shown in Figure 4, the catalyst sulphur content was similar in all cases after the catalyst was exposed to the reaction mixture. The coke content was also similar, as shown in Figure 5. Therefore, there is no conflict between our results and those of Aoshima and Wise. It appears that adjusting the catalyst sulphur content by presulphiding with CS_2 has only a temporary effect. Since both the sulphur and coke contents in the working state of the catalyst are controlled by the reaction mixture, there will probably not be any significant increase in catalyst life resulting from CS_2 presulphiding.

The Effect of Presulphiding with Materials Other than CS_2

In one series of experiments gas oil replaced CS_2 as the presulphiding material. After the presulphiding experiment was completed, two reaction experiments, one at 400°C and the other at 450°C , were performed. The properties of the liquid hydrocarbon product, wt % S, wt % N and specific gravity, obtained after presulphiding with gas oil are compared with those obtained after presulphiding with CS_2 in Table 6. Figure 4 compares the sulphur content of the catalysts after reaction. The coke contents of the catalysts are compared in Figure 5. In all instances the results obtained by gas oil presulphiding were equivalent to those obtained by CS_2 presulphiding.

Reports of industrial practice state that presulphiding improves both catalyst activity and catalyst life (3). In contrast, our comparison of CS_2 presulphiding and gas oil treatment indicates that the two procedures are equivalent. The difference between our conclusion and that reported in the literature (3) is probably due to differences in the reaction systems.

Our experiments were performed in a bottom feed reactor whereas those reported in the literature were probably obtained in top feed trickle bed reactors. The feedstock used in our experiments was composed of much higher molecular weight compounds and had a higher sulphur content than the naphtha and gas oil feedstocks with which most industrial experience has been obtained. As a result in our experiments the catalyst pellets were surrounded by liquid phase hydrocarbon having a high sulphur content. In contrast the hydrocarbon surrounding the catalyst in naphtha and gas oil hydrorefining studies is predominantly in the vapour phase. The density of molecules is much higher in the liquid phase than in the vapour phase. Therefore, the concentration of sulphur atoms at the catalyst surface will be much higher when the catalyst is surrounded by liquid. This will cause the catalyst to be converted from its oxidized form to its sulphided form much more rapidly. Therefore, when liquid phase hydrocarbon surrounds the catalyst, presulphiding may not be required.

The beneficial effects associated with presulphiding may be related to hydrogen adsorption. Massoth (20) found that the oxidized form of a hydrodesulphurization catalyst had a lower adsorption capacity for hydrogen than the sulphided form of the catalyst. Less coke would be formed if more hydrogen was adsorbed on the catalyst surface. Presumably greater activity and life would be obtained by suppressing coke formation.

When H_2S presulphiding was performed two sets of comparisons were made. In the first, H_2S presulphiding was followed by two reaction experiments, one at $400^\circ C$ and the subsequent one at $450^\circ C$. The results are shown in Table 6. The activity of the H_2S presulphided catalyst was somewhat lower than that of other presulphided catalysts. The wt % S, wt % N and specific gravity of the hydrocarbon liquid product were all slightly higher. However, significantly less coke was deposited on the H_2S presulphided catalyst.

In the second comparison two sets of four reaction experiments were performed at temperatures of $400^\circ C$, $420^\circ C$, $400^\circ C$ and $380^\circ C$. One set of experiments was preceded by H_2S presulphiding, the other was not. The properties of the liquid hydrocarbon products which were obtained are shown in Table 8. The catalyst which was not presulphided produced slightly superior specific gravity and wt % S results. The difference in wt % N results was within experimental error.

TABLE 8

Changes in Hydrocarbon Product Properties
Caused by H₂S Presulphiding

Temp. (°C)	400	420	400	380
<u>Catalyst Presulphided with H₂S</u>				
Spec. Grav. (60°/60°F)	0.942	0.932	0.941	0.952
wt % S	0.92	0.55	0.86	1.32
wt % N	0.26	0.23	0.28	0.32
<u>Catalyst not Presulphided</u>				
Spec. Grav. (60°/60°F)	0.940	0.930	0.941	0.950
wt % S	0.75	0.45	0.72	1.13
wt % N	0.27	0.24	0.31	0.33

TABLE 9

Changes in Catalyst Sulphur and Coke
Content Caused by H₂S Presulphiding

	Presulphided	Not Presulphided
Wt % S Before Reaction	2.58	0.0
Wt % S After Reaction		
benzene ext ⁿ	3.33	3.05
H ₂ ext ⁿ	3.23	2.91
Wt % Coke	2.75	2.89
Distillable Oil	42.2	46.3

The sulphur and coke contents of the two catalysts are listed in Table 9. In this comparison the amount of coke in the presulphided catalyst is almost as high as in the one which was not presulphided. It should be noted that Table 9 shows the quantities of coke obtained after four reaction experiments. In contrast, the quantities of coke obtained after two reaction experiments, shown in Table 6, indicated that H_2S presulphiding was beneficial. This suggests that the immediate effect of H_2S presulphiding is to suppress coke formation, which is in agreement with the findings of Aoshima and Wise (4). However, on prolonged exposure to the reaction mixture the sulphur content of the catalyst changes and the suppression of coke formation caused by H_2S presulphiding no longer occurs. Therefore, from the long term viewpoint, H_2S presulphiding does not appear to have any advantage over gas oil presulphiding.

CONCLUSIONS

Finally, the effects of catalyst presulphiding may be summarized as follows:

- Using various combinations of presulphiding pressure and temperature, the oxidized form of the catalyst was converted to sulphided forms having sulphur contents between 2 and 4 weight percent.
- Regardless of the presulphiding conditions, after sufficient exposure to the reaction environment, the catalyst sulphur content tended to approach the amount of sulphur required for all of the nickel and molybdenum to exist as Ni_3S_2 and MoS_2 .
- The quality of the hydrocarbon product was similar for all catalysts regardless of presulphiding conditions. This was due to all of the catalysts having essentially the same sulphur content after contacting the reaction mixture, regardless of their sulphur content after presulphiding.
- The quantity of coke formed in the catalyst was similar for all presulphiding conditions. Again this was related to the fact that all catalysts which had contacted the reaction mixture had approximately the same sulphur content.

- Finally, presulphiding with the hydrocarbon feedstock produced results which were essentially equivalent to presulphiding with other materials such as CS_2 and H_2S .

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