HYDRODESULFURIZATION OF SHOUKAIR
KEROSINE USING THREE CATALYSTS

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الخلاصة :

تمت معالجة الكيروسين المنتج من خليط حقول شقير المصرية والذي يحتوي على نسبة كبريت عالية لحدٍ ما (٢٩, ٪ وزنا) باستخدام مفاعل للهدرجة بالعامل المساعد تحت ظروف مختلفة من الضغط ودرجة الحرارة ومعدل التغذية . وقد قورنت النتائج لثلاث عوامل مساعدة مختلفة (روسي وامريكيان منتجان من قبل شركة منتجات الزيت العالمية رقم س ٦ ـ وس ٧ UOPS6, S7 وقد وجد ان أفضل عامل مساعد لمعالجة الكيروسين هو UOPS6 حيث يمكن إستخدامه عند درجة حرارة وضغط أقل من العاملين المساعدين الآخرين للحصول على نفس النتائج مما يجعل إستخدامه إقتصاديا .

ABSTRACT

Hydrodesulfurization of Egyptian Shoukair kerosine with a relatively high sulfur content (0.29% wt.) is carried out using a bench-type continuous reactor. Three catalysts are examined at different temperature, pressures, and hourly space velocities to determine the optimum desulfurization conditions for each catalyst. Two of the catalysts are produced by Universal Oil Products Co. (UOP S–6 and S–7) and the third is a Russian catalyst. Analyses of the results obtained show that UOP S–6 catalyst may be used at relatively lower temperatures and pressures than the other two catalysts for the same desulfurization level and liquid yield. This constitutes an energy saving item.

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INTRODUCTION

The application of hydrogenation to the conversion of petroleum fractions into lighter products is becoming increasingly important since these products are valuable fuels and petro-chemical feed stocks. Hydrotreating of middle distillates (kerosine and gas oil) is now an integral part of the operation of a complex refinery. Even hydrodesulfurization of residues is now being achieved successfully [1, 2]. Although acidic sulfur compounds such as mercaptans and hydrogen sulfide can be removed from petroleum fractions by chemical treatment, many other sulfur compounds which are present in crude oils and oil fractions are not susceptible to such treatment. In middle distillate fractions, sulfur may be found in the form of organic sulfides, disulfides, mercaptans, hydrogen sulfide, and thiophene [3].

The identification of types of sulfur compounds in crude oils and in fractions has been the subject of a great deal of research. However, it was determined that by selecting the right catalyst and establishing the optimum conditions for hydrodesulfurization not only removes sulfur compounds but also converts organic nitrogen compounds to ammonia and removes oxygen compounds [4, 5].

Hydrodesulfurization is also effective in removing trace quantities of metallic contaminants by adsorption with a minor loss in catalytic activity.

In general a hydrodesulfurization catalyst is a mixture of oxides or sulfides of metals from Groups III, VI B, and VIII. Some of the common compositions involve cobalt and nickel from Group VIII, molybdenum and tungsten from Group VI B and aluminum from Group III. Typical carriers for the catalysts are active charcoal, silica gel, alumina gel, clay, and bauxite. Certain promoters are added to the catalyst mixture. Fluorine and phosphorus are used as activating agents for some catalyst compositions to increase desulfurization activity.

Reaction variables are temperature, pressure, liquid hourly space velocity, and hydrogen-to-hydrocarbon ratio.

The overall hydrodesulfurization reactions are exothermic. The exothermicity increases with increased unsaturation in the feed being treated [6].

The work which is presented below is intended to establish the optimum conditions for the hydrodesulfurization of a kerosine fraction from an Egyptian crude oil with a relatively high sulfur content, and to compare the activity of three catalysts on the hydrodesulfurization of this kerosine.

EXPERIMENTAL

Charge and Catalysts

The charge to the desulfurization unit in this investigation is a kerosine fraction from Shoukair crude oil mixture. Physico–chemical analytical work was carried out to determine the important characteristics of the charge before being hydrodesulfurized (Table 1) and after being hydrodesulfurized at different temperatures, pressures, and liquid space velocities (Tables 2–4).

Three catalysts were examined:

Catalyst A: Russian catalyst
Catalyst B: UOP S–6
Catalyst C: UOP S–7

Hydrodesulfurization Test Unit

The unit used in the investigation (Figure 1) consisted mainly of a vertical tubular stainless steel re-

Table 1. Analysis of Kerosine Feed

Property	Test	Value
Density, 15/4°C	IP.160/68	0.8068
Aromatics, Vol %	145/65	20.4
Corrosion, Cu. Strip, at 50°C	154/69	1a
Flash Point, °C	170/70	43
Smoke Point, mm	57/55	24
Sulfur Mercaptan, wt %	104/53	0.0005
Doctor Test	30/56	-ve
Total Sulfur, wt. %	107/70T	0.29
Aniline Point, °C	ASTM D 1266/170 2/61	65
Total Acidity, mg KOH/100 gm sample	IP. 1/64	Nil
ASTM Distillation	123/68	
% Recovered at 200°C		45
I.B.P., °C		148
F.B.P., °C		300
Freezing Point, °C	16/68	−35

Table 2. Effect of Temperature and Pressure on Desulfurization of Kerosine using Russian Catalyst (A)

Characteristics	LHSV, l/l h⁻¹	5				5				5			
	H₂/Hydrocarbon Ratio, l/l	120				120				120			
	Pressure, kg cm⁻²	20				30				40			
	Temp., °C	320	340	360	380	320	340	360	380	320	340	360	380
Density, 15/4°C		0.805	0.804	0.805	0.805	0.804	0.805	0.805	0.803	0.805	0.804	0.804	0.803
Aromatics, Vol. %		22.5	18	23	20.5	21.5	17	24	20	23	21	24	24
Corrosion, Cu Strip, at 50°C		3a	3a	3a	1a	3a	2c	2c	2c	2a	2c	2c	3b
Flash Point, °C		50	49	48	51	49	49	49	50	49	50	48	48
Smoke Point, mm		26	25.5	26.5	25.5	26.5	26.5	25	25	27	25	26	27
Sulfur Mercaptan, wt. %		Nil	0.0002	0.0002	0.0002	0.0002	0.0002	0.0004	0.0004	0.0008	0.0005	0.0006	0.0004
Doctor Test		-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Total Sulfur, wt. %		0.050	0.038	0.014	0.016	0.050	0.040	0.015	0.015	0.040	0.023	0.013	0.011
Sulfur Removal, wt. %		82.6	86.8	95.1	94.4	82.6	86.1	94.8	94.8	86.1	92.0	95.5	96.2
Aniline Point, °C		60.6	60	60.5	62	60.2	58	62.2	62.0	61.2	61.3	60.5	61.7
Total Acidity, mg KOH/100 gm		Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ASTM Distillation													
% Recovered at 200°C		51	44	53	50	50	45		47	49	50	49	50
I.B.P., °C		152	154	151	154	152	154	163	151	155	155	154	151
F.B.P., °C		284	291	278	283	278	290	293	285	281	286	290	287
Hydrogen Consumed, l/l		7.5	8.1	8.2	8.5	7.2	8.3	9.4	11.8	8.5	9.2	10.1	12.12
Liquid, wt. %		97.1	96.3	94.6	93.8	98.1	96.2	96.2	95.3	97.3	97.4	95.1	94.5

Table 3. Effect of Pressure and Temperature on Desulfurization of Kerosine using UOP S-6 Catalyst (B)

Characteristics	LHSV, l/l h⁻¹	5				5				5			
	H₂/Hydrocarbon Ratio, l/l	120				120				120			
	Pressure, kg cm⁻²	20				30				40			
	Temp., °C	320	340	360	380	320	340	360	380	320	340	360	380
Density, 15/4°C		0.805	0.805	0.804	0.804	0.805	0.804	0.804	0.805	0.804	0.804	0.804	0.804
Aromatics, Vol. %		19	20.5	22	24	24	20.5	20.5	23	20.5	21.5	21.5	23.5
Corrosion, Cu Strip, at 50°C		1b	3a	1b	1b	1b	1a	1a	3a	2c	3a	1b	1b
Flash Point, °C		47.5	45.5	44.5	43.5	46	44	43.5	44	44.5	43.5	42.5	44
Smoke Point, mm		25.5	23	23.5	24.5	24	26	24.5	23.5	24.5	25.5	24.5	25.5
Sulfur Mercaptan, wt. %		0.0004	0.0005	0.0004	0.0004	0.0002	0.0002	0.0002	0.0003	0.0005	0.0005	0.0005	0.0005
Doctor Test		-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Total Sulfur, wt. %		0.076	0.013	0.013	0.013	0.036	0.017	0.015	0.009	0.036	0.019	0.019	0.019
Sulfur Removal, wt. %		73.5	95.5	95.5	95.5	87.5	94.1	94.8	96.9	87.5	93.4	93.4	96.2
Aniline Point, °C		52.4	51.0	52	49.8	41.0	47.9	46.4	47.5	45.2	49	45.7	50.6
Total Acidity, mg KOH/100 gm		Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ASTM Distillation													
% Recovered at 200°C		40	43	45	46	45	43	40	37	42	44	44	40
I.B.P., °C		161	159	154	151	154	152	153	161	156	154	155	159
F.B.P., °C		294	291	292	283	289	289	294	294	291	291	294	290
Hydrogen Consumed, l/l.		6.3	11.5	11.5	12.0	7.7	11.2	11.9	12.5	7.7	13.6	14.3	14.4
Yield, wt. %		95.7	94.8	94.5	94.0	96.3	97.7	96.6	95.1	97.8	97.6	96.6	95.9

Table 4. Effect of Temperature and Pressure on Desulfurization of Kerosine using UOP S–7 Catalyst (C)

Characteristics	LHSV, l/l h⁻¹: 5											
H_2/Hydrocarbon Ratio, l/l	120											
Pressure, kg cm⁻²	20	20	20	20	30	30	30	30	40	40	40	40
Temp., °C	320	340	360	380	320	340	360	380	320	340	360	380
Density, 15/4°C	0.785	0.784	0.784	0.784	0.783	0.782	0.783	0.783	0.782	0.782	0.783	0.782
Aromatics, Vol. %	20	19.5	19	20	18.5	19.5	19	20	21.5	22	19.5	20
Corrosion, Cu. Strip, at 50°C	1a	1a	1a	1a	1a	1b	1b	1a	1a	1a	1a	1a
Flash Point, °C	32	32	30	30	33	33.5	32	30	31	31	31	31
Smoke Point, mm	24	25	25	24	25.5	26.5	24	24	24.5	24	24.5	23
Sulphur Mercaptan, wt. %	0.0015	Nil	Nil	0.0001	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Doctor Test	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve	-ve
Total Sulfur, wt. %	0.0541	0.0532	0.0452	0.0406	0.0271	0.0203	0.0200	0.0187	0.0213	0.0201	0.0196	0.0168
Sulfur Removal, wt. %	81.2	81.5	84.3	85.9	90.6	92.9	93.0	93.5	92.6	90.0	93.2	94.2
Aniline Point, °C	49	51.4	49	48.6	51.2	54	54	53	48.8	48	46.8	50.2
Total Acidity, mg KOH/100 gm	0.0693	0.0462	0.0858	0.0462	0.0726	0.0264	0.0330	0.0198	0.0726	0.0264	0.0462	0.0330
ASTM Distillation												
% Recovered at 200°C	78	78	82	77	82	79	81	80	81	79	82	80
I.B.P., °C	120	123	126	131	118	125	119	127	125	126	131	125
F.B.P., °C	250	247	245	260	245	252	249	252	248	256	247	247
Hydrogen Consumed, l/l	7.4	9	9	11.5	8.5	9.0	10.5	12.0	10	10	13	15.3
Yield, wt. %	94.6	94.5	93.2	91.8	97.8	95.6	93.4	92.7	97.8	95.6	93.7	93.3

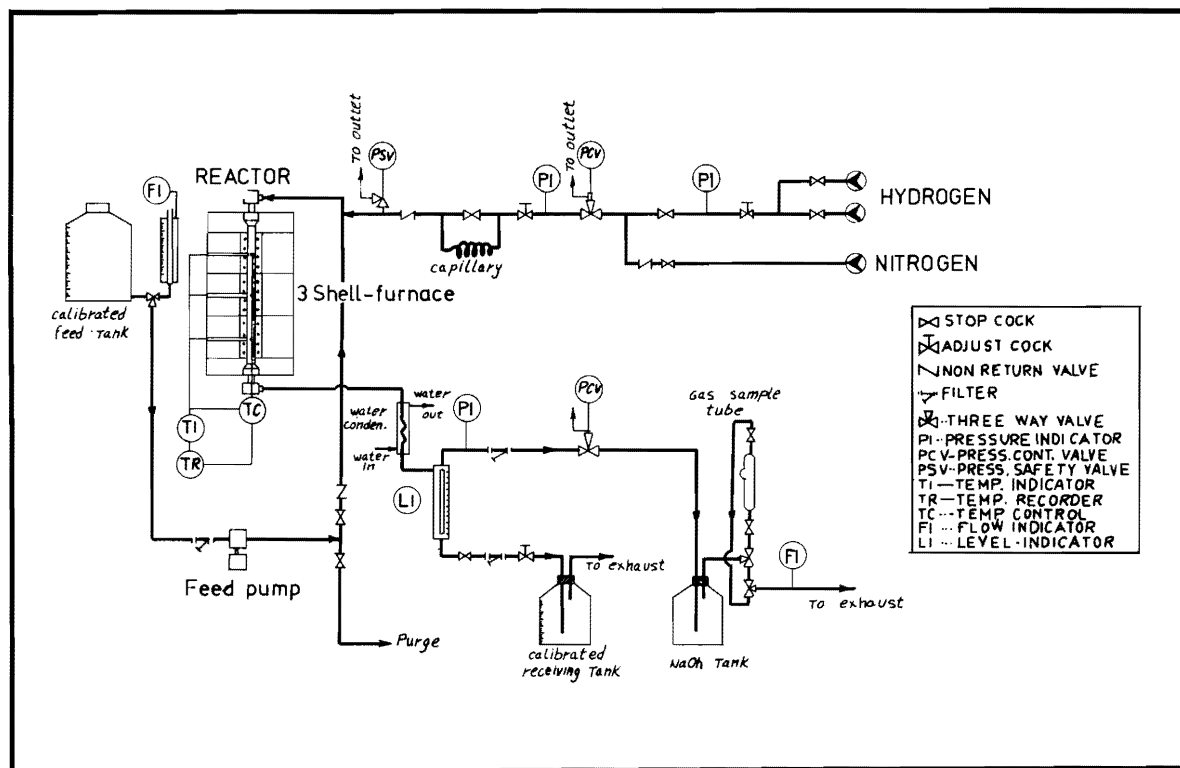*Figure 1. High Pressure Catalyst Activity Testing Unit*

actor 50cm × 1.9cm i.d. × 2.7cm o.d. The heating device for the reactor was an electrical furnace composed of three sets of heating shells. Heat for each shell was separately controlled. Twelve centimeters of the top portion of the reactor tube was filled with inert porcelain beads, the next 15cm was filled with the catalyst, forming the catalyst bed, and the rest of the tube was filled with the porcelain beads. The reactor temperature was measured by three (iron-constant) thermocouples placed at the top, center and bottom part of the catalyst bed.

The temperature of the catalyst bed was adjusted by the use of the three heating devices surrounding the reactor.

Feed was charged to the top of the reactor by the use of a piston pump. Hydrogen gas was supplied to the unit from a hydrogen cylinder.

Procedure of Operation

The unit was first flushed with nitrogen gas then kept under 100kgcm^{-2} hydrogen pressure. The catalyst was reduced for 10–12h at a temperature of 350°C and a pressure of $10–15 \text{kgcm}^{-2}$ at a hydrogen flow rate of $30–40 \text{lh}^{-1}$. The catalyst was then sulfided for 12h at a temperature of 320°C and hydrogen

pressure of 30kgcm^{-2}. The sulfiding agent was carbon disulfide injected with the feed. Hydrogen-to-hydrocarbon ratio was kept constant at 120l/l. The unit was then adjusted according to a predetermined set of operating variables. The following are the selected variables:

temperature °C	320,	340,	360,	380
pressure kg cm^{-2}	20,	30,	40	
liquid hourly space velocity (LHSV) (l/lh^{-1})	4,	5,	6	
hydrogen/hydrocarbon (l/l)	80,	120,	200	

The density of the liquid effluent after reaction was continuously measured until the reactor reached a steady state after which samples were collected for inspection.

Hydrogen and hydrocarbon gases leaving the unit were analyzed using an F & M Model 500 gas chromatograph.

The carrier gas was nitrogen at a flow rate of 50mlmin^{-1}. A thermal conductivity cell was the detector and the column temperature was kept at 30°C.

The analysis was carried out in two steps where the hydrogen was determined first by the use of a column 1.8m × 3mm i.d. packed with 40–60 mesh charcoal.

The hydrocarbon mixture was analyzed by the use of a 4.9m × 3mm i.d. column packed with 40% dimethyl sulfolane on 35–80 mesh chromosorb P, which was connected to another 3m column packed with 10% di-isodecylphthalate on chromosorb P. A flame ionization detector was used and the column temperature was kept at 30°C.

The liquid product was gently bubbled with a stream of nitrogen gas to remove H_2S and ammonia. The analysis of the desulfurized liquid was carried out according to the IP and ASTM standard testing procedures. Tables 2–4 show the desulfurization conditions, the analysis of the product kerosine, and the liquid yield from each run.

DATA AND DISCUSSION

The three catalysts investigated show different activities towards hydrodesulfurization. The results obtained using each catalyst are discussed separately. The activities of the three catalysts are then compared. The different variables studied are: temperature; pressure; liquid space velocity; and hydrogen-to-hydrocarbon ratio. The analysis of kerosine used in the investigation is shown in Table 1. Kerosine was hydrodesulfurized at three different pressure levels 20, 30, and 40kgcm^{-2}. For each pressure level the reaction has been run four times at four selected temperatures of 320, 340, 360, and 380°C. The liquid hourly space velocity was kept constant at 5 l/1h^{-1} and a hydrogen-to-hydrocarbon ratio of 120 l/l. The criteria used to evaluate the catalyst are as follows:

1. The percent desulfurization calculated from the difference between the sulfur content before and after desulfurization.
2. The temperature at which a satisfactory desulfurization level is reached.
3. The percent liquid obtained for each desulfurization run.

Catalyst A

From the percent desulfurization (Table 2), it is found that a level of 95% is reached at 360°C for the three pressure levels employed. Although at 40kgcm^{-2} the activity of the catalyst at lower temperature is better than at 20 and 30kgcm^{-2} yet, the desulfurization level reached only 92% at 340°C. Figure 2 shows the effect of changing the pressure and temperature on the percent desulfurization at constant hourly space velocity and constant hydrogen-to-hydrocarbon ratio.
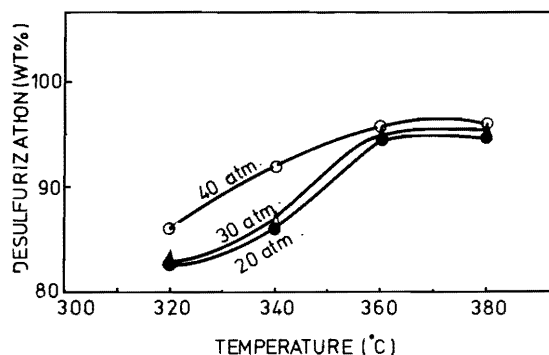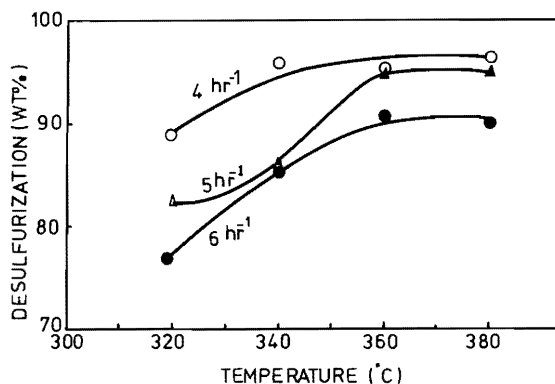

Figure 2. Effect of Temperature and Pressure on Desulfurization of Kerosine Using Russian Catalyst. LHSV: 5h^{-1}; H$_2$/Feed: 120 l/l

Under more severe conditions ($P = 40$kgcm^{-2}, $T = 380$°C) a desulfurization level of 96% is achieved.

The liquid yield varies during the investigation between 91.8 and 98.1% depending on the temperature and pressure employed. Liquid yield is generally low at low pressures and high temperatures. In general, comparing the liquid yield for desulfurization at 30 and 40kgcm^{-2} and for the same temperatures there is about 1% higher liquid yield at all temperatures at 30 than at 40kgcm^{-2} pressure. The effect of changing the hourly space velocity at the four temperatures is also studied at a constant pressure of 30kgcm^{-2} and constant hydrogen-to-hydrocarbon ratio of 120l/l. It is found that the percent desulfurization is higher for all temperatures at an LHSV of 4l/1hr^{-1}. However, a satisfactory level of 94.8% is reached at 360°C and an LHSV of 5l/1h^{-1} (Figure 3).

FIG(3)EFFECT OF TEMPERATURE & SPACE VELOSITY ON DESULFURIZATION

Figure 3. Effect of Temperature and Space Velocity on Desulfurization of Kerosine Using Russian Catalyst. Pressure: 30 kg cm^{-2}; H$_2$/Feed: 120 l/l
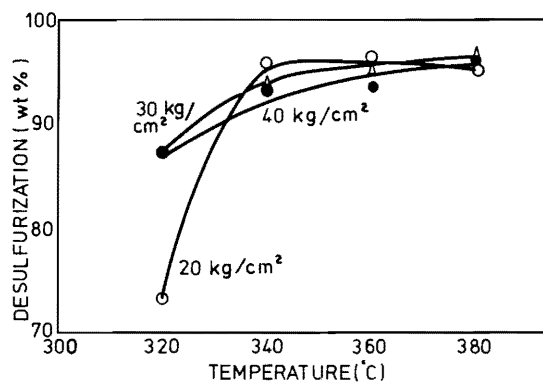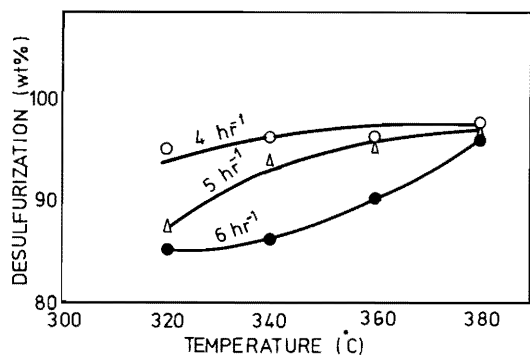
Figure 4. Effect of Temperature and Pressure on Desulfurization of Kerosine Using Catalyst UOP S–6. LHSV: $5h^{-1}$; $H_2/Feed$: 120 l/l

Catalyst B (UOP S–6)

Table 3 shows the analysis of desulfurized kerosine at different pressures and temperatures. From the percent desulfurization it may be shown that a desulfurization level of about 95% is reached for all the pressures investigated at a temperature of 340°C. A slightly better performance of the catalyst is achieved at a lower pressure of $20 kgcm^{-2}$. A sharp rise in desulfurization between 320 and 340°C is observed (Figure 4).

As expected from studying the desulfurization reaction by varying the liquid hourly space velocity and the temperature, better result are obtained at LHSV $4 l/lh^{-1}$. Acceptable results are also obtained at LHSV $5 l/lh^{-1}$, but at a higher temperature than 340°C (Figure 5) The effect of changing the hydrogen-to-feed ratio on desulfurization is also studied for two tem-

Figure 6. Effect of $H_2/Feed$ Ratio on Desulfurization of Kerosine Using Catalyst UOP S–6. Pressure: 30 $kgcm^{-2}$; LHSV: $4h^{-1}$

peratures 360°C and 380°C. The best results are obtained at 1201/1 (Figure 6).

The liquid yield ranges between 94 and 97.8% depending on the temperature and pressure used. Liquid yield is generally lower for all temperatures at 20 atmospheres. At a pressure of 30 and $40 kgcm^{-2}$, the liquid yields are comparable for all temperatures except for 320°C at which higher yield is obtained at $40 kgcm^{-2}$.

Catalyst C (UOP S–7)

Table 4 shows the analysis of desulfurized kerosine using UOP S–7 catalyst at the same temperatures and pressures used for catalysts A and B. From the results obtained, it is clear that the highest desulfurization level reached is 94.2% at $40 kgcm^{-2}$ and 380°C. The liquid yield is generally lower than for the other two catalysts. It has been observed from the analysis of-

FIG(5) EFFECT OF TEMPERATURE & SPACE VELOCITY ON DESULFURIZATION

Figure 5. Effect of Temperature and Space Velocity on Desulfurization of Kerosine Using Catalyst UOP S–6. Pressure: $30 kgcm^{-2}$; $H_2/Feed$: 120 l/l
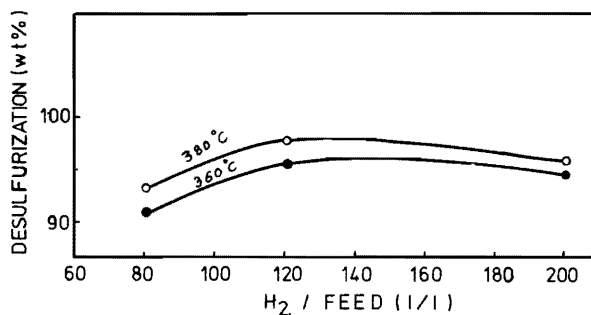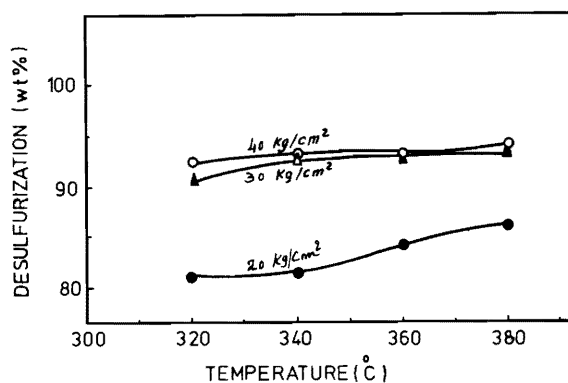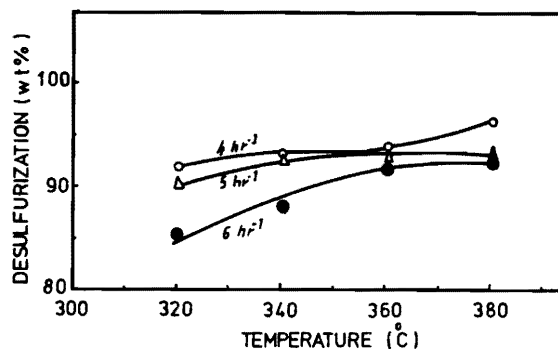

Figure 7. Effect of Temperature and Pressure on Desulfurization of Kerosine Using Catalyst UOP S–7. LHSV: $5h^{-1}$; $H_2/Feed$: 120 l/l
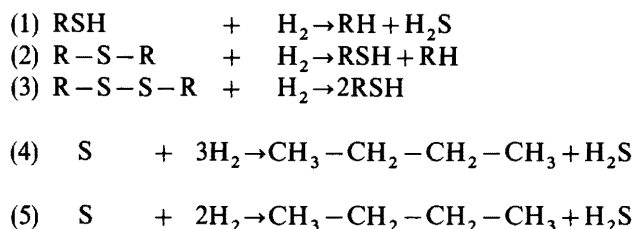
Figure 8. Effect of Temperature and Space Velocity on Desulfurization of Kerosine Using Catalyst UOP S-7. Pressure: 30 kg cm^{-2}; H$_2$/Feed: 120 l/l

mercaptan sulfur, that this catalyst promoted desulfurization of mercaptans better than catalysts A and B. The flash point, initial boiling point, and density of hydrodesulfurized kerosine are lower than the undesulfurized feed. Figures 7 and 8 show the effect of temperature, pressure as well as the liquid hourly space velocity of desulfurization.

DISCUSSION

Theoretically, sulfur compounds which are present in the kerosine fraction are mercaptans, sulfides, disulfides, and thiophene Polynuclear sulfur compounds are not expected to be in this boiling range. The desulfurization of these compounds in general is exothermic but it is expected from a thermodynamic point of view that thiopenes because of their aromatic nature are desulfurized at more severe conditions. Although equilibrium would favor this reaction at a low temperature, it is never reached under these conditions where the gas and liquid products are continuously driven out. The reactions that are anticipated to take place are as follows:

(1) $RSH \quad + \quad H_2 \rightarrow RH + H_2S$

(2) $R-S-R \quad + \quad H_2 \rightarrow RSH + RH$

(3) $R-S-S-R \quad + \quad H_2 \rightarrow 2RSH$

(4) $S \quad + \quad 3H_2 \rightarrow CH_3-CH_2-CH_2-CH_3 + H_2S$

(5) $S \quad + \quad 2H_2 \rightarrow CH_3-CH_2-CH_2-CH_3 + H_2S$

Reactions 1–3 are not pressure sensitive, unlike reactions 4 and 5. In general, reactions with heterogeneous catalysts are pressure sensitive, since the mechanism by which these catalysts react depends on the

extent of adsorption that is in turn a function of pressure, temperature, and the nature of the catalyst. An optimum temperature and pressure is always needed for the best desulfurization to take place since an equilibrium state cannot be reached for a continuous process.

From the results obtained on catalyst A, it seems that it is more active at higher temperatures than catalyst B. Liquid yields are more or less comparable at all pressures and temperatures for the two catalysts. Results of the effect of hydrogenation on aromatics are not very clear as indicated from the analysis. The difference which is observed between the feed and the desulfurized kerosine may be partially due to the production of gases, which give an average liquid yield of about 95% and partially from the reproducibility of the test itself. These results cannot be interpreted on the basis that some aromatics have been hydrogenated.

Comparing catalysts A and B, with catalyst C, it is clear that the flash point of the liquid product has been lowered as well as its specific gravity and its initial boiling point. This catalyst may have some acidic components which have promoted some hydrocracking reactions [5]. This is also clear for the liquid yield is generally less by about 1% than that obtained from each of the other two catalysts. This catalyst is apparently less active as a hydrodesulfurization catalyst for this type of kerosine.

It would appear, therefore, appropriate to mention that catalyst B is preferred to A and C for hydrodesulfurization of Shoukair kerosine due to its higher desulfurization activity at lower temperatures.

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