PRODUCTION OF LOW SULFUR FUEL OIL FROM DIFFERENT IRAQI RESIDUES CRUDES

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Abstract

Sharki Baghdad, mixture of Bai-Hassan (65vol. %) and Jambur (35vol. %), and Basrah crude oils were distillated in a laboratory distillation unit and the reduced crudes (623$^+$K) were collected. The percentage of each reduced crude was 61.91, 42.33, and 47.59 wt % of the original crude oil, respectively. The reduced crudes then treated with commercial pentane under specified conditions. The deasphaltened oils (86.30, 91.41 and 91.10 wt% of the original reduced crudes respectively) with sulfur content 4.82, 3.81 3.23 wt% were hydrotreated on commercial Co-Mo/γ -Al_2O_3 on a trickle bed reactor. The temperature varied from 573-673K with liquid hourly space velocity (LHSV) ranging from 0.69-2.90h^{-1}. Hydrogen pressure was kept constant through the experiment at 3.8MPa, with a hydrogen/ oil ratio of about 300l/l. The kinetics of HDS of the reduced crudes are well correlated with second order kinetics.

Introduction

Fuel oil is any liquid or liquefiable petroleum product burned for the generation of heat in a furnace or firebox or for the generation of power in an engine, exclusive of oils with a flash point below 310.9 K and oils burned in cotton or wool-wick burners [1].

Petroleum residual oil, such as the residue from atmospheric and vacuum distillation of crude oils, is considered to be undesirable feedstock for most refining processes because of its high metal and sulfur content. But, it is used as a cheap fuel oil.

The term heavy oil is generally applied to petroleum products with an American petroleum institute (API) gravity of less than 20° and usually, but not always, has a sulfur content higher than 2 % by weight [2].

They usually contain substantial portion of asphaltenes and resins which are nonvolatile fractions of petroleums and which contain the highest proportions of hetroatoms (i.e. sulfur, nitrogen, and oxygen) [3].

The two major characteristics of residua and heavy oil, which distinguish them from distillates, are that residua and heavy oil contain, (1) Asphaltenes and other high-molecular weight, highly aromatic, structures, and (2) Ash-forming constituents, including organometallic compounds, with nickel and vanadium being the predominant metals. The first characteristic, Asphaltenes have a marked effect on refining and result in the deposition of high yields of coke during the various thermal processes. The second characteristic of residua and heavy oils pertinent to hydrodesulfurization is the presence of organometallic compounds (of which nickel and vanadium are the principle constituents) that are present to varying degree in all residua and heavy oils. The deposition of these metals in any form on the catalyst leads to catalyst deactivation is still subject to speculation [4].

Hydrodesulfurization process of atmospheric and vacuum residues is used by refiners to produce low sulfur fuel oils. Hydrotreating upgrade oils by removing and cracking heavy molecules in the feed to produce lighter product oils. The amount of impurities removed depends on the feed and on the product specifications desired by the refiner. Sulfur removal greater than 95 percent, metal removal greater than 70 percent, carbon residue reduction greater than 70 percent and cracking of vacuum residue as high as liquid percent have been commercially demonstrated[2,5].

Hydrodesulfurization (HDS) is a catalytic process in which a crude oil fraction is passed with hydrogen, over or through a catalyst bed at elevated temperature and pressures [2].

Residual hydrodesulfurization (HDS) is quite evolved from distillate desulfurization. The HDS of heavy oils is more difficult than the HDS of petroleum distillates because they contain appreciable amount of metals and asphaltenes, which reduce the oils amenability to hydroprocessing, which caused deposit coke and metallic impurities on the catalyst. The general range of condition for hydrotreating process is wide and the choice is governed by the feedstock, desired products, available of hydrogen and economic consideration in addition to the related process operating conditions such as temperature,

LHSV, pressure, catalyst activity and H_2 to oil ratio [6]. Catalyst technology, operating / design experience and understanding of reaction kinetics are important stones toward residual HDS [7].

In this study an attempt was made to produce low sulfur fuel oils from different reduced crudes and to gain some insight into the role of asphaltenes in the HDS process.

Experimental Work

The feedstocks in this study were Sharki Baghdad, mixture of Bai-Hassan (65 vol %) and Jambur (35 vol %), and Basrah reduced crudes. Each reduced crude was obtained by distillation of the crude oil in a laboratory distillation unit. The percentage of each one was 61.91, 42.33, and 47.59 wt % of the original crude oil, respectively. The properties of the original and reduced crudes are given in Table 1 and Table 2, respectively.

Table 1 The Properties of Crude Oils

Specifications	Crude Oil		
	Sharki Baghdad	Mix. of (65%) Bai-Hassan & (35%) Jambur	Basrah
Specific Gravity at 15.6/15.6 °C	0.940	0.847	0.856
API	19	35	33.2
Viscosity 37.8 °C (cSt)	26.7	5.4	6.2
Pour Point °C	-15	-39	-39
Sulfur (wt. %)	4.5	2.2	1.9
CCR (wt. %)	10.0	4.3	6.2
Vanadium (wt. ppm)	76	27	26
Nickel (wt. ppm)	30	15	14
Ash (wt %)	.08	0.004	0.005
n-C7 Asphaltenes (wt. %)	6.2	1.1	1.3

Table 2 The Properties of Reduced Crudes

Specifications	Crude Oil		
	Sharki Baghdad	Mix. of (65%) Bai-Hassan & (35%) Jambur	Basrah
Specific Gravity at 15.6/15.6 °C	0.998	0.962	0.967
API	10.28	15.53	14.82
Viscosity 50 °C (cSt)	235.3	215	220
Sulfur (wt. %) (by X-Ray)	6.1	4.5	3.89
CCR (wt. %)	12.7	8.35	9.15
Vanadium (wt. ppm)	117	52	48
Nickel (wt. ppm)	45	31.1	27.71
Ash (wt %)	0.15	0.018	0.021
n-C7 Asphaltenes (wt. %)	8.97	6.1	6.33

Preparation of Hydrodesulfurization Feedstocks

Four feedstocks were hydrotreated in HDS pilot plant unit. Mixture of Bai-Hassan and Jambur, and Basrah deasphaltened reduced crudes were prepared at solvent-to-oil ratio 7, temperature 293 K, 45min mixing time using commercial pentane fraction, while the Sharki Baghdad deasphaltened reduced crude was prepared at solvent-to-oil ratio 10, temperature 293 K, 45min mixing time using the same solvent and the fourth oil was Sharki Baghdad reduced crude (RC). The percent of deasphaltened oils in Sharki Baghdad, mixture of Bai-Hassan and Jambur, and Basrah are 86.30, 91.41 and 91.10 wt % of the original reduced crudes respectively. The properties of the deasphaltened oils are given in Table 3.

Table 3 The Properties of Deasphaltened Reduced Crudes

Specifications	Crude oil		
	Sharki Baghdad	Mix. of (65%) Bai-Hassan & (35%) Jambur	Basrah
Specific Gravity at 15.6/15.6 °C	0.977	0.949	0.953
API	13.33	17.60	16.98
Viscosity C (cSt)	213.71	190.50	198.89
Sulfur (wt. %)	4.82	3.81	3.23
CCR (wt. %)	6.51	3.85	5.62
Vanadium (wt. ppm)	9.00	11.40	10.00
Nickel (wt. ppm)	7.00	5.20	4.41
Ash (wt %)	0.006	0.001	0.001
n-C5 Asphaltenes (wt. %)	13.97	8.59	7.89

Catalyst

The catalyst employed for the HDS process in this study was the commercial Co-Mo/γ-Al_2O_3 type catalyst. The properties of this catalyst are given in Table 4.

75 cm^3 of fresh catalyst was charged to the HDS reactor between two layers of inert material after drying at 393 K for 2 hours.

Table 4 Properties of Catalyst Commercial Co-Mo/γ Al_2O_3.

MoO_3, wt. %	15.0
NiO, wt. %	3.0
SiO_2 wt. %	1.1
Na_2O, wt %	0.07
Fe, wt %	0.04
SO_4, wt. %	2.0
Al_2O_3, wt. %	Balance
Form	Extrude
Surface Area, m^2/g	180
Pore Volume, cm^3/g	0.5
Bulk Density, g/cm^3	0.67
Mean particle diameter, mm	1.8
Mean particle length, mm	4.0

Hydrodesulfurization of Deasphaltened and Reduced Crudes

The hydrotreating experiments were performed in a pilot plant continuos high-pressure unit employing an up-flow cocurrent. The unit shown in Fig. (1) consists of the feed pump, reactor, high-pressure separator, and cooler.

The reactor used is a stainless steel (316-heat resistance) with 19-mm inside diameter i.d, 2-mm thickness and 773-mm length. The reactor was heated and controlled automatically by steel-jacket heaters. The thermocouples measured the temperature profile along the full length of the reactor. The separator was made of stainless steel with 350-mm length and 20-mm i.d.

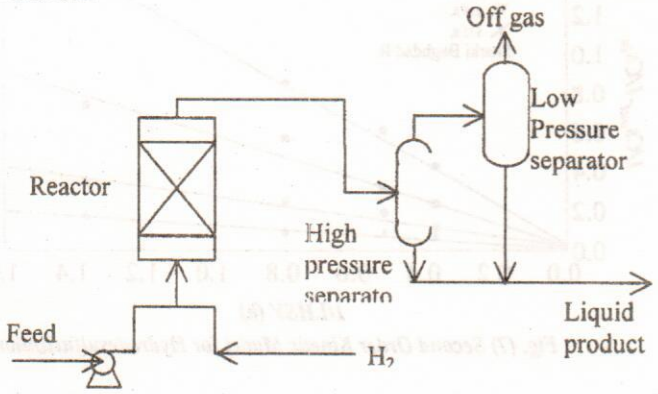


Fig. (1) General Scheme of heavy HDS Unit

The hydrodesulfurization reaction conditions employed are temperatures of 573 to 673 K, pressure 3.8 Mpa, Liquid hourly space velocity (LHSV) of 0.69-2.86 h^{-1} and hydrogen to oil ratio of 300 l/l. The products of reactions were cooled in a condenser cooler and separate from hydrogen and H_2S and the hydrocarbon gases. The gases then vented to the exterior through a gas flow meter. Final products were collected only after steady state operation was established and initial products were discarded.

Tests for the Feedstocks and Products

The sulfur contents of the feedstocks were determined by X-Ray fluorescence (ASTM: D 2622) while the sulfur contents of deasphaltened oil and the hydrotreated products obtained by quartz tube method (IP 63/55). The metal content of the reduced crudes, deasphaltened oils and hydrotreated products were evaluated using atomic absorption spectrophotometer (ASTM: D3327). n-Heptane asphaltenes of reduced crudes were determined by standard method (ASTM: D3279). The composition of solvents was obtained using gas chromatography (GC) analysis. Other tests such as the specific gravity, flash point, kinematic viscosity, ash content, Conradson carbon residue of the feedstocks and the products of each stage were carried out using IP 120/64, IP 15/67, IP 319/75, IP 4/75, and IP 3/66 respectively.

Results and Discussions

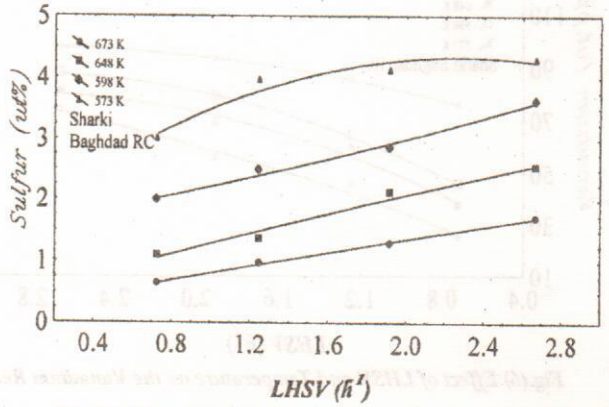
Hydrodesulfurization Process

Effect of Temperature and LHSV on Hertoatoms Removal

HDS process of residual oils has many variables, which effect the extent of hetroatoms removal. Temperature, pressure, LHSV, and hydrogen to oil volumetric ratio are the main process variables.

Throughout this study hydrogen pressure and hydrogen to oil ratio were kept constant at 3.8 Mpa and 300 l/l respectively. HDS experiments were carried out in the temperature range 573 to 673K over liquid hourly space velocities ranging from 0.69 to 2.86 h^{-1}

The removal of sulfur increases with increasing temperature, and decreasing LHSV as shown in Figs. (2-5). These results are in well agreement with other studies on the HDS of several residues [2, 8, 9, 10]. The increasing sulfur removal at higher reaction temperature may be attributed to several reasons. Firstly, at high reaction temperature the unreactive sulfur compounds become activated enough to react with hydrogen. Secondly, the large molecules are decomposed into smaller molecules, which can more easily diffuse into the catalyst micropores and reach the inner active sites where the desulfurization reaction occurs. Thirdly, the decreases in the viscosity increase the oil diffusivity through the catalyst micropores [11]. Metals removal or demetalization reactions occur simultaneously with the desulfurization reaction. For Sharki Baghdad reduced crude the removal of vanadium increases with increasing temperature, and decreases LHSV as shown in Figs. (6). This is due to increasing in destructive of large molecules especially asphaltenes, which is carried the major portion of the reduced oil metals.



Fig(2) Effect of LHSV and Temperature on the Sulfur Remov

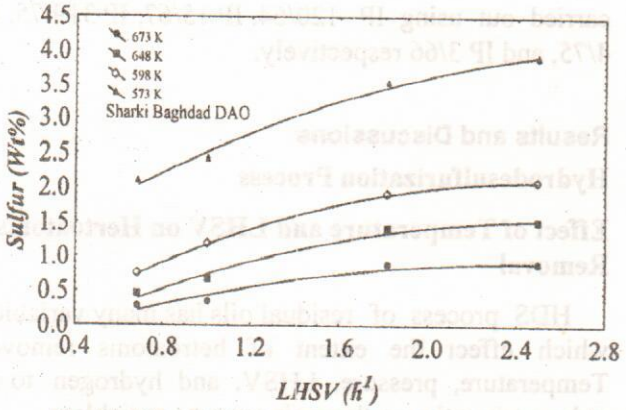


Fig. (3) Effect of LHSV and Temperature on the Sulfur Remo

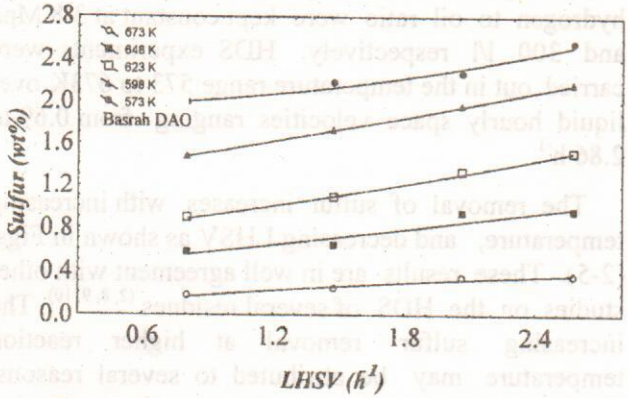


Fig. (4) Effect of LHSV and Temperature on the Sulfur Remov

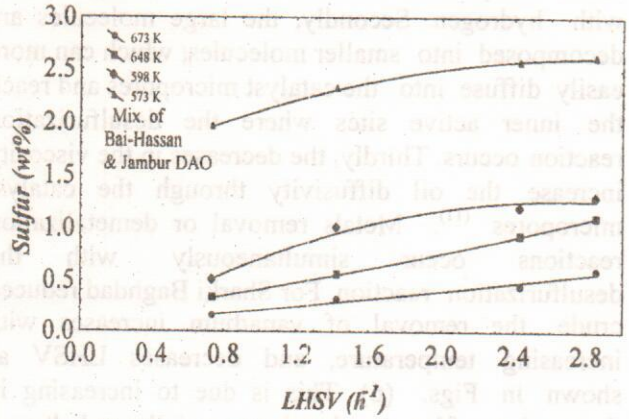


Fig.(5) Effect of LHSV and Temperature on the Sulfur Remov

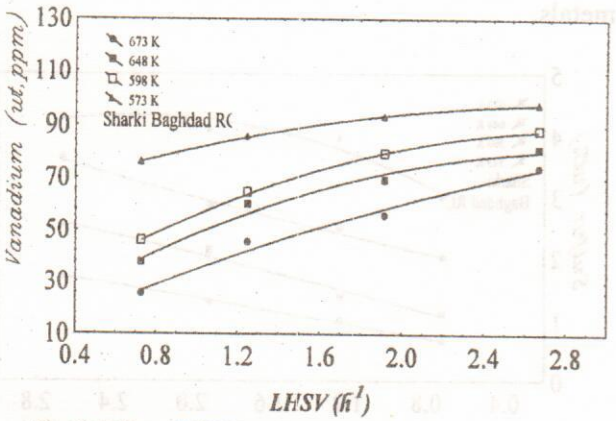


Fig.(6) Effect of LHSV and Temperature on the Vanadium Remo

Kinetics of the Hydrodesulfurization Process

Kinetics of Hydrodesulfurization

Data obtained from the pilot-plant unit for the desulfurization of the deasphaltened oils were analyzed by using $\frac{1}{CA_{out}} - \frac{1}{CA_{in}} = \frac{K}{LHSV}$ second order kinetic model to fit the obtained data by plotting $1/C_{out}$-$1/C_{in}$ vs. 1/LHSV as shown in Figs. (7-10). These plots give straight lines with slopes equal to rate constants.

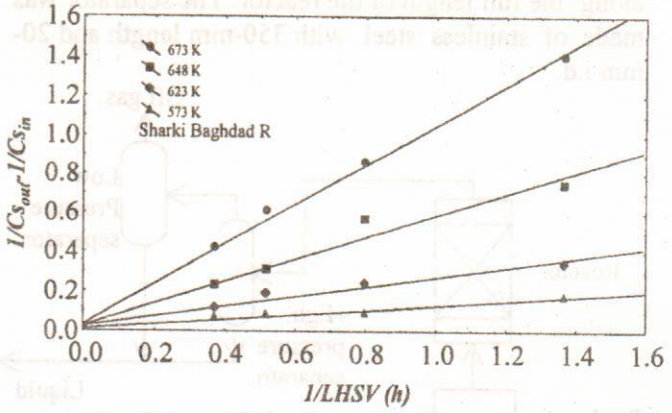


Fig. (7) Second Order Kinetic Model for Hydrodesulfurization.

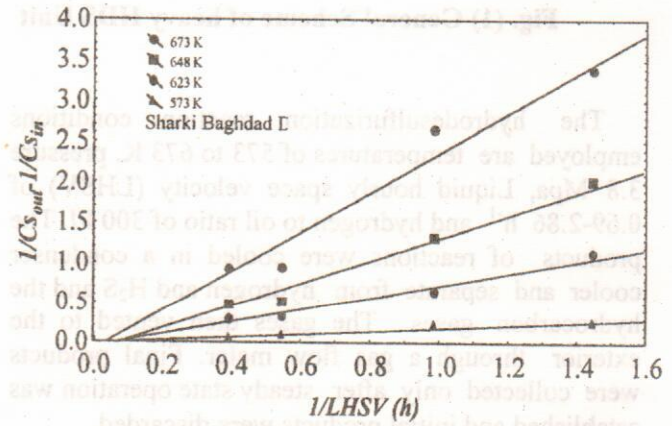


Fig. (8) Second Order Kinetic Model for Hydrodesulfurization

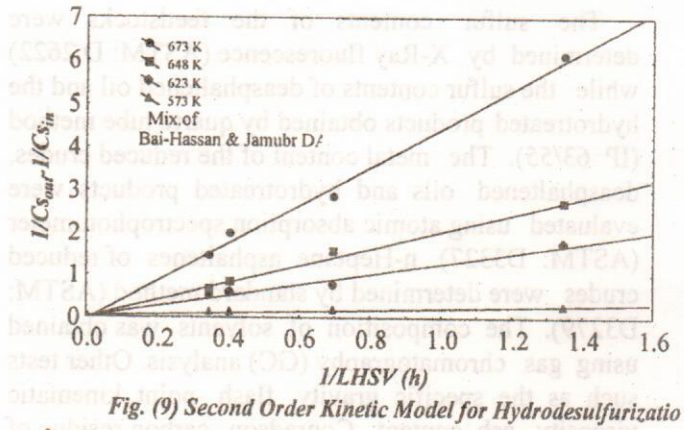


Fig. (9) Second Order Kinetic Model for Hydrodesulfurizatio

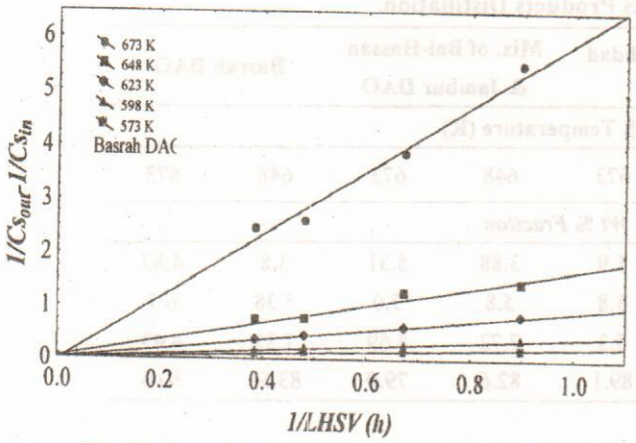


Fig. (10) Second Order Kinetic Model for Hydrodesulfurization

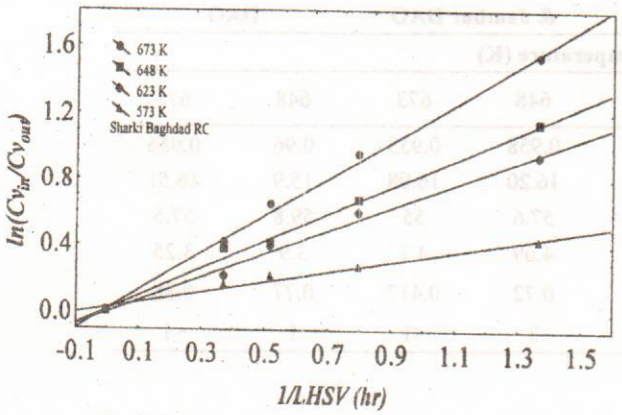


Fig. (11) First Order Kinetic Model for Vanadium Removal.

Kinetics of Demetalization:

Sharki Baghdad reduced crude was used for the study the kinetic of demetalization. The vanadium removal appeared to obey the $\ln\left(\frac{CA_{in}}{CA_{out}}\right)=\frac{K}{LHSV}$ ideal first order kinetics equation with negligible deviation from plug flow.

Plots of $\ln(Cv_{in}/Cv_{out})$ vs. 1/LHSV at different temperatures for Sharki Baghdad reduced crude gives straight lines with slops equal to rate constants as shown in Fig. (11).

Fuel Oil Production

Environmental control regulation, pollution, price, and economic limit the specifications of the burned fuel oils [1, 5].

Table (5) shows the specifications of commercial fuel oils used in United States, Canada and Japan.

According to these specifications, fuel oils obtained from reduced crudes and solvent deasphaltening process can not cover these specifications for fuel oils used in power stations and most industrial purposes because the sulfur content of these products is higher than that required by specifications as shown in Table (5). It is possible to produce fuel containing sulfur 2.36 % wt. (no.6) by mixing the deasphaltened oil from mixture of Bai-Hassan and Jambur of 55 vol % with gas oil containing 1 % sulfur produced from atmospheric distillation of crude oils.

The HDS is the only choice to produce low sulfur fuel oil. In order to produce low sulfur fuel oil from the deasphaltened oils and Sharki Baghdad reduced crude with reasonable CCR and low impurities level, hydrodesulfurization was carried out at temperatures 648 and 673 K, LHSV $1h^{-1}$, and at constant pressure (3.8 MPa) and hydrogen to oil ratio (300l/l). Table (6) shows the results of HDS products distillation, while Table (7) shows the properties of 623^{+}K distillated from hydrotreated different feedstocks.

Table 5 Specifications of some Commercial Fuel Oils [5].

Specifications	Commercial Fuel Oils						
	No.1	No.2	N0.3	No.4	No.5	No.6	No.7
Gravity, at 15.6/15.6 °C	0.948	1.008	0.986	1.001	1.00	0.967	0.973
°API	18.1	8.9	11.8	9.9	10	14.8	13.9
CCR, wt. %	5.70	5.58	10.19	12.91	10.40	10.70	22.65
Sulfur, wt. %	0.34	0.58	1.44	1.79	2.14	2.36	2.86
Nickel, ppm	-	-	14	15	26	20	23
Vanadium, ppm	<1	0.7	53	71	167	417	98
Ash, wt. %	-	0.016	0.044	0.051	0.055	0.073	0.15

Table 6 Material Balance of HDS Products Distillation.

Fractions	Sharki Baghdad DAO		Sharki Baghdad RC		Mix. of Bai-Hassan & Jambur DAO		Basrah DAO	
	HDS Temperature (K)							
	648	673	648	673	648	673	648	673
	Wt % Fraction							
Naphtha (-423K)	3.22	3.4	1.79	1.9	3.88	5.31	3.8	4.87
Kerosene (423-523 K)	3.48	4.3	2.61	3.8	5.8	7.0	5.38	6.7
Gas Oil (523-623 K)	4.8	5.5	4.2	5.3	7.72	8.69	7.31	8.43
Residue (623^+K)	88.5	86.8	91.4	89.1	82.6	79.0	83.51	80.0

Table 7 Properties of the HDS Distillate products Fuel Oils (623^+ K).

Specifications	Sharki Baghdad DAO		Sharki Baghdad RC		Mix. of Bai-Hassan & Jambur DAO		Basrah DAO	
	HDS Temperature (K)							
	648	673	648	673	648	673	648	673
Sp. Gr.	0.982	0.979	0.991	0.985	0.958	0.953	0.96	0.956
°API	12.59	13.00	11.29	12.15	16.20	16.98	15.9	16.51
Flash Point °C	93.5	89.7	68.5	71.4	57.6	55	59.8	57.5
CCR (wt. %)	5.47	5.15	5.89	5.72	4.69	4.1	3.9	3.25
S (wt. %)	1.39	0.44	1.53	1.15	0.72	0.417	0.77	0.38
V (wt. ppm)	5	2	46	27	3	<1	1	<1

Fuel oil with the following grades could be produced from hydrotreated residues 623^+K:

1. Fuel oil confirming the specifications of fuel no.1 with sulfur content 0.38 wt % from hydrotreared DAO of Basrah residue 623^+ K at temperature 673 K and LHSV 1 h^{-1}.
2. Fuel oil confirming the specifications of fuel no.3 with sulfur content 1.44 wt % from hydrotreated DAO of Sharki Baghdad 623^+ K at temperature 648 K and LHSV $1h^{-1}$.

Furthermore, fuel oil confirming with commercial fuel oil no.7 could be produced by 50 % blending Sharki Baghdad DAO with 50 % Sharki Baghdad hydrotreated DAO (623^+K) at temperature 673 K and LHSV 1 h^{-1}. This fuel oil has low price comparing with hydrotreated fuel oil.

Notation

DAO Deasphaltened reduced Crud

C	Concentration, weight percent	wt %
CCR	Conradson Carbon Residue	wt %
kv	Pseudo first order reaction rate constant	s^{-1}
L	Length of catalyst bed	m
LHSV	Liquid hourly space velocity	m^3 liquid/h.m^3 catalyst
R	Universal gas constant	8.314 kJ/kmole.K
S	Sulfur concentration in equation	wt. %
T	Temperature	K

Subscript

in	Inlet
out	Outlet
S	Sulfur
V	vanadium

Reference

1. Guthrie, B.V., "Petroleum Products Handbook", 2nd Ed., 1969
2. Speight J. G., "The Desulfurization of Heavy Oils and Residua", (1981).
3. Speight J. G., Am. Chem. Soc., 23-28, 1981.
4. Arey, W. F., Jr., Blackwell, N. E., and Reichle, A. D., Seventh World Petroleum Congress, 1968, 4, 167.
5. Meyers R. A., "Handbook of Petroleum refinery Processes", 2nd Ed.,(1996).
6. Shalit, H., and Schuman, S. C., Catalysis Review, 3, 300, 1971.
7. "Annual Book of ASTM Standards; American Society for Testing and Materials, No. D-396-67. 1989
8. Mohammed A-H. A-K., Hankish K. and Abbas K., Fuel Science and Technology Int., 65, (6) 1022, 1985.
9. Mohammed A-H. A-K. and Hankish K., J. Petrol. Res., 4 (2), 37, 1985.
10. Parayannakos N., Applied Catalysis, 24, 99, 1986.
11. Weisser, O., and Landa, S., "Sulphide Catalyst, their Properties and Applications", 1973.