

DEPARTMENT OF ENERGY, MINES AND RESOURCES MINES BRANCH OTTAWA

THE HYDRODESULPHURIZATION OF HEAVY GAS-OILS (650-975° F) DERIVED FROM ATHABASCA BITUMEN

P.S. SOUTAR, E.C. McCOLGAN, W.H. MERRILL AND B.I. PARSONS

FUELS RESEARCH CENTRE

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THE HYDRODESULPHURIZATION OF HEAVY

GAS-OILS (650-975°F) DERIVED FROM

ATHABASCA BITUMEN

by

P. S. Soutar*, E. C. McColgan*, W. H. Merrill** and B. I. Parsons**

ABSTRACT

The hydrodesulphurization characteristics of three heavy gas-oils derived from Athabasca bitumen were determined and compared. The experimental work was undertaken in a bench-scale flow system at 2000 psi with the oil and hydrogen percolating up through a fixed-bed of cobalt molybdate catalyst, i.e., the system was operated in a bottom-feed, mixed-phase mode. The range of temperatures investigated was from 320 to 420°C at liquid hourly space velocities of 1, 2, and 3 with a hydrogen flow rate of 5000 scf/bbl. The reference feed stock was a gas-oil prepared commercially (500-850°F) from Athabasca bitumen by delayed coking. This was compared to two experimentally produced gas-oils (650-975°F) generated by the thermal and catalytic hydrocracking of Athabasca bitumen in a Mines Branch pilot plant.

The reaction characteristics of the three gas-oils were found to be very similar. Products comparable to ASTM Grades 4 and 5 fuel oils containing 0.3 to 1% sulphur could be produced at all the space velocities investigated at low reaction temperatures 340 to 400°C. Slightly more lightends were produced with the lower-boiling coker gas-oil than with the higher-boiling hydrocracked gas-oils but the amounts involved were not large. No significant catalyst deactivation was observed with any of the feed stocks over the 45-50 operating hours involved in any of the series of experiments.

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Bulletin technique TB-179 de la Direction des mines

HYDRODESULFURATION DU GAS-OIL LOURD (650-975°F)

DERIVE DU BITUME DE L'ATHABASCA

par

P.S. Soutar*, E.C. McColgan*, W.H. Merrill** et B.I. Parsons**

RESUME

Les auteurs déterminent et comparent les caractéristiques d'hydrodésulfuration de trois types de gas-oil dérivés du bitume de l'Athabasca. Le travail a été entrepris à l'aide d'un système d'écoulement à échelle expérimentale à une pression de 2,000 livres par pouce carré avec du pétrole et de l'hydrogène passant à travers un lit fixe d'un catalyseur à molybdate de cobalt, i.e. le système a été exploité selon le mode d'alimentation par le bas, en phase mixte. L'échelle des températures de l'expérience était de 320 à 420°C aux vitesses spatiales liquide par heure de 1, 2, et 3 avec un débit d'hydrogène de 5,000 pieds cubes normaux/baril. Le stock d'alimentation de référence était un gas-oil préparé commercialement (500-850°F) à partir du bitume de l'Athabasca par cokéfaction différée. On l'a comparé à deux types de gas-oil expérimentaux qui sont le produit de l'hydrocraquage thermique et catalytique du bitume de l'Athabasca à l'installation d'essai de la Direction des mines.

Les caractéristiques de la réaction des trois types de gas-oil ont semblé être tout-à-fait semblables. On pourrait obtenir des produits comparables aux huiles combustibles de l'ASTM de qualités de 4 et 5 contenant de 0.3 à 1% de soufre à toutes les vitesses spatiales expérimentées à basses températures de réaction de 340 à 400°C. On a produit un peu plus de fractions légères avec le gas-oil de l'unité de cokéfaction à bas point d'ébullition qu'avec les types de gas-oil hydrocraqués à un point d'ébullition plus élevé, mais les quantités en question n'étaient pas importantes. On n'a pas observé de déactivation du catalyseur chez aucun des stocks d'alimentation après les 45-50 heures d'opération pour chacune des séries d'expériences.

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INTRODUCTION

The objective of the following work was to demonstrate the ease with which high-boiling gas-oils derived from tar sands bitumen can be hydrodesulphurized and converted to low-sulphur fuel oils. Partly as the result of more strict environmental regulations and partly because of the general increase in energy requirements, the demand for low-sulphur fuel oils for commercial applications and electric power generation is growing rapidly. The market potential for heavy fuel oils (approximately equivalent to ASTM fuel oil Grades 4 and 5) is large and it is logical to look to the huge tar sands and other bitumen deposits in northern Alberta as a source of supply.

Attempts to hydrodesulphurize the Alberta bitumens directly to produce "residual-class" fuel oils have encountered many difficulties (1, 2). At moderate pressures (1000 - 2000 psi) catalyst effectiveness has generally been found to be low and catalyst life quite short. The reasons for this have not been established with certainty, but are believed to be associated with the high molecular weight material in the feed and/or the high concentrations of combined metals and residual mineral matter. Increasing the operating pressure of the hydrodesulphurization process up to 5000 psi (3) greatly improves catalyst life but, unfortunately, also results in a prohibitive increase in capital and operating costs.

To circumvent the high costs connected with a direct catalytic process, most upgrading schemes for asphaltic feed stocks first convert the bulk of the residuum material into distillate fractions by thermal coking (4) or by low pressure thermal hydrocracking (5). The refining process is then completed by hydrodesulphurizing the distillate. The asphaltic and resinous hydrocarbon material, metals and minerals are removed in the thermal processes and catalyst activity and life with the distillate fractions is generally good. The over-all yield of liquid fuels is less by this two-step procedure (because of pitch or coke formation in the thermal pretreatment) but the economic penalty of this loss is not as great as that associated with direct catalytic processing*. A very real advantage of the two-step procedure is that the hydrocarbon quality of the heavy fuel oils produced is considerably better than the usual oils marketed as Grades 4, 5, and 6 residual fuels. No residuum material or metals are present in distillate fuels.

^{*}This is the situation at the present time. An increase in the value of crude petroleum or petroleum products could change the economics drastically.

As a consequence of the two-step approach, more and more attention is being focused on techniques for distilling hydrocarbon mixtures to higher temperatures, i.e., cutting deeper into the residuum fraction to produce more, and heavier, gas-oils. Most older industrial vacuum or steam distillation systems have a temperature limit of approximately 850°F equivalent temperature at one atmosphere. The latest proposal for bitumen upgrading indicates that the limit is now 975°F (5). In the following work the desulphurization characteristics of two higher-boiling gas-oils (650-975°F) produced from bitumen were determined and compared to those of the heaviest fraction currently produced and desulphurized commercially (500-850°F). The object was to establish whether extraordinary conditions are required for the heavier fraction or, if not, the relative ease of desulphurization with a view to producing clean oils approximately equivalent to ASTM Grades 4 or 5 fuel oil.

EXPERIMENTAL

Genera1

The experimental work was undertaken in a bench-scale flow system with the oil and hydrogen percolating <u>up</u> through a fixed-bed of cobalt molybdate catalyst. In a bottom-feed arrangement, the high-boiling components of the feed stock are present in the catalyst bed in the liquid phase and progress through the reaction system mainly by displacement. The operational advantages of a bottom-feed over a top-feed system have been outlined in an earlier bulletin (6). The major components of the apparatus together with the general method of operation and the analytical procedures applied to the products are described in Mines Branch Research Report R-194 (7).

The range of reaction temperatures investigated was from 320 to 420°C at liquid hourly space velocities (LHSV) of 1, 2 and 3. All the experiments were made at 2000 psi with a hydrogen flow rate of 5000 standard cubic feed per barrel (scf/bbl). The catalyst used was 1/8-inch pellets of cobalt molybdate on alumina manufactured by the Harshaw Chemical Co. of Cleveland, Ohio. A fresh charge of catalyst was placed in the reaction vessel for each series of experiments. The initial high activity of the

catalyst (characteristic of the first few hours of operation) was dampened by pretreating each charge for five hours at 400°C, 2000 psi and LHSV = 1. The activity of the catalyst after each series of tests was checked by repeating the first experiment in the series and comparing the result. The average running time for each experiment was approximately four hours.

Feed Stocks

The general properties of the gas-oil feed stocks are shown in Table 1. The boiling range of each is shown with the products of the desulphurization experiments (see Tables 2 to 4 in the following section). The standard, or reference feed stock for the investigation was the gas-oil prepared from Athabasca bitumen by delayed coking in the refinery of Great Canadian 0il Sands Ltd. at McMurray, Alberta (4). At the present time, this is the heaviest distillate fraction (500-850°F) produced commercially from any of the Alberta bitumens. Two higher-boiling gas-oils (650-975°F) were distilled from Athabasca bitumen that had been a) thermally and b) catalytically hydrocracked in a pilot plant flow system at the Mines Branch. The average conversion level of the residuum (+975°F) in the hydrocracking experiments was about 70%* and the operating pressure was 1000 psi. The catalyst used in the hydrocracking experiments was cobalt molybdate on alumina.

EXPERIMENTAL RESULTS AND DISCUSSION

In very broad terms, the hydrodesulphurization characteristics of the two high-boiling hydrocracked gas-oils and the medium-range coker gas-oil were quite similar. The main results of the investigation are summarized in Figures 1 and 2. With all of the feed stocks, the bottom-feed system was easy to operate, temperature control in the reaction vessel was good, and flexibility was high. Fuel oil type products containing 0.3 to 1% sulphur could be produced over a range of space velocities (1 to 3) at low reaction temperatures (320 to 395°C) with the coker gas-oil. Slightly greater reaction temperatures were required to achieve the same level of desulphurization with the two high-boiling gas-oils, but the temperature increases were small (5 to 20°C) and well below the temperature where coking is a problem with a cobalt molybdate catalyst. No significant catalyst deactivation was observed

^{*}This is to be compared to the 45-50% conversion level reported for delayed coking (4).

Table 1

The General Properties of the Feed Stocks

Details of Analyses	Coker Gas-Oil (500-850°F)	Thermally Hydrocracked Gas-Oil (650-975°F)	Catalytically Hydrocracked · Gas-Oil (650-975°F)
Specific Gravity 60/60°F	0.950	0.975	0.960
Sulphur (wt %)	3.38	3.44	2.20
Nitrogen (wt %)	0.26	0.33	0.40
Conradson carbon (wt %)	0.21	0.77	0.42
Ash (wt %)	t	t	t
Vanadium (ppm)	2	<1	<1
Viscosity, Kinematic (cSt) at 100°F	18.8	77.6	67.1

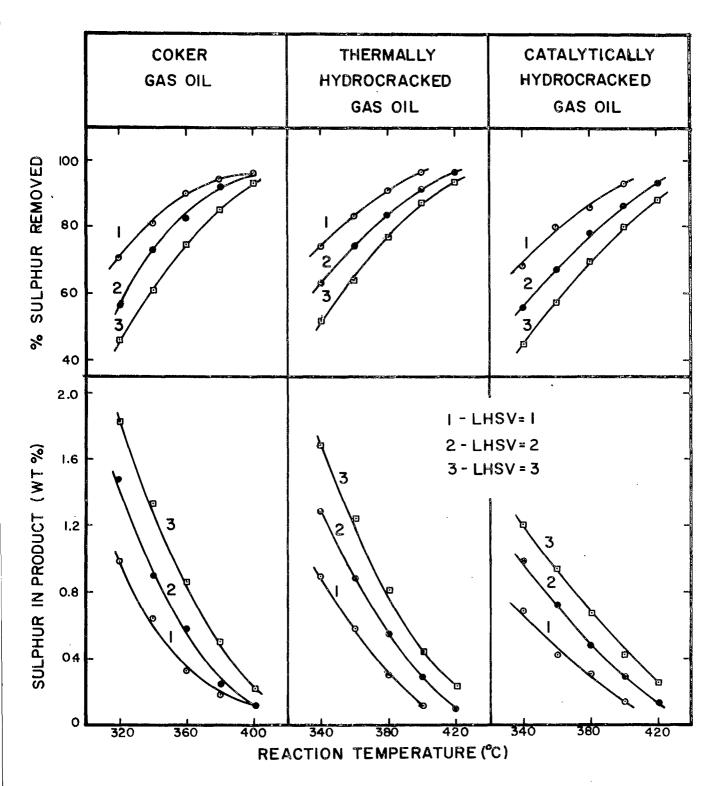


Figure 1. - The effect of space velocity and reaction temperature on desulphurization.

(pressure = 2000 psi; hydrogen flow rate = 5000 scf/bbl)

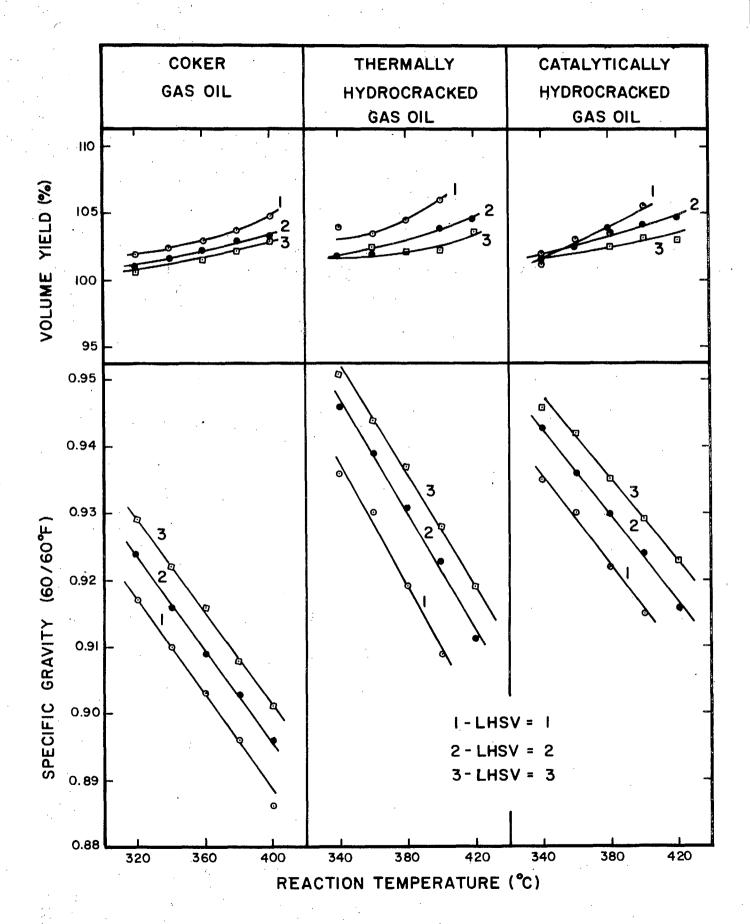


Figure 2. - The effect of space velocity and reaction temperature on the volume yield and specific gravity of the products.

(pressure = 2000 psi; hydrogen flow rate = 5000 scf/bbl)

with any of the feed stocks over any series of experiments (totalling 45-50 operating hours) and no deposits of any kind, tar or coke, were detected on the catalyst pellets at the conclusion of any of the tests.

The low reaction temperatures required and the comparative insensitivity of the system to changes in the boiling range of the feed stock are important advantages. An oil refinery combines many processes and considerable equipment, i.e., reactor and distillation systems, pumps, etc., not all of which operate at top efficiency all the time. The results of the present study indicate that substantial changes (or disruptions) in either the boiling range or operating conditions could be tolerated without appreciable change in the product.

An interesting aspect of the investigation to note with the two 650-975°F gas-oils is that the reaction conditions required to form lowsulphur products (0.7 to 0.2% sulphur) were, for all practical purposes, independent of the initial sulphur concentration. For example, the reaction temperatures required to produce oil products containing 0.5% sulphur at LHSV = 2 from the thermally hydrocracked and catalytically hydrocracked gasoils differed by only 4°C (383° and 379°C respectively) even though the initial sulphur concentration of one feed stock was 60% greater than the other (3.5% and 2.2% S respectively). Where the extent of desulphurization was less, of course, the reaction temperatures required with the catalytically produced gas-oil were significantly lower. The point to be made is that a catalytic hydrocracking pretreatment of a feed stock like the Athabasca bitumen does not materially lessen the severity at which the secondary desulphurization process must be operated*. There may be advantages inherent in the catalytic hydrocracking process itself, such as increased liquid yield or stability in storage, etc. but at high desulphurization rates the severity at which the secondary hydrodesulphurization units must be operated is dictated by the sulphur level required in the final product.

The combined weight yield of liquid product and sulphur removed was either equal to, or slightly greater than, 100% for all the experiments. Considerable lowering of the specific gravity accompanies desulphurization with the result that the volume yield of liquid product always exceeded 100%. At high desulphurization levels (where the sulphur remaining in the liquid product was of the order of 0.5%) the volume yield was 103-104%. The usual

^{*}And, by inference, increase the catalyst life in the secondary process.

commercial practice is to sell fuel oils on a volume basis, i.e., per gallon or per barrel. The selling price for low-sulphur No. 5 fuel oil in the Chicago area is currently \$5.45 per barrel (8). A 4% increase in volume represents a processing gain of 21 cents per barrel.

The results of distillation and sulphur analyses on typical products formed from the three gas-oils are shown in Tables 2 to 4. The reaction conditions selected for the comparison were LHSV = 1, 2 and 3 at 380°C. More light ends (boiling up to 392°F) were formed with the 500-850°F coker gas-oil than either of the 650-975°F hydrocracked gas-oils. The amounts involved were not large, i.e., a maximum of 3.5% for the coker gas-oil at LHSV = 1 compared with 1% for the hydrocracked gas-oil under similar conditions. It would appear that the larger amount of light-ends produced from the coker gas-oil is due almost entirely to the presence of the lower-boiling components, the 500-650°F fractions, in the feed stock. With the higher-boiling gas-oils the amount of light-ends produced was negligible even under high desulphurization conditions.

The results of the distillation analyses show that a general lowering of the average boiling point accompanies desulphurization ... the extent of lowering increasing with reaction severity (greatest at low space velocities and least at the highest space velocity). The fraction most affected in every instance was the high-boiling hydrocarbon, the +790°F material. For example, as shown in Table 3 for the thermally hydrocracked gas-oil at 380°C, the +790°F fraction decreased from 44% (in the feed) to 35% at LHSV = 3 and 2, and 27% at LHSV = 1. Minimal change occurred between LHSV = 2 and 3 with all three gas-oils which suggests immediately that for heavy fuel production the reaction conditions at a space velocity of one and 380°C are too severe. At high desulphurization levels, the feed rate to the system and the corresponding residence time of the heavy oil components in the catalyst bed undoubtedly have an important bearing on the extent of hydrocracking which occurs after desulphurization as well as in the course of desulphurization. It is difficult to predict exactly where and when the (excessive) hydrocracking is taking place but the present work would indicate that at LHSV = 1 some hydrocracking is occurring after desulphurization. a space velocity of one, the theoretical residence time of the feed stock in the catalyst bed of a bottom-feed system is about 20 minutes*; at LHSV = 2 and 3 the theoretical residence times are 10 and 7 minutes respectively.

^{*}The void-space in the packed bed being approximately one third of the total volume of the reaction zone.

Table 2

The Yield and Sulphur Content of the Product

Fractions Formed from the Coker Gas-Oil at 380°C

(Note: The fractions are expressed as weight % of feed)

	Feed	Stock	LHSV	= 1	LHSV	= 2	LHSV	= 3
Boiling Range of Fraction Equiv. Temp. at one atm (°C) (°F)	wt % of Fraction	wt % of Sulphur						
RT-100 RT-212	_	-	· -	-	_	-	-	_
100-200 212-392	-	-	3.5	-	2.0	-	1.0	-
200-250 392-482	1.2	-	4.4	0.04	4.5	0.03	3.5	0.12
250-275 482-527	5.8	2.67	11.0	0.03	10.0	0.07	7.6	0.18
275-332 527-630	26.5	2.90	32.8	0.07	32.5	0.15	33.4	0.32
332-361 630-682	24.8	3.25	23.1	0.06	24.2	0.33	24.3	0.58
361-391 682-736	14.4	3.54	6.8	0.19	7.8	0.42	9.7	0.63
391-421 736-790	17.7	3.73	11.5	0.19	11.3	0.51	12.8	0.76
+421 +790	9.6	4.01	3.7	0.26	4.6	0.48	4.8	0.78
Sulphur Removed	-	-	3.2		3.1		2.9	
Totals	100		100		100		100	

Table 3

The Yield and Sulphur Content of the Product Fractions

Formed from the Thermally Hydrocracked Gas-Oil at 380°C

(Note: The fractions are expressed as weight % of feed.)

-	Feed	Stock	LHSV	= 1	LHSV	= 2	LHSV	= 3
Boiling Range of Fraction Equiv. Temp. at one atm (°C) (°F)	wt % of Fraction	wt % of Sulphur						
RT-100 RT-212	-	-	<u>-</u>	-	-	-	-	***
100-200 212-392	-	-	1.0	-	0.9	-	0.9	-
200-250 392-482	1.9	-	1.4	-	2.0	0.16	2.0	0.17
250-275 482-527	1.2	-	2.9	0.1	2.5	0.17	2.3	0.15
275-332 527-630	5.0	2.87	12.8	0.27	8.9	0.36	8.5	0.50
332-361 630-682	13.2	3.09	17.8	0.20	15.8	0.38	19.2	0.60
361-391 682-736	13.7	3.27	10.0	0.21	13.6	. 0.49	11.1	0.73
391 - 421 736-790	20.8	3.36	23.8	0.26	18.4	0.62	17.9	0.86
+421 +790	44.2	3.83	27.1	0.38	35.0	0.77	35.4	1.04
Sulphur Removed	-	-	3.2	į	2.9		2.7	
Totals	100		100	.	100		100	

Pressure = 2000 psi

Hydrogen Flow Rate = 5000 scf/bb1

Table 4

The Yield and Sulphur Content of the Product Fractions

Formed from the Catalytically Hydrocracked Gas-Oil at 380°C

(Note: The fractions are expressed as weight % of feed.)

	. Feed	Stock	LHSV	= 1	LHSV	= 2	LHSV	= 3
Boiling Range of Fraction Equiv. Temp. at one atm (°C) (°F)	wt % of Fraction	wt % of Sulphur						
RT-100 RT-212	-	-	-	-	-	-	-	-
100-200 212-392	-	-	0.9	-	0.3	-	0.3	-
200-250. 392-482	0.6	-	1.3	-	1.1	-	0.9	-
250-275 482-527	1.1	-	1.7	-	1.9	0.11	1.4	0.18
275 - 332 527-630	3.8	1.75	11.3	0.25	8.6	. 0.23	9.4	0.34
332-361 630-682	14.1	1.86	16.6	0.16	16.8	0.32	14.5	0.43
361-391 682-736	14.7	2.03	15.1	0.25	14.6	0.37	15.3	0.55
391-421 736 - 790	21.2	2.15	20.7	0.32	20.1	0.49	20.9	0.69
+421 +790	44.5	2.46	30.5	0.35	34.9	0.59	35.8	0.83
Sulphur Removed	_	-	1.9		1.7		1.5	
Totals	100		100		100		100	

Pressure = 2000 psi

Hydrogen Flow Rate = 5000 scf/bb1

The optimum space velocity in the present bottom-feed experimental arrangement appears to be 2 to 3. It is unlikely that still higher space velocities would be practical on an industrial scale because of the difficulty of removing the heat generated by the (exothermic) desulphurization reaction.

The viscosity, cloud and pour points of typical products formed from the three gas-oils at a liquid hourly space velocity of 2 are shown in Table 5. The viscosity and pour point of all the low-sulphur products (less than 1% sulphur) from the coker gas-oil meet the ASTM specifications of a Number 4 fuel oil (9) where no preheating is usually required for handling or burning. The products from the 650-975°F hydrocracked gas-oils do not meet the Number 4 pour point specifications (maximum 20°F) but fall well below the maximum viscosity requirements for a Number 5 (light) fuel oil. By all reasonable standards the low-sulphur products from any of the gas-oils would be good fuel oil for an electrical power generation station or any commercial application. They are all distillate fuels containing virtually no residuum or chemically combined metals, and are (potentially) available in multibillion barrel quantities from bitumen reserves in the Athabasca, Peace River, Cold Lake, and Lloydminster areas.

POSTSCRIPT

The mention of specific brand names for equipment and materials is made for information purposes only and does not imply endorsement by the Mines Branch.

Table 5 The General Properties of Typical Products Formed at LHSV = 2

Feed Stock	Reaction Temp. (°C)	Specific Gravity (60/60°F)	Sulphur in Product (wt %)	Cloud Point (°F)	Pour Point (°F)	Viscosity at 100°F (cSt)
Coker	400	0.896	0.11	26	5	8.2
Gas-Oil 3.38% Sulphur	380	0.903	0.25	22	15	9.5
	340	0.916	0.92	22	15	11.6
Thermally	420	0.911	0.10	46	40	14.6
Hydrocracked	380	0.931	0.55	44	45	31.8
Gas-Oil 3.44% Sulphur	360	0.939	0.89	70	40	37.6
Catalytically	420	0.916	0.14	56	45	19.4
Hydrocracked	380	0.930	0.48	58	50	35.7
Gas-Oil 2.20% Sulphur	340	0.943	0.99	66	50	46.2
Pressure = 2,000 psi		, ,	Hydrog	en Flow Ra	te = 5,000	scf/bbl

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