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HYDROCRACKING OF ATHABASCA BITUMEN: EFFECT OF OPERATING CONDITIONS
ON SULPHUR-TYPE DISTRIBUTION IN THE NAPHTHA FRACTION OF PRODUCT

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HYDROCRACKING OF ATHABASCA BITUMEN: EFFECT OF OPERATING CONDITIONS ON SULPHUR-TYPE DISTRIBUTION IN THE NAPHTHA FRACTION

by

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INTRODUCTION

The upgrading of Athabasca bitumen requires the use of pyrolytic processes. Coking processes are wasteful and hence alternates are being sought by the Department of Energy, Mines and Resources. One of the alternatives is hydrocracking (1), and this report deals with the effect of increasing the severity of hydrocracking of this asphaltic sulphurous bitumen (Table 1) on sulphur analysis in the products, and sulphur compound-type distribution in the naphtha fraction up to 200°C.

Further removal of different sulphur compounds in the hydrocracked liquid product by hydrotreating is dependent on the type and general structure of these compounds. Processing high-sulphur products reduces the capacity of the refining process and increases the cost of the final products. Furthermore, most sulphur compounds have unfavourable effects on the service properties of fuels: reducing storage stability, decreasing engine life, and lowering engine performance. A knowledge of the total sulphur in products is important; however the chemical group composition is also very important, as some sulphur structures are more harmful for certain applications than others. On the other hand, complete removal of sulphur compounds from fuels will not always lead to an improvement and may lead to impairment of certain important service properties of the fuels, e.g., thiophenes have high thermal oxidation stability and can be used as anti-oxidant additives; also they are less corrosive than other sulphur types. But regardless of what form of sulphur compound is present, the combustion products will contain sulphur oxides that pollute the environment.

The presence of considerable amounts of olefins in the naphtha fraction of hydrocracked Athabasca bitumen (12) presents an analytical problem in sulphide sulphur determination, and this was dealt with in this investigation.

The sulphur content distribution in the thermal and catalytic liquid products and asphaltenes, as well as the sulphur-type distribution in the naphtha fraction boiling up to 200°C, were investigated.

EXPERIMENTAL PROCEDURES

Thermal Hydrocracking

The hydrocracking pilot plant and its operation on Athabasca feed have been described in a previous report (1). The reactor is a vertical vessel into which the Athabasca bitumen and hydrogen are fed at the bottom. The resulting products, both liquid and vapour, flow from the top of the reactor to a hot separator. The condensed material in this separator is withdrawn continuously as a heavy-oil product, through a pressure reducing valve into an atmospheric receiver. The uncondensed vapours flow from the hot separator to a cold receiver where the light-oil product is withdrawn continuously. The gas stream from the cold receiver, consisting mainly of hydrogen and containing impurities such as uncondensed hydrocarbon gas, hydrogen sulphide and ammonium sulphide is water-and oil-scrubbed. The scrubbed hydrogen is joined by fresh make-up hydrogen and is then recycled to the reactor at a constant controlled rate.

Four liquid samples of the light- and heavy-oil products representing increasing degrees of hydrocracking were selected for investigation. The samples are representative of steady state conditions at a liquid hourly space velocity of 2 and temperatures of 410, 420, 430 and 470°C, and are designated in this report as Samples 1, 2, 3 and 4. All the samples resulted from processing at 2000 psi operating pressure except the sample of 470°C which was at 3500 psi. Experimental conditions and further details for these samples are given in References 2 and 3.

Catalytic Hydrocracking

A coal-base catalyst, described in a previous CANMET report (4), was used at 460°C, 2000 psi, and a space velocity of 2 h⁻¹ to elucidate the effect of catalyst on the sulphur compound-type distribution of the gasoline product, compared to the non-catalytic product. The catalyst was made using Co(NO₃)₂·6H₂O and (NH₄)₆ Mo₇O₂₄·4H₂O dissolved in water and then mixed with Al₂O₃·H₂O gel. The resulting gel was then mixed with coal to give a catalyst with 15% by weight of metal oxides and 85% coal. The sample from this run was designated as 5(C).

Distillation

The light oil was distilled (ASTM D216-54) to separate the naphtha up to 200°C, and the fraction boiling above 200°C was combined with the de-asphalted heavy-oil product in the correct proportion.

Deasphalting

The asphaltene portion of the heavy-oil product was precipitated by the addition of 20 volumes of pentane to one volume of oil. The asphaltenes were separated by filtration, extracted with pentane in a Soxhlet extractor and dried first on a water bath and then under reduced pressure at 50°C. The main pentane solubles and washings were combined and n-pentane was completely evaporated from these maltenes.

Analytical Methods for Sulphur Compound Types

Prior to any sulphur-type determination, hydrogen sulphides was removed from all the samples by shaking with an equal volume of 10% CdCl₂ solution in water.

For a complete scheme of sulphur group analysis, the method described by Rubenshtein et al. (5) was adopted with slight modifications. This method is based on potentiometric titration of different groups of sulphur in presence of each other.

Total Sulphur

The INAX X-ray fluorescence spectrometer was used for total sulphur content determination in all the products except sulphur in asphaltenes which was determined by the IR-33 LECO sulphur determinator.

Elemental Sulphur

A modification of Sommer's semiquantitative colour test (6) and a method based on the reaction of free sulphur with cyanide-ferric chloride reagent, which gives a coloured ferric-thiocyanate complex that absorbs at 465 m μ (7), were used. The latter is sensitive to 2 ppm of elemental sulphur.

Mercaptans

This sulphur type was determined argentometrically by means of potentiometric titration using silver sulphide and calomel electrodes (5).

Total Sulphides

According to a detailed review of methods of determining sulphur compounds (8), potentiometric titration is the most effective method for sulphide sulphur determination. In this investigation, sulphides were potentiometrically titrated against potassium iodate in a solvent of 60 ml acetic acid and 50 ml benzene, and the solvent was saturated prior to use with dry hydrogen chloride to the maximum possible concentration of about 2 mol/l (see the discussion section). A platinum and a calomel electrode were used in the titration.

Aliphatic Sulphides

The aliphatic sulphides (open chain and cyclic) were determined from the ultra-violet spectrophotometric absorptions (Beckman model DK-2) of the iodine-aliphatic sulphide complexes at 310 m, according to the procedure described by Hastings (9) and modified by Drushel et al. (10). Interference from olefinic materials is negligible because the absorption of their iodine complex at 310 m μ is low relative to the absorption of the sulphide complex.

Aromatic Sulphides

This group was calculated as the difference between the values of total sulphides and aliphatic sulphides.

Residual Sulphur (Unreactive)

Sulphur present in complex chemical structures that are not covered by the above group types is termed "residual sulphur". The thiophenic compounds are incorporated within this group. Residual sulphur is calculated as the difference between the values of total sulphur and the sum of sulphur types determined potentiometrically.

RESULTS AND DISCUSSION

This work deals with the naphtha fraction boiling up to 200°C, obtained from the hydrocracking of Athabasca bitumen under conditions of increasing severity. The gross composition of the products is shown in Table 2. The naphtha fraction increased steadily from 3.9% in the product from mild hydrocracking conditions (Sample 1) to 21.6% in the most severely-treated product (Sample 4). The amount of oil and resin fraction distilling above 200°C was equal in the catalytic product (Sample 5C) and in Sample 3, in spite of the considerable difference in their pitch conversion (conversion of heavier fractions to fractions boiling below 524°C equivalent atmospheric boiling temperature). The asphaltene content decreased steadily with the increase of the severity of hydrocracking. The sum of naphtha, oil and resins, and asphaltenes does not add up to 100% in Table 2. The difference is due to gaseous product and errors in measurements. The lighter fractions were swept from the reactor with the hydrogen stream as formed, therefore their residence time was limited. This allowed substantial amounts of the relatively thermally-unstable compounds to survive cracking.

Sulphur Conversion

Sulphur removal from the total liquid product increased with the increase in severity of hydrocracking from Samples 1 to 4 (Table 3), but was substantially higher in the catalytic product (72.7%). This trend is reflected in the sulphur contents of the two fractions, oil plus resins and asphaltenes, for all the products (Tables 4 and 5), Figures 1 and 2. On the other hand, the total amount of sulphur in the naphtha fraction from 100 grams of total product (Table 5) increased substantially with hydrocracking in spite of the progressive decrease in the percentage sulphur content of the samples. This was caused by the increasing quantity of naphtha in the products. The liquid products of the catalytic sample (Sample 5C) were of markedly lower sulphur content than the non-catalytic samples.

Sulphur Compound-Types

The effect of increasing the severity of hydrocracking on the sulphur compound-type distribution is shown in Tables 6 and 7. Elemental sulphur was absent in all the naphtha products, as would be expected under the applied reducing conditions.

Mercaptans

Mercaptan content in the hydrocracked products is low because these compounds are relatively thermally unstable. It is interesting to point out that mercaptans make up a substantially greater percentage of the total sulphur types found in Sample 5C (Table 8), which suggests that mercaptan formation may be an intermediate step in the desulphurization reaction (11).

Total Sulphides

Because of the presence of substantial amounts of olefins (12) in the samples (14 to 27%), the conventional aqueous method for oxidizing sulphides, involving the reaction



had to be modified. The extent of reaction is monitored by the potential of the iodine-chloride electrode (13) formed in the initial stages of the reaction. As the iodine chloride is readily consumed by the olefins, meaningful potential readings could not be obtained. Therefore, a non-aqueous system described by Gulyayeva and Bolkh (13) was applied. The solvent was saturated with dry hydrogen chloride prior to use to prevent a concentration drop of iodine-chloride in the reaction mixture due to the undesirable influence of olefins.

Aliphatic Sulphides

These compounds represent the second largest sulphur-type present in the hydrocracked products. They decreased steadily with increasing severity of hydrocracking (Table 6 and Figure 1), but their content based on total product increased progressively from Samples 1 to 3, then remained constant in Sample 4 (Table 7 and Figure 2). These sulphur compounds are composed of paraffinic and aliphatic cyclic structures and are relatively less thermally stable. This is evidenced by the more pronounced decrease of this group, relative to the change of aromatic sulphides or residual sulphur contents in the most severely-cracked product (Tables 6 and 8).

Introduction of catalyst results in lower aliphatic sulphides compared to aromatic sulphides, as shown by comparison of Samples 4 and 5C in Table 7, Figure 2.

Aromatic Sulphides

The quantity of aromatic sulphides in the total product (Table 7) increased from Sample 1 to 4. Nevertheless, their amount dropped sharply because of the catalyst effect (Samples 4 and 5C in Table 7).

Residual Sulphur

This sulphur group, which includes the thiophenic structures, is the most thermally-stable sulphur type, as evidenced by its high representation in all the non-catalytically-cracked samples (Tables 6 and 8). Also, its amount in the total hydrocracked product increases (Table 7) progressively at a higher rate than any other sulphur compound-type.

It is interesting to note that the residual sulphur compounds are equally or more amenable to the catalytic effect than even the aliphatic sulphides, followed by the aromatic sulphides in a decreasing order.

CONCLUSIONS

Although the percentage sulphur content decreases in all the liquid fractions and asphaltenes of the bitumen, when the severity of hydrocracking is increased, the amount of sulphur present in the naphtha fraction increases steadily because of the increase of this fraction in the product. The main sulphur compound-types in the naphtha product are residual sulphur, aliphatic sulphides and aromatic sulphides, in descending order. These sulphur groups show the same trend as the total sulphur on increasing the severity of hydrocracking, except in the most severely-treated product where the aliphatic sulphides remain constant.

The catalytic product has a higher mercaptan content, and lower concentration of residual sulphur, aliphatic sulphides and aromatic sulphides than the non-catalytically-cracked product at nearly the same pitch conversion. This suggests that the formation of mercaptans could be an intermediate step in the desulphurization process.

A modification for the procedure of potentiometric titration of sulphides, in hydrocracked products that have a high olefinic content, has been described in this report.

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TABLE 1

TYPICAL PROPERTIES OF ATHABASCA BITUMEN

Specific gravity, 60/60°F	1.009
Sulphur, wt %	4.63
Ash, wt %	0.68
Viscosity, cSt at 210°F	152.2
Conradson carbon residue, wt %	12.8
Asphaltene (pentane insolubles), wt %	15.3
Benzene insolubles, wt %	0.9
Nickel, ppm	70
Vanadium, ppm	190

TABLE 2

GROSS COMPOSITION OF THE HYDROCRACKING PRODUCTS
(wt % of Total Bitumen Product)

Sample No.	Operating Temp. °C	Pitch Conversion wt %	Hydrogen Chemical Consump. m ³ API/t	Naphtha up to 200°C	Oil & Resins above 200°C	Asphaltenes
1	410	26.1	28.2	3.9	82.2	10.8
2	420	36.8	37.9	7.8	80.4	10.4
3	430	49.3	54.0	10.6	76.3	9.8
4	470	89.1	212.7	21.6	68.8	4.3
5C*	460	83.5	179.3	18.2	76.5	3.9

* Catalytic hydrocracking product (cobalt-molybdena oxides on coal base)

TABLE 3
EFFECT OF HYDROCRACKING ON TOTAL
SULPHUR CONVERSION

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Sulphur content in feed, wt %	4.48	4.48	4.48	4.77	4.48
Liquid yield, wt %	96.6	98.0	96.1	89.3	91.9
Sulphur content in liquid product, wt %	3.72	3.58	3.35	2.23	1.33
Percentage sulphur conversion	19.78	21.69	28.14	58.25	72.72

TABLE 4
SULPHUR CONTENT IN THE
HYDROCRACKED PRODUCTS

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Sulphur content in naphtha (up to 200°C), wt %	1.80	1.79	1.57	0.87	0.32
Sulphur content in oil and resins (above 200°C), wt %	3.81	3.74	3.56	2.60	1.65
Sulphur content in asphaltenes, wt %	6.87	6.72	6.56	4.18	4.26

TABLE 5

SULPHUR CONTENT IN THE
HYDROCRACKED PRODUCTS

(Milligrams Sulphur in 100 grams Total Product)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Sulphur from naphtha (up to 200°C)	70.2	139.6	166.4	187.9	158.2
Sulphur from oil and resins (above 200°C)	3131.8	3006.9	2716.3	1788.8	1262.2
Sulphur from asphaltenes	742.0	698.9	642.9	179.7	166.1

TABLE 6

SULPHUR-TYPE DISTRIBUTION IN NAPHTHA PRODUCT

(wt % of Sulphur in Sample)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Mercaptans	0.052	0.067	0.056	0.010	0.037
Aliphatic sulphides	0.64	0.52	0.43	0.21	0.07
Aromatic sulphides	0.28	0.28	0.26	0.14	0.09
Residual sulphur	0.83	0.92	0.82	0.51	0.12
Total sulphur	1.80	1.79	1.57	0.87	0.32

TABLE 7

SULPHUR-TYPE DISTRIBUTION IN NAPHTHA PRODUCT

(Milligrams Sulphur as Specified Sulphur-Type
in Naphtha, per 100 grams Total Product)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Mercaptans	2.0	5.2	5.9	2.16	6.7
Aliphatic sulphides	25.0	40.6	45.6	45.4	12.7
Aromatic sulphides	10.9	21.8	27.6	30.2	16.4
Residual sulphur	32.4	71.8	86.9	110.2	21.8

TABLE 8

SULPHUR-TYPE DISTRIBUTION IN NAPHTHA PRODUCT
(Sulphur-Type as Percentage of Total Sulphur)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Mercaptans	2.9	3.8	3.6	1.2	11.7
Aliphatic sulphides	35.5	29.1	27.4	24.1	22.1
Aromatic sulphides	15.5	15.7	16.6	16.1	28.4
Residual sulphur	46.1	51.4	52.4	58.6	37.8