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# EFFECT OF HYDROCRACKING ATHABASCA BITUMEN ON SULPHUR-TYPE DISTRIBUTION IN THE NAPHTHA FRACTION

A.E. GEORGE, B.B. PRUDEN AND H. SAWATZKY

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# EFFECT OF HYDROCRACKING ATHABASCA BITUMEN ON SULPHUR-TYPE DISTRIBUTION IN THE NAPHTHA FRACTION

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A.E. George\*, B.B. Pruden\*\* and H. Sawatzky\*\*\*

## ABSTRACT

The effect of increasing hydrocracking severity of Athabasca bitumen on sulphur content of the products and on sulphur compound type distribution in the naphtha fraction boiling at temperatures up to 200°C has been investigated. Products from both thermal and catalytic hydrocracking were compared.

Increased severity of hydrocracking increased the proportion of lighter products and decreased the overall amount of sulphur. Another factor which affected sulphur content was the migration of sulphur from heavier to lighter fractions. It was apparent that measured sulphur content of hydrocracked products reflected a combination of the above factors.

The main sulphur compound types in the naphtha product in descending order were residual sulphur, aliphatic sulphides and aromatic sulphides. The catalytic product has a higher mercaptan content and lower concentrations of residual sulphur, aliphatic sulphides and aromatic sulphides than the noncatalytically-cracked product.

A modification of the procedure for potentiometric titration of sulphides in hydrocracked naphtha products that have high olefinic content is described.

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# L'EFFET DE L'HYDROCRAQUAGE DU BITUME D'ATHABASCA SUR LA DISTRIBUTION DU COMPOSE-TYPE DE SOUFRE DANS LA FRACTION DE NAPHTE

#### par

#### A.E. George\*, B.B. Pruden\*\* et H. Sawatzky\*\*\*

#### RESUME

L'effet de la sévérité croissante de l'hydrocraquage du bitume d'Athabasca sur la teneur en soufre des produits et sur la distribution du composé-type de soufre dans la fraction de naphte, à une température d'ébullition pouvant aller jusqu'à 200°C, a été analysé. On compare les produits provenant de l'hydrocraquage thermique ainsi que catalytique.

La sévérité accrue de l'hydrocraquage a fait augmenter la proportion de produits plus légers et diminuer la quantité globale de soufre. Un autre facteur qui a influencé la teneur de soufre est la migration du soufre des fractions plus lourdes aux fractions plus légères. Il est évident que la teneur de soufre que l'on mesure dans les produits d'hydrocraquage reflète une combinaison des facteurs mentionnés plus haut.

Les principaux types de composés de soufre retrouvés dans le produit de naphte en ordre décroissant sont le soufre résiduel, les sulfures aliphatiques et les sulfures aromatiques. Le produit catalytique a une plus forte teneur de mercaptan et des concentrations plus basses de soufre résiduel, de sulfures aliphatiques et aromatiques que le produit ayant subi un craquage sans l'aide de catalyseurs.

On décrit une modification de la procédure de titration potentiométrique des sulfures dans les produits de naphte par l'hydrocraquage ayant une teneur élevée d'oléfine.

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#### INTRODUCTION

On the basis of pilot plant-scale runs the thermal hydrocracking process has been found to give a high distillate yield and to eliminate the production of waste coke in the processing of Athabasca bitumen (1). In keeping with departmental (EMR) policy of encouraging maximum utilization of non-renewable resources, the Canada Centre for Mineral and Energy Technology (CANMET) has supported research on hydrocracking of Athabasca bitumen. This report is the first in a series dealing with the effect of increasing the severity of hydrocracking of this asphaltic sulphurous bitumen (Table 1) and of heavy oils on sulphur analysis in the products; it also deals with sulphur compound-type distribution in the naphtha and gas oil fractions. The ultimate objective of this series of studies is to provide a basis for choosing the optimal conditions for hydrocracking and hydrotreating these heavy oils and synthetic fuels to meet certain market specification requirements. The removal of certain types of sulphur compounds or their conversion to less deleterious types should constitute a part of refinery practice in upgrading synthetic fuels.

Further removal of different sulphur compounds in the hydrocracked liquid product by hydrotreating is affected by the type and general structure of these compounds. High-sulphur feeds reduce refining capacity and increase product cost. Platforming catalysts are extremely sensitive to the toxic effects of sulphur. Furthermore, most sulphur compounds have unfavourable effects on service properties of fuels, such as on storage stability, engine life, and engine performance. Knowledge of the total sulphur content in products is important; however, the chemical group composition is also important as some sulphur structures are more harmful than others for certain applications. On the other hand, complete removal of sulphur compounds from fuels will not always lead to improvement and may lead to impairment of certain important service properties, e.g., thiophenes have high thermal oxidation stability and can be used as anti-oxidant additives, and are also 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 presents an analytical problem in sulphide sulphur determination, and this was dealt with in this investigation (12).

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 at temperatures up to 200°C, were investigated.

#### EXPERIMENTAL PROCEDURES

#### Thermal Hydrocracking

The hydrocracking pilot plant and its operation on Athabasca feed have been described in previous report (1). The reactor is a vertical vessel into which the bitumen and hydrogen are fed at the bottom. 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. 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 such impurities as uncondensed hydrocarbon gas, hydrogen sulphide and ammonium sulphide is water- and oil-scrubbed. The scrubbed hydrogen, together with fresh make-up hydrogen, is recycled to the reactor at a constant rate.

Four liquid samples of the light- and heavy-oil products representing increasing degrees of hydrocracking were selected for investigation. The samples, representing steady state conditions at a liquid hourly space velocity of 2 and temperatures of 410, 420, 430 and 470°C, are designated in this report as Samples 1, 2, 3 and 4 respectively. All the samples resulted from processing at 13.79 MPa (2000 psi) operating pressure except the 470°C sample which was at 24.13 MPa (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 and 13.79 MPa (2000 psi) pressure to determine its effect on the sulphur compound-type distribution of the naphtha. The sample from this run was designated 5C.

## Distillation

The light oil was distilled (ASTM D216-54) to separate the naphtha and the fraction boiling above 200°C was combined with the deasphaltened heavy-oil product proportionally as produced from the pilot plant.

#### Deasphalting

The asphaltene portion of the heavy-oil product was precipitated by adding 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.

Table 1 - Typical properties of Athabasca bitumen

| Specific gravity, 15.5/15.5°C         | 1.009 |
|---------------------------------------|-------|
| Sulphur, wt %                         | 4.63  |
| Ash, wt %                             | 0.68  |
| Viscosity, cSt at 98.9°C              | 152.2 |
| Conradson carbon residue, wt %        | 12.8  |
| Asphaltene (pentane insolubles), wt % | 15.3  |
| Benzene insolubles, wt %              | 0.9   |
| Nickel, mg/kg (ppm)                   | 70    |
| Vanadium, mg/kg (ppm)                 | 190   |

#### Analytical Methods for Sulphur Compound-Types

Prior to sulphur-type determination, hydrogen sulphide was removed from all the samples by shaking with an equal volume of 10%  $CdC1_2$  solution in water.

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

## Total Sulphur

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

## Elemental Sulphur

A modification of Sommer's semiquantitative colour test was used (6) as well as 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 mm (7). The latter is sensitive to 2 mg/kg (2 ppm) of elemental sulphur.

## Mercaptans

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

#### Total Sulphides

According to a detailed review of methods for determining sulphur compounds (8), potentiometric titration is the most effective method for sulphide sulphur. 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 discussion). Platinum and calomel electrodes were used in the titration.

## Aliphatic Sulphides

The open chain and cyclic aliphatic sulphides were determined from the ultra-violet spectrophotometric absorptions of the iodinealiphatic sulphide complexes at 310 nm using the Beckman model DK-2 instrument 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 nm is low relative to 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 in 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

The gross composition of the products is shown in Table 2. The naphtha fraction increased steadily from 3.9% in the product from mild hy-

drocracking conditions in Sample 1 to 21.6% in the most severely treated product in Sample 4. The amount of oil and resin fraction distilling above  $200^{\circ}C$  in the catalytic product in Sample 5C was equal to that in Sample 3, in spite of the considerable difference in pitch conversion i.e., the conversion of heavier fractions to fractions boiling below 524°C equivalent atmospheric boiling temperature. Asphaltene content decreased steadily with increased hydrocracking. The sum of naphtha, oil and resins, and asphaltenes in Table 2 is less than 100% because of the formation of gaseous products and errors in measurements. The lighter fractions were swept from the reactor with the hydrogen stream as they formed. As their residence time was limited, substantial amounts of the relatively thermally unstable compounds survived cracking.

#### Sulphur Conversion

Sulphur removal from the total liquid product increased with increased hydrocracking severity from Samples 1 to 4 (Table 3), but was substantially higher in the catalytic product at 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, 5, Fig. 1, 2). On the other hand, the total amount of sulphur in the naphtha fraction resulting from 100 g of total product (Table 5) increased substantially with hydrocracking in spite

| Sample | Operating | Hydrogen chemi-      | Pitch      | Naphtha | 0il & resins |             |
|--------|-----------|----------------------|------------|---------|--------------|-------------|
| No.    | temp.     | cal consump.         | conversion | up to   | above        | Asphaltenes |
|        | °C        | m <sup>3</sup> API/t | wt %       | 200°C   | 200°C        |             |
|        |           |                      |            | wt % of | total bitume | n product   |
| 1      | 410       | 28.2                 | 26.1       | 3.9     | 82.2         | 10.8        |
| 2      | 420       | 37.9                 | 36.8       | 7.8     | 80.4         | 10.4        |
| 3      | 430       | 54.0                 | 49.3       | 10.6    | 76.3         | 9.8         |
| 4      | 470       | 212.7                | 89.1       | 21.6    | 68.8         | 4.3         |
| 5C*    | 460       | 179.3                | 83.5       | 18.2    | 76.5         | 3.9         |

Table 2 - Gross composition of hydrocracked products

\*Catalytic hydrocracking product.

Table 3 - Effect of hydrocracking on total sulphur conversion

| Characteristic                |       | Sample |       |       |           |  |  |
|-------------------------------|-------|--------|-------|-------|-----------|--|--|
|                               | 1     | 2      | 3     | 4     | <u>50</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 hydrocracked products

| · · · · · · · · · · · · · · · · · · · | ·    |      |      | 1    |      |   |
|---------------------------------------|------|------|------|------|------|---|
| Product                               |      |      | Samp | Le . |      |   |
|                                       | 1    | 2    | 3    | 4    | 50   |   |
| Naphtha (up to 200°C), wt %           | 1.80 | 1.79 | 1.57 | 0.87 | 0.32 |   |
| 0il and resins                        | 3.81 | 3.74 | 3.56 | 2.60 | 1.65 |   |
| (above 200°C), wt %                   |      |      |      |      |      |   |
| Asphaltenes, wt %                     | 6.87 | 6.72 | 6.56 | 4.18 | 4.26 |   |
|                                       |      |      |      |      |      | - |

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 run in Sample 5C were of markedly lower sulphur content than those from the noncatalytic runs.

#### Sulphur Compound-Types

The effect of increasing hydrocracking severity on 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 unstable thermally. Note however, that mercaptans make up a substantially greater percentage of the total sulphur types found in Sample 5C (Table 8), suggesting that mercaptan formation may be an intermediate step in the desulphurization reaction (11).

## Total Sulphides

Because samples contained from 14 to 27% olefins (12), the conventional aqueous method for oxidizing sulphides involving the reaction

 $KIO_3 + 2R_2S + 2HC1 \rightarrow KC1 + H_2O + 2R_2SO + IC1$ 

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

#### Aliphatic Sulphides

These compounds represent the second most abundant sulphur-type present in the hydrocracked

| Source of sulphur     |        |        | Sample |        |        |  |  |  |
|-----------------------|--------|--------|--------|--------|--------|--|--|--|
|                       | 1      | 2      | 3      | 4      | 50     |  |  |  |
| Naphtha (up to 200°C) | 70.2   | 139.6  | 166.4  | 187.9  | 158.2  |  |  |  |
| 0il and resins        | 3131.8 | 3006,9 | 2716.3 | 1788.8 | 1262.2 |  |  |  |
| (above 200°C)         |        |        |        |        |        |  |  |  |
| Asphaltenes           | 742.0  | 698.9  | 642.9  | 179.7  | 166.1  |  |  |  |

# Table 5 - Sulphur content in hydrocracked products (milligrams sulphur in 100 g total product)

Table 6 - Sulphur-type distribution in naphtha product (wt % of sulphur in sample)

| Sulphur type        |       |       | Sample |       |       |
|---------------------|-------|-------|--------|-------|-------|
|                     | 1     | 2     | 3      | 4     | 5C    |
| 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 g total product)

| Sulphur type        |      |      | Sample |       |      |
|---------------------|------|------|--------|-------|------|
|                     | 1    | 2    | 3      | 4     | 5C   |
| 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)

| Sulphur type        |      |      | Sample |      |      |
|---------------------|------|------|--------|------|------|
|                     | 1    | 2    | 3      | 4    | 5C   |
| 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 |

products. They decreased in content steadily with increasing hydrocracking severity (Table 6 and Fig. 1) but, based on total product, increased progressively from Samples 1 to 3 then started to decrease in Sample 4 (Table 7 and Fig. 2). These sulphur compounds are composed of paraffinic and aliphatic cyclic structures and are relatively less stable thermally as shown 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 with aromatic sulphides, as shown by comparing Samples 4 and 5C in Table 7 and in Fig. 2.

#### Aromatic Sulphides

The quantity of aromatic sulphides in the total product changed in the same pattern as the



Fig. 1 - Effect of hydrocracking on sulphur-type distribution in the naphtha product

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aliphatic sulphides (Table 7). 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 thermallystable sulphur type, as shown by its high representation in all the non catalytically cracked samples (Tables 6 and 8). Also, its amount in the total hydrocracked product increases progressively at a higher rate than any other sulphur compound type (Table 7).

Residual sulphur compounds are more amenable to the catalytic effect than even the aliphatic sulphides, which in turn are more amenable than the aromatic sulphides. However because of contributions to the naphtha sulphur types from



Fig. 2 - Effect of hydrocracking on the amount of sulphur-type per 100 g total naphtha product

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hydrocracking of the higher boiling fractions, such a conclusion can only be regarded as tentative.

## CONCLUSIONS

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

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

The content of mercaptans, which are potentially the most corrosive, is reduced significantly with severity of hydrocracking. The product from catalytic hydrocracking has more mercaptans than the product from a higher conversion thermal experiment. This is in spite of the fact that total sulphur removal was higher in the catalytic product - 72% versus 58%. It appears that from migration alone, perhaps combined with resistance to conversion, the residual sulphur has increased with the severity of hydrocracking.

This residual sulphur which includes thiophenic compounds, is resistant to hydrotreating and could have an advantageous effect on the oxidation-resistant properties of jet fuels if mild hydrotreating conditions are chosen.

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#### REFERENCES

- Merrill, W.H., Logie, R.B. and Denis, J.M. "Pilot-scale investigation of thermal hydrocracking of Athabasca bitumen"; Department of Energy Mines and Resources, Mines Branch [since renamed Canada Centre for Mineral and Energy Technology (CANMET)]; <u>Research</u> Report R281; 1973.
- 2. Logie, R.B., Pruden, B.B. and Denis, J.M. "Low conversion thermal hydrocracking of Athabasca mined bitumen"; CANMET, Energy, Mines and Resources Canada; <u>Lab Report</u> ERP/ERL 77-121(R); 1977.
- Pruden, B.B., Logie, R.B., Denis, J.M. and Merrill, W.H. "Thermal hydrocracking of Athabasca bitumen - reduction of reactor fouling"; CANMET, Energy, Mines and Resources Canada; <u>CANMET Report</u> 76-33; 1976.
- 4. Khulbe, C.P., Pruden, B.B. and Denis, J.M. "Hydrocracking of Athabasca bitumen: Effect of coal-base catalyst on pilot plant operation"; CANMET, Energy, Mines and Resources Canada; <u>CANMET Report</u> 77-35; 1977.
- Rubinshtein, I.A., Kleimnova, Z.A. and Sobolev, E.P. Metody Analyiza, Organ Soeden, Nefti, Ikh Smesei, Acad. U.S.S.R., Inst. Neftekhem Sinteza; 74:1; 1960.
- Mapstone, G.E. "Detection of elemental sulphur in gasoline by the Sommer test"; <u>Ind Eng</u>

Chem Anal Ed; 18:8:498-499; 1946.

- Bartlett, J.K. and Skoog, D.A. "Colorimetric determination of elemental sulfur in hydrocarbons"; <u>Anal Chem</u>; 26:6:1008-1011; 1954.
- Luk'yanitsa, V.G. "Progress in science chemistry of petroleum and gas - volume 2"; Edited by G.D. Gal'pern; Moscow; 1958.
- 9. Hastings, S.H. "Spectrophotometric determination of aliphatic sulfides"; <u>Anal Chem</u>; 25:3:420-422; 1953.
- Drushel, H.V. and Miller, J.F. "Spectrophotometric determination of aliphatic sulfides in crude petroleum oils"; <u>Anal Chem</u>; 27:4:495-501; 1955.
- 11. George, A.E. "Hydrodesulphurization of distillates of heavy crude oil"; Ph.D. thesis, Cairo University (Egypt); 1967.
- 12. George, A.E., Smiley, G.T. and Sawatzky, H. "Chemical changes during thermal hydrocracking of Athabasca bitumen"; <u>Symposium on Oil</u> <u>Sand and Oil Shale</u>; organized by American Chemical Society, division of Fuel Chemistry, Montreal, May 29-June 2, 1977; p. 140-157; 1977.
- 13. Gulyayeva, L.I. and Bolkh, N.V. "Potentiometric determination of organic sulphur compounds in cracked gasolines"; <u>Pet Chem</u> <u>U.S.S.R.</u>, 9:2:308-313; 1969.

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