Oil Shale, 2000, Vol. 17, No. 1
pp. 25-30
ISSN 0208-189X

UPGRADING OF ESTONIAN SHALE OIL DISTILLATION FRACTIONS. 5. HYDROGENATION OF HEAVY MAZUTE

H. LUIK, N. VINK
E. LINDARU, L. MARIPUU

Tallinn Technical University,
Institute of Chemistry
15 Akadeemia St., Tallinn
12618 Estonia

Upgrading of Estonian shale oil heavy mazute fraction boiling over 320 °C and characterized by high content of high-polar and heteroatomic compounds (46.6 %) and by low content of aliphatic hydrocarbons (6.6 %) was carried out in an autoclave at 370 °C using Co-Mo and Ni catalysts. Both catalysts gave high recovery (over 90 %), but when Co-Mo catalyst was used more volatiles with higher conversion level and less coke were obtained. The content of high-polar and heteroatomic compounds in hydrogenisate was decreased twice and that of aliphatic hydrocarbons was increased just as much, and as a result also other properties of heavy mazute were significantly altered.

The results of hydrogenation of Estonian shale oil lighter fractions, so-called "diesel fraction", and light mazute were discussed in [1-4]. In this work the most viscous and high-boiling part of Estonian shale oil – heavy mazute – was submitted to hydrogenation with the aim to investigate the effect of hydrogenation on the yield, composition and properties of oil obtained. Hydrogenation was carried out in an autoclave during 2 hours at 370 °C, the initial pressure of hydrogen being 100 at. Experimental and analysis see in [1]. In parallel to Co-Mo catalyst also Ni catalyst was used.

Results and Discussion

Hydrogenation of heavy mazute results in its high recovery (90 %), while coke, gas and water together make less than 10 % of reaction products

Table 1. **The Yield of Heavy Mazute Hydrogenation Products**

Product	Yield, wt.%	
	Co-Mo catalyst	Ni catalyst
Refined oil	91.1	90.2
Gas	3.4	1.3
Water	3.4	4.9
Coke	2.1	3.6

(Table 1). More coke but less water and gas were formed when Ni catalyst was used. So it is preferable to use Co-Mo catalyst that gives more volatiles with higher conversion level.

The composition of initial and hydrogenated samples of heavy mazute was analysed using infrared spectroscopy, thin-layer chromatography and capillary gas chromatography. The results are presented in Figs. 1 and 2, and Table 2.

In Fig. 1, one can see intensive absorptions at 724, 747, 1380, 1470, 2860-2880, and 2930-2960 cm^{-1} belonging to methyl and methylene groups in aliphatic chains, and also complex absorptions at 750, 820, 880, 1020, 1080, 1600, and at nearby 3000 cm^{-1} belonging to aromatic compounds. These absorptions are characteristic for every spectrum, but in the spectrum of the hydrogenated sample these signals seem to be amplified indicating the formation of an additional quantity of aliphatic and aromatic hydrocarbons during hydrogenation. Absorptions at 1720 and 3450 cm^{-1} belong to the oxygen-containing functional groups, to carbonyl and carboxyl groups, respectively. Significant weakening of the signal at 3450 cm^{-1} and vanishing of the signal at 1720 cm^{-1} indicate the instability of carbonyl and carboxyl functional groups on hydrogenation.

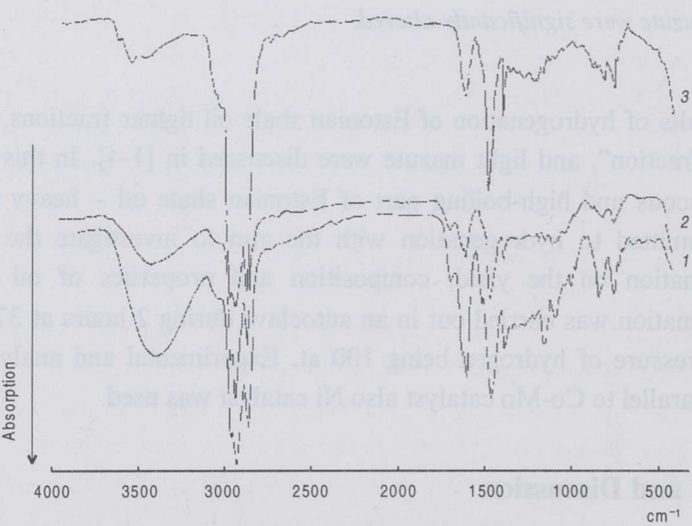

Fig. 1. Infrared spectra of initial (*1*), dephenolated (2), and dephenolated then hydrogenated (*3*) heavy mazute

Table 2. **Chemical Group Composition of Heavy Mazute, wt.%**

Compounds	Fraction		
	Initial	Dephenolated	Dephenolated then hydrogenated
Aliphatic hydrocarbons	6.6	10.4	21.3
Aromatic hydrocarbons	27.3	43.0	53.8
Among them:			
Monocyclic	2.7	4.3	6.1
Polycyclic	24.6	38.7	47.7
Neutral oxygen compounds	14.4	22.6	10.5
High-polar compounds	15.2	24.0	14.4
Phenols	36.5	0.0	0.0

The chemical group composition of oils (Table 2) shows that the composition of hydrogenisate is significantly altered as compared with that of the initial sample. The latter, unlike previously investigated "diesel fractions" and light mazute, is characterized by low content of aliphatic hydrocarbons and high content of phenols and other oxygen-containing compounds. Dephenolated fraction submitted to hydrogenation contains only 10.4 % of aliphatic hydrocarbons, but 46.6 % of neutral oxygen compounds and high-polar components.

As compared with "diesel fraction" and light mazute, the fraction under study – heavy mazute – contains 3-5 times less aliphatic hydrocarbons and twice more neutral oxygen compounds and high-polar compounds. Significantly more hydrogen was expected to be consumed for heavy mazute hydrogenation, and that is why the initial pressure of hydrogen was elevated up to 100 at, the sample weight being kept the same. As a result of hydrogenation the total concentration of hydrocarbons increased from 57.7 to 81.2 % (the content of aliphatic hydrocarbons being increased twice), and the total concentration of neutral oxygen compounds and high-polar compounds decreased from 46.6 down to 24.9 %.

The individual composition of nonaromatic hydrocarbons in hydrogenisate was investigated by capillary gas chromatography and the chromatogram is presented in Fig. 2. One can see that a lot of various saturated hydrocarbons are formed as a result of hydrogenation. *n*-Alkenes were totally hydrogenated. The peaks of *n*-alkanes prevail in the chromatogram, the intermediate peaks belonging to different *iso*- and cycloalkanes. The most of them have been already identified [5].

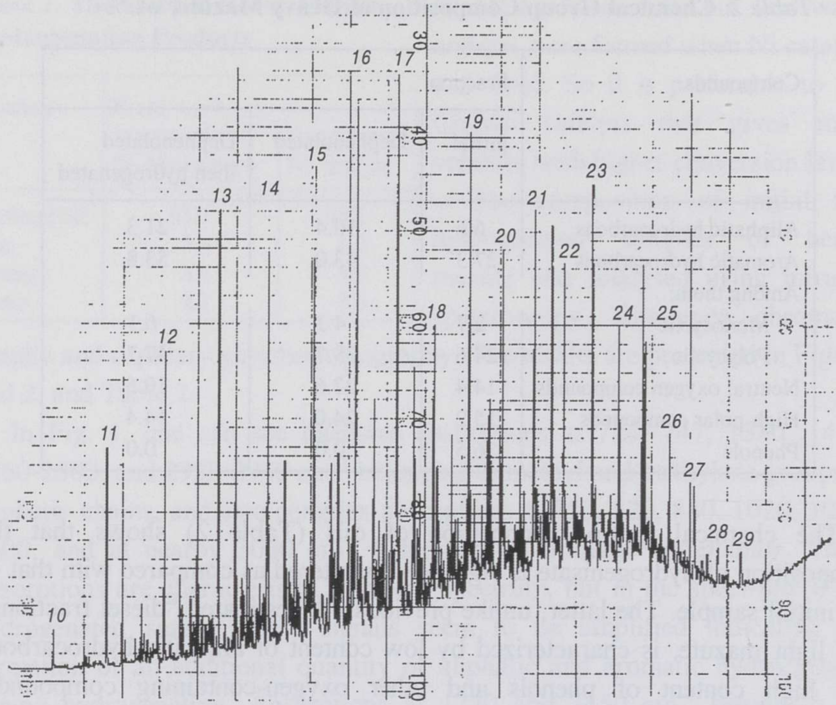

Fig. 2. Chromatogram of nonaromatic hydrocarbons in heavy mazute hydrogenisate. Numbers 10-29 on the peaks of *n*-alkanes indicate the number of carbon atoms in the molecule

One can see that as a result of hydrocracking the boiling range of the fraction was widened and almost 30 % of heavy mazute was transformed into the “diesel fraction”.

Table 3. **Heavy Mazute Qualities**

Characteristic	Heavy mazute		
	Initial	Dephenolated	Dephenolated then hydrogenated
Specific weight, kG/m^3, at 20 °C	1025	969	936
Refraction index at 20 °C	1.5190	1.5004	1.5000
Kinematic viscosity, cSt, at 20°C	1407.0	49.4	11.7
Elemental composition, %:			
C	84.0	84.7	85.5
H	9.7	10.0	11.4
Atomic ratio H/C	1.39	1.42	1.59
Sulfur, wt.%	0.82	0.58	0.29
Carbon residuum on 10 %, %	2.05	1.05	0.69
Existent gum content, wt.%	7.47	4.63	1.07
Water, vol.%	0.32	0.37	0.22
Mechanical impurities, wt.%	0.002	0.00	0.00
Ash, wt.%	0.30	0.30	0.02
Flash point, °C	195	172	118
Pour point, °C	–16	–19	–21
Copper strip corrosion	+ + –	– – –	– – –
Water-soluble acids and alkalis	0.00	0.00	0.00
Iodine number	84	74	43

Table 4. **Distillation Data**

	Initial sample	Dephenolated sample	Dephenolated then hydrogenated sample
	Temperature, °C		
Initial boiling point	298	307	179
Distilled, %:			
5	320	330	260
10	332	336	282
20	342	345	307
30	349	350	325
40	353	353	338
50	358	357	350
60	361	359	360
70	365	364	370
80	366	365	–
90	375	376	–
End point	380	381	378
Recovery, %	91.8	91.3	78.6
Residue, %	6.7	7.2	19.4
Loss, %	1.5	1.5	2.0

Conclusion

Heavy mazute – a fraction of Estonian shale oil boiling above 320 °C – is a very viscous, moderately sulfurous and oxygen-rich liquid which hydrogenation after its prior dephenolation results in sulfur removal by 50 % and in transformation of 50 % of high-polar and neutral oxygen compounds when the Co-Mo catalyst was used. Hydrogenated oil contains 75 % of hydrocarbons and 30 % of over 320 °C boiling compounds. Also other oil characteristics were altered significantly.

Acknowledgements

The research was financially supported by Estonian Science Foundation, Grant No. 2630.

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Presented by V. Yefimov
Received February 19, 1999