

<https://doi.org/10.3176/oil.1999.4.05>

UPGRADING OF ESTONIAN SHALE OIL DISTILLATION FRACTIONS 3. HYDROGENATION OF LIGHT MAZUTE

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

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

Upgrading of Estonian shale oil fraction boiling at 240-320 °C, the so-called light mazute characterized by sulfur content 0.62 % and polar heteroatomic compound content 30.8 % after dephenolation, was effected by hydrogenation in an autoclave at 370 °C using a Co-Mo catalyst. The composition and properties of initial, dephenolated and hydrogenated light mazute were determined. Olefinic double bonds in oil were totally saturated and most oxygen and sulfur were eliminated as a result of hydrogenation, 90% of oil consisting in hydrocarbons only.

In our previous works [1-2], the lightest Estonian shale oil distillation fraction produced industrially in Kohtla-Järve, the so-called “diesel fraction”, was hydrogenated to change its chemical composition and properties. In this work the middle fraction – light mazute, compounds boiling between 240-320 °C, was hydrogenated in an autoclave with the aim to investigate the effect of hydrotreating on the yield, composition and properties of hydrogenate – the upgraded product obtained. Experimental conditions, methods and oil analysis see in [1]. Unlike [1], hydrogenation of light mazute was carried out at an initial pressure of hydrogen 80 at.

Results and Discussion

Hydrogenation of the light mazute results, similarly to the “diesel fraction”, in a high yield of refined oil, but unlike the “diesel fraction”, some amounts of coke are formed (see Table 1).

Table 1. The Yield of Light Mazute Hydrogenation Products

Product	Yield, wt. %
Refined oil	89.0
Gas	2.9
Water	2.0
Coke	6.1

Infrared spectroscopic analysis was accomplished to determine the distribution of functional groups in initial and chemically treated oil samples (Fig. 1). Every spectrum displays absorptions at 724, 747, 1380, 1470, 2860, 2880, 2930, and 2960 cm^{-1} caused by methyl and methylene groups in aliphatic chains, and complex absorptions at 750, 820, 880, 1020, 1080, 1600, and at nearby 3000 cm^{-1} characteristic for aromatic compounds.

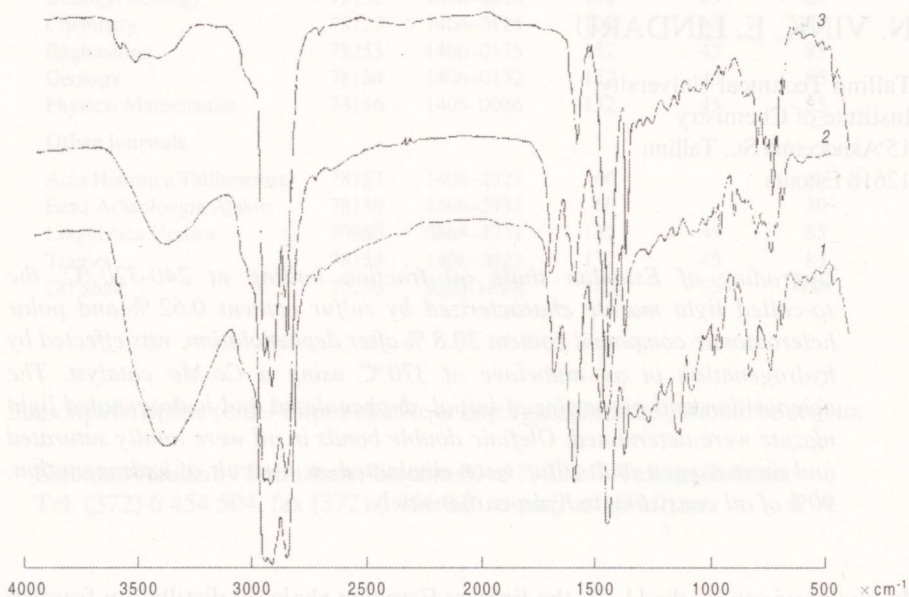


Fig. 1. Infrared spectra: 1 – initial light mazute, 2 – dephenolated light mazute, 3 – dephenolated then hydrogenated light mazute

The spectrum of the initial sample differs from others by intense absorptions at 3400 cm^{-1} (characteristic for hydroxyl groups), and at 1600 cm^{-1} (referring to benzene derivatives) indicating a significant concentration of phenols in the initial sample of light mazute. The remnant parts of the spectra of the initial and dephenolated samples are similar both having absorptions at 1650 and at 3000-3050 cm^{-1} (indicating the presence of olefinic double bonds), and an intense absorption at 1720 cm^{-1} belonging to carbonyl groups. These absorptions are absent or almost absent in the spectrum of the hydrogenated sample. So, it could be concluded that dephenolation significantly decreases the absorption intensities at 3400 and 1600 cm^{-1} as phenolic hydroxyl groups and some part of benzene nuclei are removed, double bonds

are totally saturated and most of hydroxyl and carbonyl groups are eliminated.

Table 2. Chemical Group Composition of Light Mazute, wt. %

Compounds	Initial fraction	Dephenolated fraction	Hydrogenated fraction
Nonaromatic hydrocarbons	21.0	31.2	50.8
Aromatic hydrocarbons	25.7	38.0	39.6
Among them:			
monocyclic	3.5	5.2	13.0
polycyclic	22.2	32.8	26.6
Neutral oxygen compounds	12.0	17.7	3.6
High-polar compounds	8.9	13.1	6.0
Phenols	32.4	0.0	0.0

Table 3. Light Mazute Qualities

Characteristic	Light mazute		
	initial	dephenolated	dephenolated then hydrogenated
Specific weight, kg/m^3 , at 20 °C	957	918	874
Refraction index at 20 °C	1.5020	1.5000	1.4989
Kinematic viscosity, cSt, at 20 °C	34.85	9.42	2.81
Elemental composition, %:			
C	84.2	83.2	84.8
H	10.8	11.4	12.2
Atomic ratio H/C	1.54	1.64	1.73
Sulfur, wt. %	0.74	0.62	0.35
Carbon residuum on 10 %, %	1.71	0.99	0.51
Existent gum content, wt. %	4.57	2.66	1.57
Water, vol. %	0.36	0.17	0.20
Mechanical impurities, wt. %	0.024	0.00	0.00
Ash, wt. %	0.03	0.00	0.00
Flash point, °C	91	89	86
Pour point, °C	-40	-40	-45
Copper strip corrosion	++-	---	---
Water soluble acids and alkalis	0	0	0
Iodine number	95	77	38

The group composition of refined oil as well as that of the initial and dephenolated light mazute are presented in Table 2. One can see that the initial light mazute is characterized by a high content of phenols (32.4 %) indeed, but after dephenolation it consists of almost equal parts of aliphatic hydrocarbons (31.2 %), aromatic hydrocarbons (38.0 %) and heteroatomic compounds (30.8 %). Hydrogenation increases the total content of hydrocarbons including both aliphatic and aromatic ones from 69.2 up to

90.4 % on account of the decrease in the content of neutral oxygen compounds and high-polar heterocompounds. The first ones show a five-fold and the latter a double decrease. The content of aliphatic hydrocarbons increases significantly.

The phenols whose concentration in the light mazute fraction is significant (32.4 %) are removed by dephenolation. Neutral oil becomes richer in hydrocarbons and more paraffinaceous at hydrogenation. Both processes influence markedly the properties of the light mazute (see Table 3). Dephenolation as well as hydrogenation both lead to a marked change in oil physical and chemical parameters (specific weight, kinematic viscosity, refraction index, and sulfur content all decrease). Unsaturation, coking, corrosive and resin-forming properties diminish, and hydrogen-to-carbon ratio in oil increases.

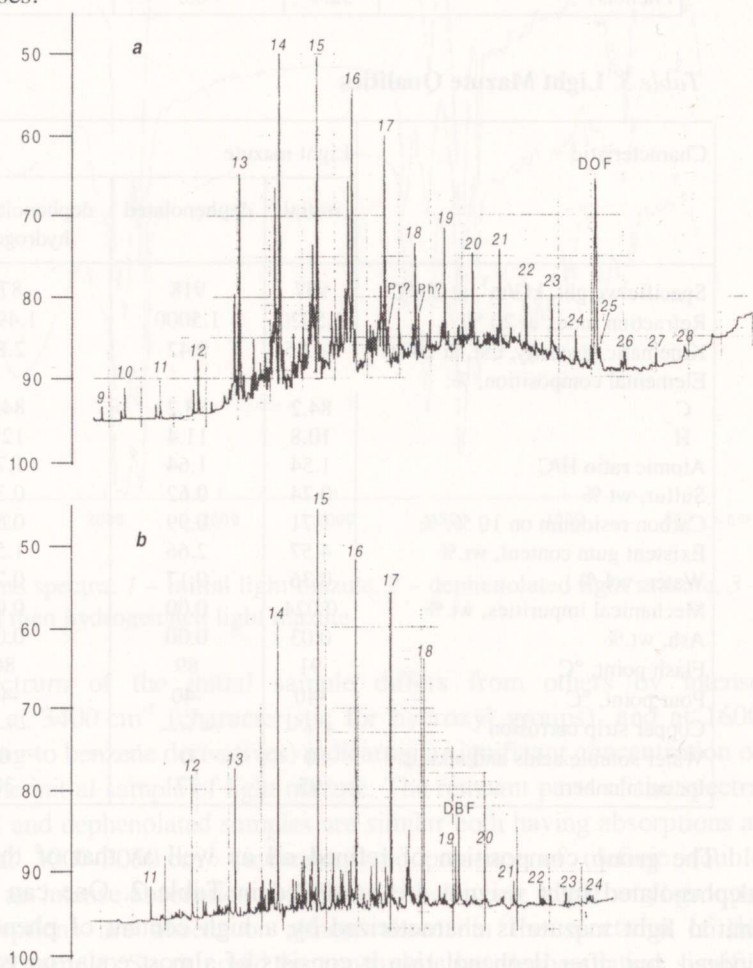


Fig. 2. Chromatograms of nonaromatic hydrocarbons separated from dephenolated light mazute (a) and from dephenolated then hydrogenated light mazute (b) by thin-layer chromatography

The individual composition of aliphatic hydrocarbons before and after hydrogenation of light mazute was investigated using gas chromatography. The chromatograms are presented in Fig. 2, and one can see that *n*-alkanes C_{11} - C_{24} , C_{14} - C_{18} in especially high concentrations are the main components in both chromatograms. In the chromatogram of the non-hydrogenated fraction the peaks of *n*-alkenes abreast with the peaks of *n*-alkanes, and an abundance of non-identified peaks belonging to various *iso*- and cycloalkanes can also be seen.

As a result of hydrogenation, the composition of aliphatic hydrocarbons becomes significantly simpler. The concentration of *n*-alkanes higher than C_{18} decreases significantly, and among *n*-alkanes C_{11} - C_{17} , typical for kukersite oils, the concentrations of C_{15} , C_{17} and C_{18} are elevated. These long chains are formed at hydrogenation and may partly be originated from cracking of alkylbenzenes.

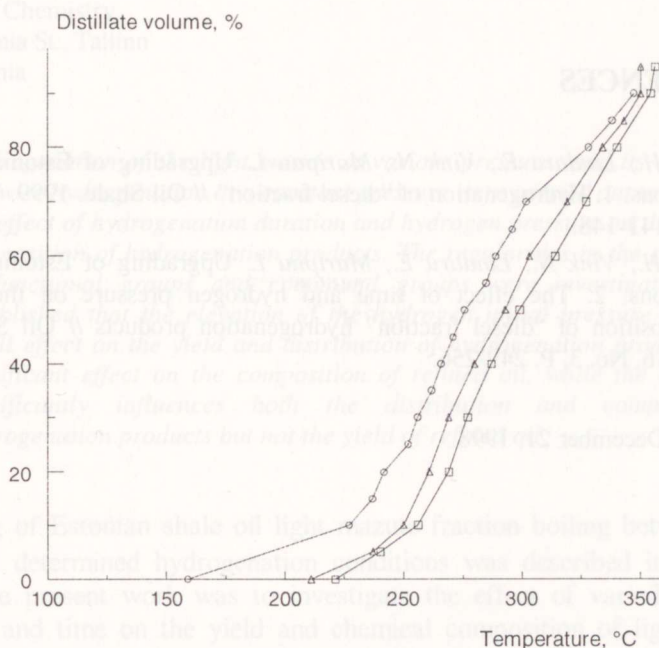


Fig. 3. Boiling curves of the initial (□), dephenolated (∇), and dephenolated then hydrogenated (○) light mazute

Boiling curves of the initial, dephenolated and hydrogenated light mazute are presented in Fig. 3. As a result of both, dephenolation and hydrogenation, the oil becomes lighter – the content of low-boiling compounds increases significantly. At hydrogenation not much gasoline fraction (boiling below 180°C) was formed, but the content of compounds boiling over 300°C decreased essentially. The oil 70 % point was replaced from 350°C in the initial oil to 300°C in the hydrogenated oil.

Conclusion

Estonian shale oil fraction boiling at 240-320 °C – light mazute – is characterized by a high content of heteroatomic constituents (phenols, neutral oxygen compounds and high-polar compounds). As a result of hydrogenation of dephenolated light mazute a 90 % yield of refined oil was obtained, oil consisting mainly of hydrocarbons, while the content of heteroatomic compounds was eight-fold reduced.

Acknowledgements

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

REFERENCES

1. Luik H., Lindaru E., Vink N., Maripuu L. Upgrading of Estonian shale oil fractions. 1. Hydrogenation of "diesel fraction" // Oil Shale. 1999. Vol. 16, No. 2. P. 141-148.
2. Luik H., Vink N., Lindaru E., Maripuu L. Upgrading of Estonian shale oil fractions. 2. The effect of time and hydrogen pressure on the yield and composition of "diesel fraction" hydrogenation products // Oil Shale. 1999. Vol. 16, No. 3. P. 249-256.

Received December 21, 1998