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UPGRADING OF ESTONIAN SHALE OIL DISTILLATION FRACTIONS

1. HYDROGENATION OF THE "DIESEL FRACTION"

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The kukersite oil obtained industrially in vertical retorts was chemically separated into neutral oil and phenols. Hydrocracking of the total oil as well as its constituents was performed, chemical composition and the properties of the products were determined [1-3]. Besides chemical separation, also distillative fractionation is practised in industry to obtain oils of different properties. This series of works deals with the upgrading of Estonian shale oil fractions obtained in industry using catalytical hydrogenation methods.

Shale oil fractions boiling at 180-240°, 240-320°, and above 320 °C - so-called "diesel fraction", fuel oil and heavy fuel oil, respectively, were hydrogenated under various reaction conditions to establish the optimum ones under which the yield of refined oil of desired composition will be maximum. The effect of initial parameters on the yield, composition and properties of products obtained was investigated. The aim of this work was to study the composition of the "diesel fraction" and the effect of hydrogenation on the yield, composition and properties of the products obtained.

Experimental

Objects

Specific characteristics and chemical composition of shale oil fractions produced in *Kiviter AS* (Kohtla-Järve) were determined. After dephenolation and before hydrogenation no other chemical or thermal treatment of samples was carried out.

Methods and Analyses

The catalytical hydrogenation method was worked out and applied for upgrading shale oil fractions. The optimum conditions for each fraction

were found taking into account the yield of thermally hydrotreated oil obtained and the quantum of hydrogen consumed. Experimental conditions applied for "diesel fraction" hydrogenation are presented in Table 1.

Table 1. Experimental Conditions

Parameter	Value
Autoclave volume, cm ³	500
Shale oil volume, cm ³	120
Initial pressure of hydrogen, MPa	5
Temperature, °C	370
Time of hydrogenation, h	2
Catalyst Co-Mo/Al ₂ O ₃ , %	5

Ultimate analysis, chromatographic and spectroscopic methods were used for the characterization of initial and modified oils. In some cases, preliminary dephenolation of oils was carried out.

Ultimate analysis of oil samples was performed using a 186 CHN *Hewlett Packard* analyzer. Infrared spectroscopic method was used to characterize the content of functional groups in oils.

Preparative thin-layer chromatographic method, using 24 × 24 cm plates coated with a 2 mm layer of silica gel (40 μm) and *n*-hexane as eluent, was applied for investigating the group composition of oils.

Gas chromatography on a *Chrom 4* analyzer with temperature programming was used for determination of the individual composition of volatiles in preparatively separated oil fractions.

Dephenolation included the consecutive treatment of oils with 10 % sodium hydroxide, 10 % hydrochloric acid, and diethyl ether. As a result, phenols and neutral oil were obtained.

Physical and chemical characteristics were determined meeting ISO-standards.

Results and Discussion

The degree of hydrogenation depends on the sufficiency of activated hydrogen and on the other hand, on the readiness of oil to react with hydrogen. The yield of hydrogenation products is presented in Table 2. One can see that the yield of refined oil is high and those of water and gas are low. It is noteworthy that no coke was formed.

Table 2. The Yield of Hydrogenation Products of the "Diesel Fraction"

Product	Yield, wt. %
Refined oil	94.9
Gas	3.8
Water	1.3
Coke	0

Judging by the group composition of compounds (Table 3), "diesel fraction" does not contain much heteroelements; high-polar and neutral oxygen compounds as the main source of heteroelements constitute only one fifth of the total fraction. The industrial "diesel fraction" consists mainly of hydro-

carbons and their content increases still as a result of hydrogenation (from 55 to 69 %). Data in Table 3 show that hydrogenation of the "diesel fraction" changes essentially its group composition; hydrogenisate contains 6-7 times less high-polar and neutral oxygen compounds and 8 times less monocyclic aromatic compounds, but 3 times more polycyclic aromatic compounds.

Table 3. Chemical Group Composition of the "Diesel Fraction", mass%

No.	Compounds	"Diesel fraction"		
		Initial	Dephenolated	Dephenolated then hydrogenated
1	Nonaromatic hydrocarbons	52	55	69
2	Aromatic hydrocarbons	23	25	28
	Among them:			
	Monocyclic hydrocarbons	16	17	2
	Polycyclic hydrocarbons	7	8	26
3	Neutral oxygen compounds	7	7	1
4	High-polar compounds	12	13	2
5	Phenols	6	0	0

The main reactions occurring on hydrogenation of the "diesel fraction" seem to be saturation of unsaturated bonds and removal of heteroelements. High-polar and neutral oxygen compounds, the latter consisting mainly of *n*-alkanones and *n*-2-alkanones, give an additional amount of aromatic and aliphatic hydrocarbons, respectively, after the removal of heteroelements. At the same time also monocyclic aromatic hydrocarbons (mainly alkylarenes) have been submitted to hydrogenation yielding cyclohexane derivatives.

Functional Group Analysis

The composition of functional groups of the "diesel fraction" present in its initial, dephenolated as well as in dephenolated and then hydrogenated at various hydrogen pressures state was characterized by infrared spectroscopy (Fig. 1).

In Figure 1, one can see that dephenolation manifests itself in a significant decrease in the number of hydroxyl groups (absorption at 3650 cm^{-1}). Due to the low content of phenols in the initial "diesel fraction" (only 6%), it is difficult to find any other difference between the initial and dephenolated fractions. Further hydrogenation of the dephenolated fraction leads to total elimination of hydroxyl groups and to immense decrease in the number of carbonyl groups (absorption at 1720 cm^{-1}).

In the spectrum of the dephenolated fraction, one can see an intense signal at 1650 cm^{-1} characteristic for the double bond, which is absent in the spectrum of the hydrogenated fraction, indicating that as a result of hydrogenation olefinic bonds are saturated.

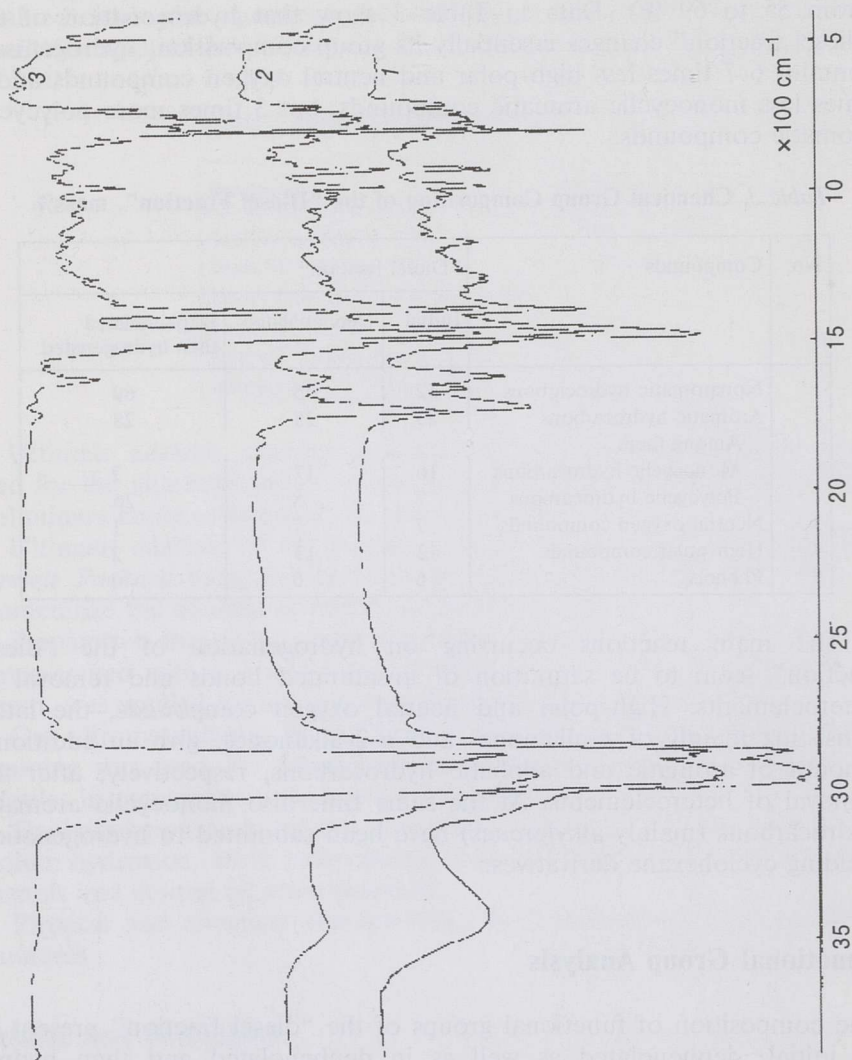


Fig. 1. Infrared spectra: 1 - initial "diesel fraction", 2 - dephenolated "diesel fraction", 3 - dephenolated "diesel fraction", then hydrogenated "diesel fraction"

Strong absorptions at 725, 745, 1380, 1470, 2870, and 2960 cm^{-1} are characteristic for methyl and methylene groups in aliphatic structures and absorptions at 750, 820, 880, 1020, 1080, 1600, and 3000 cm^{-1} indicate aromatic compounds. Infrared spectroscopic analysis data conform to those obtained from the chromatographic group analysis; as a result of hydrogenation, the content of hydrocarbons increases at the cost of oxygenous compounds.

Nonaromatic hydrocarbons dominate in both initial and hydrogenated sample, constituting more than a half of the total "diesel fraction" (55 and 69 %, respectively). Their individual composition was investigated by capillary gas chromatography, and the chromatograms are presented in Fig. 2.

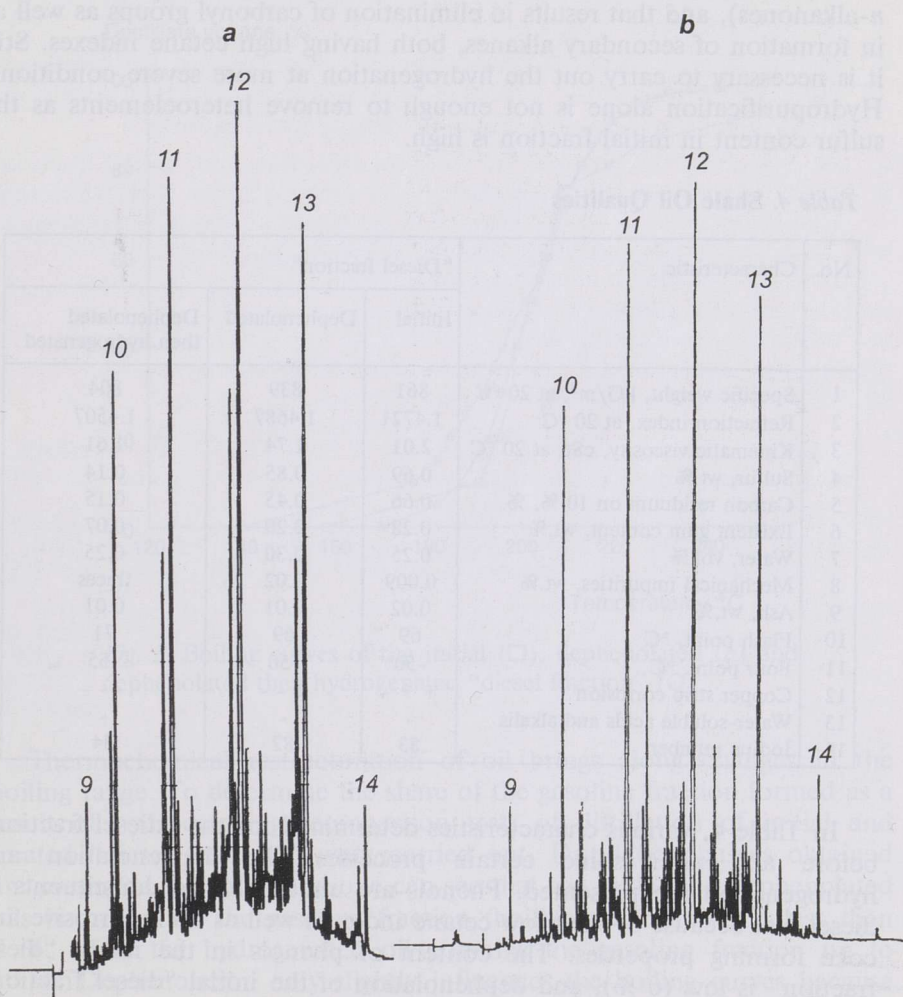


Fig. 2. Chromatograms of non-aromatic hydrocarbons separated by thin-layer chromatography from dephenolated "diesel fraction" (a) and from dephenolated then hydrogenated "diesel fraction" (b)

One can see that the initial "diesel fraction" includes *n*-alkanes and *n*-alkenes from C₉ up to C₁₄, the latter being completely hydrogenated as a result of hydrogenation.

Both chromatograms display the peaks of iso- and cycloalkanes in significant concentrations. In Estonian shale oil, straight-chain alkanes and alkanones are the best constituents of diesel fuel. Formed as a result of hydrogenation of secondary *n*-alkanes, branched alkanes and cycloalkanes, they have also higher cetane index as compared with *n*-alkenes and aromatic compounds present in the initial oil.

It could be expected that hydrogenation of the "diesel fraction" leads, besides to the improvement of oil properties, also to the increase in its cetane index. At the same time the removal of heteroelements during hydrogenation includes also the removal of oxygen (located mainly in *n*-alkanones), and that results in elimination of carbonyl groups as well as in formation of secondary alkanes, both having high cetane indexes. Still it is necessary to carry out the hydrogenation at more severe conditions. Hydropurification alone is not enough to remove heteroelements as the sulfur content in initial fraction is high.

Table 4. Shale Oil Qualities

No.	Characteristic	"Diesel fraction"		
		Initial	Dephenolated	Dephenolated then hydrogenated
1	Specific weight, kG/m ³ , at 20 °C	861	839	804
2	Refraction index, at 20 °C	1.4721	1.4687	1.4507
3	Kinematic viscosity, cSt, at 20 °C	2.01	1.74	1.61
4	Sulfur, wt. %	0.69	0.85	0.14
5	Carbon residuum on 10 %, %	0.66	0.45	0.15
6	Existent gum content, wt. %	0.28	0.20	0.07
7	Water, vol. %	0.25	0.30	0.25
8	Mechanical impurities, wt. %	0.009	0.02	traces
9	Ash, wt. %	0.02	0.01	0.01
10	Flash point, °C	69	69	71
11	Pour point, °C	-50	-50	-55
12	Copper strip corrosion	+ + -	+ - -	- - -
13	Water-soluble acids and alkalis	-	-	-
14	Iodine number	83	82	34

In Table 4, various characteristics determined for the "diesel fraction" before and after some certain processes like dephenolation and hydrogenation are presented. Phenols are undesirable as constituents of diesel fuel because of their low cetane index as well as their corrosive and coke forming properties. The content of phenols in the initial "diesel fraction" is low (6 %), and dephenolation of the initial "diesel fraction" manifests itself in only a slight increase in cetane index, but in a significant decrease in specific weight, refraction index, kinematic viscosity, existent gum content, carbon residuum and copper strip corrosion. Dephenolation includes alkali-acid treatment and other

procedures with water solutions which influence the content of water, mechanical impurities and ash of the fraction, as well as the content of water-soluble acids and alkalis partly removed during the dephenolation process.

Hydrogenation leads to essential changes in the chemical composition of the "diesel fraction", as we could become convinced above, and these changes strongly influence the oil properties. In Table 4, one can notice marked alterations in oil properties. Specific weight, refraction index, kinematic viscosity, carbon residuum, the content of sulfur, existent gum, mechanical impurities and ash; flash and pour points, iodine number, corrosive and coking properties of the hydrogenated "diesel fraction" are significantly lower than those of the initial or dephenolated "diesel fraction".

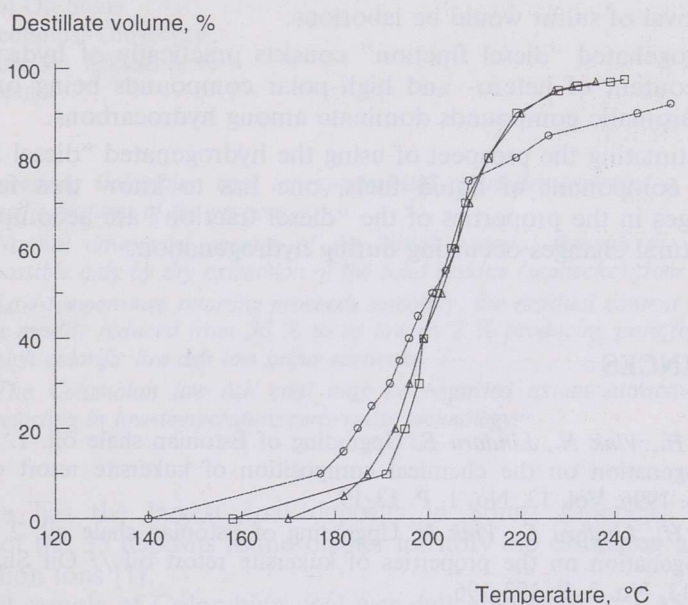


Fig. 3. Boiling curves of the initial (□), dephenolated (Δ) and dephenolated then hydrogenated "diesel fraction" (○)

Thermochemical restructuring of oil brings along changes in the boiling range. To determine the share of the gasoline fraction formed as a result of hydrocracking, comparison tests of distillation of initial and treated "diesel fractions" were carried out. Distillation curves obtained are presented in Fig. 3, and one can see that the initial and dephenolated oils both contain the gasoline fraction (boiling up to 180 °C) less than 5 %, while the hydrogenated oil contains the gasoline fraction up to 10 %. Dephenolation only slightly influences the boiling curves because the content of phenols eliminated was low (6 % only). 50 %-points are practically equal for each one of oils (at 201-203 °C), but as a result of hydrogenation the amount of compounds boiling below 200 °C,

especially boiling between 170-200 °C, increases essentially. No significant cracking of long alkyl chains in alkanes and alkanones was observed (see the chromatograms).

Conclusions

- Estonian shale oil fraction boiling at 180-240 °C, the so-called “diesel fraction”, separated from the industrial retort oil and dephenolated, hydrogenates readily at 370 °C in the presence of a Co-Mo catalyst without forming coke.
- The main reactions of hydrogenation of the “diesel fraction” are saturation of double bonds and active elimination of oxygen. Removal of sulfur would be laborious.
- Hydrogenated “diesel fraction” consists practically of hydrocarbons, the content of hetero- and high-polar compounds being only 3 %. Nonaromatic compounds dominate among hydrocarbons.
- At estimating the prospect of using the hydrogenated “diesel fraction” as a component of liquid fuels, one has to know that favourable changes in the properties of the “diesel fraction” are accompanied by structural changes occurring during hydrogenation.

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