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UPGRADING OF ESTONIAN SHALE OIL

1. EFFECT OF HYDROGENATION ON THE CHEMICAL COMPOSITION OF KUKERSITE RETORT OIL

H. LUIK
N. VINK
E. LINDARU

Institute of Chemistry
Tallinn, Estonia

Upgrading of Estonian shale oil — changing the chemical composition and correcting the boiling range — was effected by hydrogenation in an autoclave at 370 °C using a Co-Mo catalyst. Refined oil which yield reached 93 % is rich in different aliphatic, alicyclic and aromatic hydrocarbons and contains considerably less high-polar heterocompounds and alkanones as compared with unupgraded oil. Nevertheless, compound groups similar to those present in initial oil and, mainly, same individual components were identified in the composition of upgraded oil, the content of the groups as well as of single components in groups being strongly different.

As a result of moderate hydrogenation, the chemical composition of Estonian shale oil becomes closer to that of natural crude oil, enabling to widen essentially the possible fields of use of shale oil.

Shale oil produced industrially in Estonia from local oil shale - kukersite - in vertical retorts and also, in some measure, in units with solid heat carrier, is characterized by a high content of oxygen compounds. The content of phenols and neutral oxygen compounds of total oil may reach 65 %. Though atomic ratio H : C = 1.4-1.5 is relatively high for a substance like shale oil, the total kukersite oil is rich in unsaturated compounds. More than 60 % of oil is high-boiling (above 320 °C).

Taking into account the specificity of Estonian shale oil and its oxygeneous character, a moderate hydrogenation technique to depress too intensive water formation is to be worked out and used for total oil. It would be practical to separate phenols as products also upgraded from total oil prior to hydrogenation, decreasing in that way the content of oxygen in oil and, simultaneously, the consumption of hydrogen.

The aim of this work was to investigate the effect of hydrogenation on the chemical composition of kukersite retort oil.

Experimental

Moderate conditions (Table 1) and Co-Mo/Al_2O_3 as a catalyst were used for hydrogenation of kukersite retort oil. Both total and dephenolated oil were subjected to hydrogenation. Reaction time was measured from the point of reaching the reaction temperature. During the hydrogenation period the working pressure was regularly recorded. It was found that the consumption of hydrogen proceeds similarly for both total and dephenolated oil - actively during the first hour and more slowly during the second one (Fig. 1). At the end of the heating period the system was cooled down to the room temperature and residual pressures 37 and 25 at for total and dephenolated oil, respectively, were registered. Amounts of unreacted hydrogen and reaction gases - 15.4 and 8.8 dm^3, respectively, - were measured volumetrically. After that the autoclave was opened and liquid and solid products were separated by filtration.

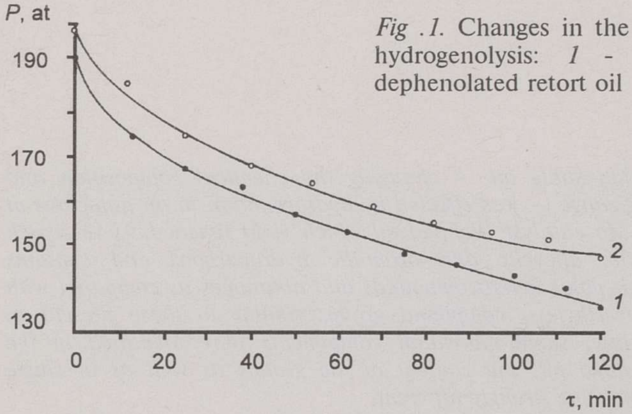

Fig .1. Changes in the working pressure during hydrogenolysis: *1* - total retort oil, *2* - dephenolated retort oil

Ultimate analysis of oils was performed by using a 186 CHN Hewlett Packard analyzer, infrared spectra were taken on a Specord 75 IR spectrophotometer.

The oils were separated into groups of compounds by thin-layer chromatography (TLC) on silica gel. TLC fractions were analyzed by gas chromatography with temperature programming using columns of different polarity.

Results and Discussion

The balance of products obtained on hydrogenation at conditions given in Table 1 is presented in Table 2.

It can be seen that considerably more gas is formed on hydrogenation of dephenolated oil than from the initial oil - 16.1 and 2.1 %, respectively, the coke yield being the same. This result supports the view that hydrogen primarily is expended on dehydroxylation of phenols present in the initial oil (increased amounts of formed water indicate the same phenomenon).

Table 1. **Hydrogenation Parameters**

Parameter	Value
Autoclave volume, cm^3	500
Ratio catalyst/shale oil, g/g	0.1
Temperature, °C	370
Initial pressure of hydrogen, at	97-103
Duration, h	2

Table 2. **Products Obtained on Hydrogenation and Their Yield**

Object of hydrogenation	Product, mass %			
	Refined oil	Water	Gas	Coke
Total retort oil	93.1	4.2	2.1	0.6
Dephenolated oil	80.2	3.1	16.1	0.6

When oil contains no phenols, process is directed to hydrogenolysis of neutral oil resulting in the formation of a lot of gas. One may assume that for effective hydrogenation of phenols present in retort oil the supply of hydrogen must be elevated and the process must run longer than in case of dephenolated oil.

Infrared and gas chromatographic analyses were carried out for estimating chemical changes in oil composition. Fig. 2 presents infrared spectra of the initial and hydrogenated oils. Structures typical for Estonian shale oil in all spectra were recorded and differences between the initial, dephenolated and hydrogenated oils were detected. A very strong absorbance in the region 2960-2850 cm^{-1} and at 1460 and 1380 cm^{-1} testifies the presence of numerous and various aliphatic and alicyclic groups. These bands are still boosted in the spectra of hydrogenisates as compared with the spectra of the initial oil, indicating the increase in the content of aliphatic and alicyclic CH_3-, CH_2- and CH-groups as a result of hydrogenation. Bands at 745, 770, 795, 820, 880, 1020, 1080, 1600, and 3000 cm^{-1} indicate the presence of aromatic systems of different degree of condensation and substitution. Bands at 1580 and 1500 cm^{-1} may originate from aromatic rings functionalized with substituents having either free electron pairs (e.g. phenolic oxygen) or unsaturated groups (e.g. carbonyl groups). Broad absorption bands with a maximum at 3450 cm^{-1} belong to the stretching vibrations of phenolic OH-groups. The infrared spectrum of the dephenolated thereafter hydrogenated oil is, in contrast to the other spectra, distinguishable by the absence of a bond corresponding to phenolic OH-groups. At the same time the spectra of dephenolated not hydrogenated and hydrogenated not dephenolated retort oils show, like the spectra of total retort oil, the presence of OH-groups. In the first case that could be caused by neutral phenols not separated from oil during alkali treatment. In the latter case the presence of OH-groups indicates either

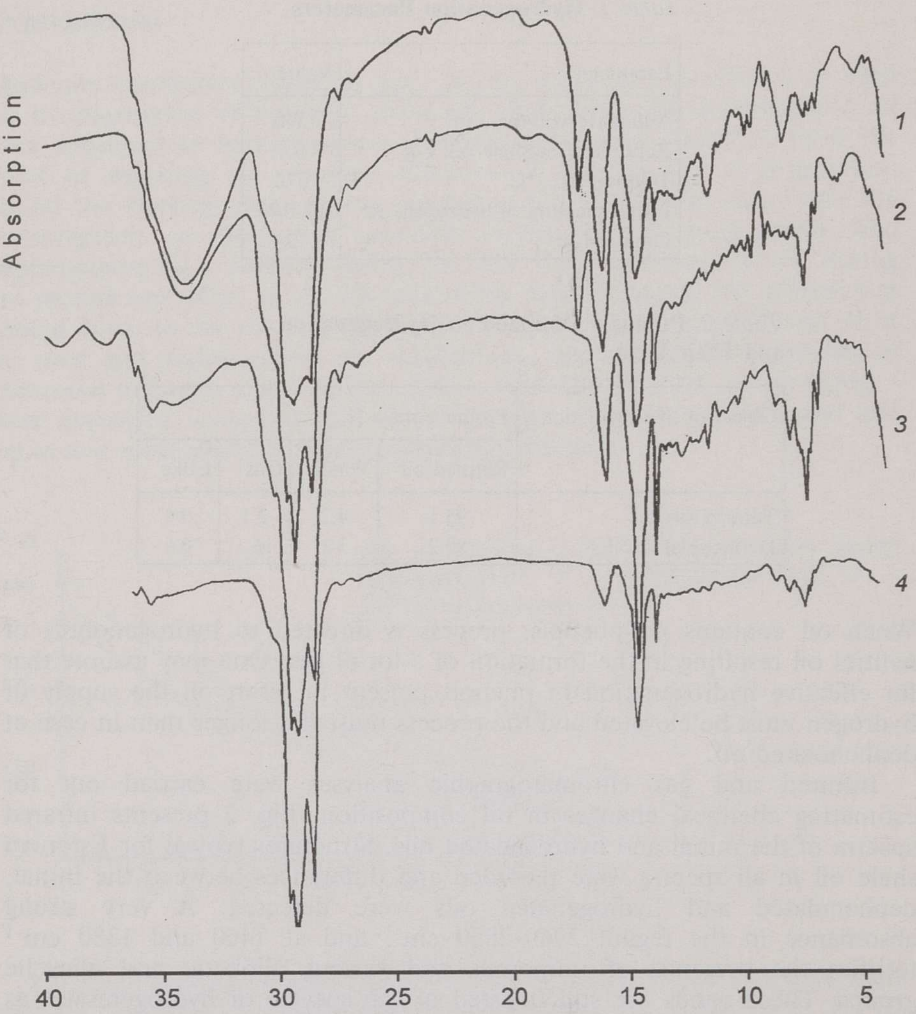

Fig. 2. Infrared spectra of initial oils and their hydrogenisates: *1* - total retort oil, *2* - dephenolated retort oil, *3* - hydrogenated retort oil, *4* - dephenolated, thereafter hydrogenated retort oil

the formation of secondary phenols from the primary ones or presence of a part of phenols remained in the oil after hydrogenation; this relatively weak absorption may also originate, to some extent, from water formed during hydrogenation. One may resume that for a more complete elimination of OH-groups both dephenolation and hydrogenation are needed. Also, it looks like only typical - slightly acidic - but not neutral phenols produce secondary phenols, as in the spectrum of dephenolated and thereafter hydrogenated retort oil no absorption of phenolic OH-groups at 3450 cm^{-1} has been noticed. A strong and sharp band at 1720 cm^{-1}, missing in the spectra of hydrogenisates, as well as diffuse and poorly shaped bands at 1250, 1100, and 1040-1020 cm^{-1} originate from carbonyl groups of the initial retort oils. As we can see, hydrogenation proceeds more readily with heteroatomic compounds. The spectral patterns of oxygenic systems in the initial and hydrogenated oils differ markedly, the latter ones being characterized by the absence or at most a very low content of polar groups such as O−H and C=O.

The results of TLC (Table 3) also confirm the conclusions stated above.

Table 3. **Chemical Group Composition of Compounds Present in Initial and Hydrogenated Oils**

Compounds	Retort oil, %			
	Initial	Dephenolated	Hydrogenated	Dephenolated, thereafter hydrogenated
Non-aromatic hydrocarbons	11.1	15.0	32.7	35.7
Alkylarenes	5.4	7.3	1.7	2.1
Polycyclic (alkyl)arenes	23.1	31.2	41.1	40.9
Alkanones	16.7	22.6	12.5	8.7
High-polar heterocompounds	17.7	23.9	10.4	11.9
Phenols	26.0	0	1.6	0.7

As a result of hydrogenation, the content of heterocompounds (S, N, and mainly oxygen atom-containing high-polar compounds, alkanones and especially phenols) significantly decreases. At the same time the content of hydrocarbons in hydrogenisates increases. This increase is especially great in case of the non-aromatic ones (2-3 times). It is obvious that just the above-mentioned heterocompounds - high-polar ones as well as alkanones and phenols - serve as precursors of aliphatic, alicyclic and aromatic compounds on hydrogenation.

It is of a special interest to observe the changes in the composition of phenols and guess possible pathways of their alteration. Almost all phenols totally decompose on hydrogenation, and their residual content in hydrogenisates does not surpass 1.6 % (Table 3). Hydrogenation of phenols as well as of other compounds is accompanied by various reactions like cracking, dealkylation, cleavage of functional groups (dehydroxylation), which may occur prior to and after hydrogenation as well as simultaneously, and as a result various final products are formed.

The formation of phenols in previously dephenolated oil on hydrogenation was somewhat unexpected. Appearance of acidic properties of dephenolated shale oil not having them before was explained as a result of dealkylation of neutral phenols and cracking of ether groups [1]. Nevertheless, that phenomenon as well as possible alterations of multifunctional phenols, e.g. alkylresorcinols, under the hydrogen pressure and presence of a Co-Mo catalyst need special and more detailed research.

The individual composition of different compound classes present in hydrogenisate of the initial retort oil separated by TLC (Table 3) is represented in Fig. 3.

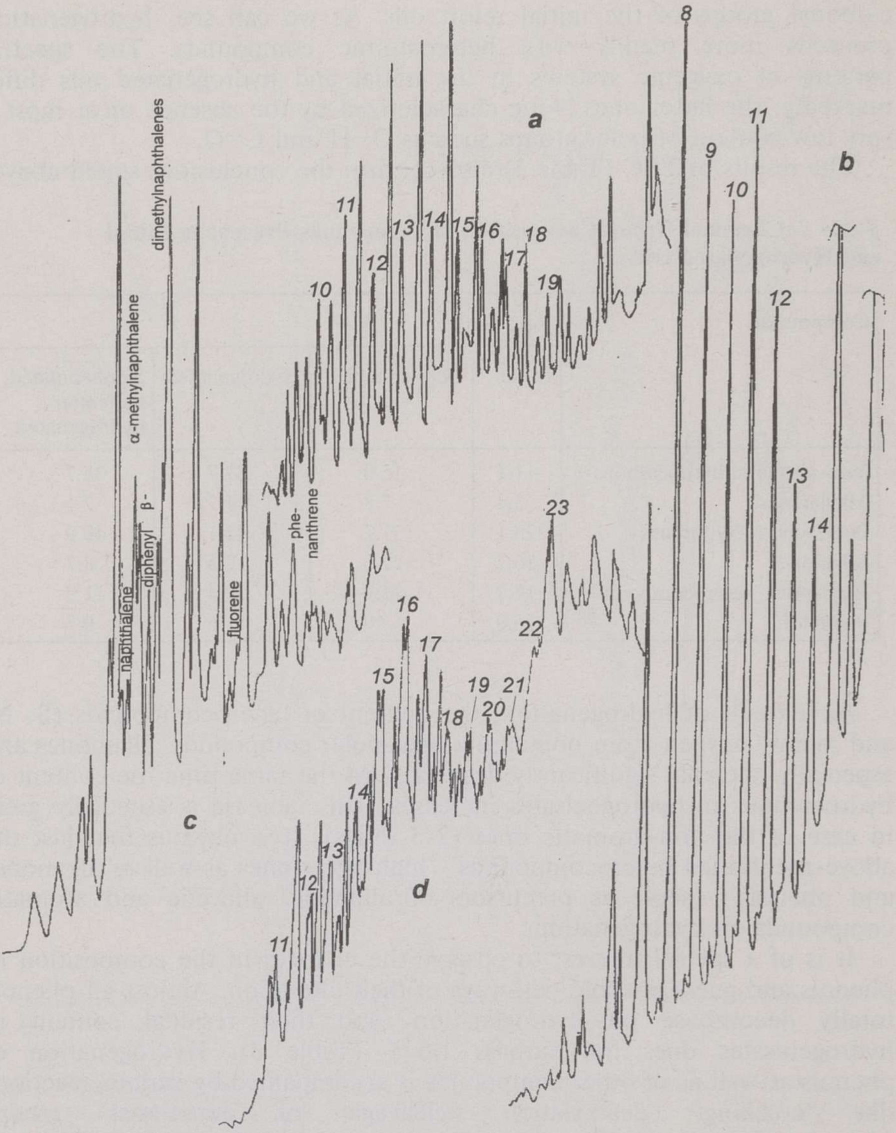

Fig. 3. Chromatograms of compounds separated from hydrogenated total retort oil by TLC: *a* - non-aromatic hydrocarbons, *b* - alkylarenes, *c* - polycyclic (alkyl)arenes, *d* - alkanones. Numbers *8-23* indicate the carbon atoms number in the alkyl chain of a compound

The fraction of **non-aromatic hydrocarbons** consists mainly of *n*-alkanes, having up to 21 carbon atoms in chain, and even-numbered homologs prevail as compared with initial retort oil. The marked decrease in the share of odd-numbered *n*-alkanes is caused by the saturation of alkenes (even-numbered alkenes dominate in the initial oil) and by formation of secondary *n*-alkanes (mainly even-numbered) *via* hydrocracking reactions. In the chromatogram, peaks of isoalkanes and alicyclic hydrocarbons (most of them of technological origin with significant concentration maximums) are located between the peaks of *n*-alkanes.

Monocyclic alkylarenes are represented by alkylbenzenes with the maximum length of the alkyl chain (number of carbon atoms) 17, typical for Estonian shale oil.

Polycyclic arenes consist mainly of compounds with 2-4 condensed cycles and their methyl and ethyl derivatives: naphthalene, dimethylnaphthalenes, 1-naphthol, 2-naphthol, pyrene, phenanthrene, diphenyl, fluorene, acenaphthene, etc.

Alkanones are presented by regular twin peaks indicating to the homologous series of *n*-2-alkanones and dialkylalkanones which have a carbonyl group near the centre of the chain. Though entangled as a result of partial hydrogenation, the maximum length of the alkyl chain is 23 in alkanones.

Basing on chromatographic data it was established that the composition of alkanones and arenes present in hydrogenisates and in the initial retort oil is similar.

Conclusions

1. A method for moderate hydrogenation of Estonian shale oil has been worked out. During hydrogenation of dephenolated oil a lot of gas and less water was formed as compared with hydrogenation of total oil while coke yield was the same.
2. Among different secondary products of saturation, derivation and substitution formed as a result of hydrogenation, in the composition of upgraded oil mostly compounds similar to those present in primary oil or remained after hydrogenation were detected. The individual and group concentration of respective aliphatic and aromatic hydrocarbons as well as of alkanones in hydrogenisates and initial oil differ markedly. Hydrogenisates are characterized by a significantly higher content of non-aromatic hydrocarbons and a lower content of heteroatomic compounds.
3. As a result of hydrocracking the phenols totally decompose forming gas, water, various hydrocarbons and also secondary phenols.

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