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UPGRADING OF ESTONIAN SHALE OIL
2. EFFECT OF HYDROGENATION ON THE PROPERTIES OF KUKERSITE RETORT OIL

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Upgrading of Estonian shale oil - improving the properties and correcting the boiling range - was effected by hydrogenation in an autoclave at 370 °C using a Co-Mo catalyst. Characteristic parameters for initial kukersite retort oil as well as for its hydrogenisates were determined. It was concluded that it is prospective to upgrade Estonian shale oil into diesel fuel or diesel fuel additive.

In [1], the effect of hydrogenation on the chemical composition of kukersite retort oil was investigated. It was established that the hydrogenation of Estonian shale oil proceeds readily at moderate procedural conditions. Essential alterations in the oil composition occur and as a result of hydrogenation heteroatomic compounds are partly and phenols totally decomposed, double bonds are saturated and the content of different non-aromatic hydrocarbons in oil markedly increases.

The aim of this article was to explain in what manner the chemical changes in oil structure influence the oil properties and to suggest possible fields of application of the upgraded oil. To that end several characteristics for initial as well as for dephenolated and/or hydrogenated oils were determined (Table).

Data in Table show that the hydrogenation of Estonian shale oil results in marked alterations of oil properties - with increasing the H : C ratio oil density, molecular weight, viscosity, iodine number, flash and pour points, the content of sulphur, resins and mechanical admixtures, corrosive and coking properties decrease significantly.

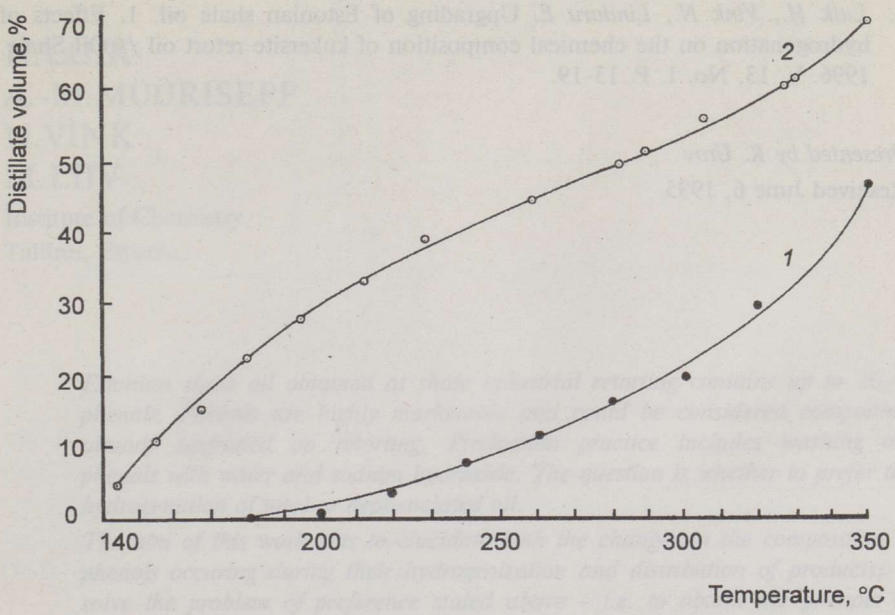
Oil Qualities

No.	Characteristic	Retort oil			
		initial	dephenolated	hydrogenated	dephenolated then hydrogenated
1	Density at 20 °C, g/cm^3	0.9520	0.9219	0.8860	0.8829
2	Index of refraction at 20 °C	1.5100	1.5060	1.4989	1.4978
3	Kinematic viscosity at 20 °C, cSt	81.54	32.25	7.56	6.47
4	Atomic ratio H : C	1.43	1.44	1.68	1.65
5	Sulphur, wt.%	1.03	1.07	0.48	0.60
6	Carbon residuum on 10 %	3.1	1.6	0.9	0.1
7	Molecular mass	245	251	200	195
8	Existent gum content, wt. %	16.83	11.20	6.84	3.03
9	Water, vol.%	0.37	0.45	0.33	0.30
10	Mechanical impurities, wt. %	0.1	0.1	0.03	-
11	Ash, wt. %	0.03	0.03	0.01	-
12	Flash point, °C	92	91	73	71
13	Pour point, °C	-17	-21	-40	-35
14	Copper strip corrosion	+++	+	-	-
15	Iodine number	-	91	40	33
16	Water soluble acids and alkalis	+	-	-	-

Dephenolation of initial retort oil manifests itself only in a slight decrease in refraction index, flash and pour points as well as corrosive properties; at the same time the decrease in density, viscosity, carbon residue and resins content is significant. Dephenolation practically has no effect on H : C ratio, molecular weight and the content of sulphur, ash and mechanical admixtures in retort oil.

In Figure, the boiling curves of the initial and hydrogenated retort oils are presented. The phenols as well as their hydrogenation products are uniformly distributed between the oil fractions so the respective boiling curves of dephenolated and not dephenolated oils get covered by each other. As it could be seen in Figure, the initial retort oil as compared with the hydrotreated oil contains considerably less fractions boiling up to 350 °C. As a result of hydrocracking, high-boiling compounds in retort oil decompose and modify into lighter ones so markedly increasing the share of low-boiling fractions. We can see that the total content of fractions boiling up to 200, 250, and 300 °C in the initial and hydrogenated retort oils are as follows: 2 and 30, 10 and 42.5, 20 and 54 %, respectively. The content of compounds boiling above 350 °C is decreased during hydrogenation from 54 to 30 %, and almost a half of them are converted into compounds boiling below 350 °C at hydrogenation conditions used.

In practical aspect, the obtained total oils could be characterized by the content of technical raw fractions like gasoline (up to 180 °C), diesel (180-325 °C) and mazut (above 325 °C) ones. The initial retort oil contains no gasoline fraction, 28 % diesel and more than 70 % mazut fraction while upgraded retort oil contains the same fractions in the amounts of 22.5, 40 and 37.5 %, respectively.



Boiling curves of the initial (*1*) and hydrogenated (*2*) retort oil

So, hydrogenation of Estonian shale oil results not only in the improvement of oil qualities but in the correction of boiling range as well.

Conclusion

- Taking into account the specificity of Estonian shale oil and alterations occurring in its composition and properties on hydrogenation, its upgrading into diesel fuel or diesel fuel additive is prospective.
- Upgraded Estonian shale oil contains moderately neutral oxygen compounds (ketones) and a lot of different aliphatic hydrocarbons both groups of compounds having a high cetane number.
- It seems to be preferable to separate the phenols prior hydrogenation as they are highly marketable compounds already upgraded on retorting, so essentially decreasing the consumption of hydrogen.

- To bring shale oil qualities closer to natural oil and to obtain diesel fuel meeting the standards, hydrogenation technique as well as processing schemes should be improved.

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