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## UPGRADING OF ESTONIAN SHALE OIL DISTILLATION FRACTIONS

### 2. THE EFFECT OF TIME AND HYDROGEN PRESSURE ON THE YIELD AND COMPOSITION OF "DIESEL FRACTION" HYDROGENATION PRODUCTS

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*Upgrading of Estonian shale oil fraction boiling at 180-240 °C, the so-called "diesel fraction", characterized by sulfur content 0.85 % and polar heteroatomic compound content 20 % after dephenolation, was effected by hydrogenation in an autoclave at 370 °C using a Co-Mo catalyst. Chemical group composition and changes in the composition of functional groups occurring at hydrogenation of the "diesel fraction" were determined. Hydrogen consumption potential of the "diesel fraction" was estimated in multistep hydrogenation experiments. It was concluded that hydrogenation proceeds rapidly, non-aromatic hydrocarbons being formed dominantly.*

### Experimental

Upgrading of the Estonian shale oil "diesel fraction" at determined hydrogenation conditions is described in [1]. The effect of variations in hydrogen pressure and time on the yield and chemical composition of the hydrogenation products is the issue of this work.

The work was aimed at investigating hydrogenation velocity and hydrogen consumption potential of the "diesel fraction".

Two series of hydrogenation experiments were carried out in a 0.5 dm<sup>3</sup> autoclave at 370 °C:

1. Experiments at varied hydrogen pressures, 50, 85 and 100 at (accuracy of measurement  $\pm 1$  at) during 2 hours, the other parameters of hydrogenation – temperature, time, sample and catalyst weights – being constant.
2. Consecutive two-step hydrogenation at  $80 \pm 1$  at: after the end of a 2-hour hydrogenation at  $80 \pm 1$  at (1st step) the autoclave was cooled

down, gases (reaction gases and unreacted hydrogen) were removed and the autoclave was charged again with a new equal amount of pure hydrogen up to  $80 \pm 1$  at, and a new 2-hour hydrogenation under the same conditions (2nd step) was proceeded.

Hydrogenation at varied hydrogen pressures as well as the multistep consecutive hydrogenation offer the possibility to investigate both problems given above and also to investigate the effect of time and hydrogen pressure on the yield and composition of the products obtained.

The characterization of the hydrogenated samples, other parameters of hydrogenation, and the scheme of hydrogenisate analysis find in [1].

## Results and Discussion

### 1. Hydrogenation at Varied Hydrogen Pressures

To estimate the hydrogenation velocity and hydrogen consumption at various initial pressures of hydrogen, the changes in the pressure in autoclave were observed and depicted in Fig. 1. One can see that the consumption of hydrogen is very intensive during the first hour when the pressure decreases significantly. The lower the initial hydrogen pressure, the steeper the slope in the pressure curve at the beginning. During the second hour the hydrogen consumption stabilizes being somewhat balanced and shadowed by other compounds formed as a result of

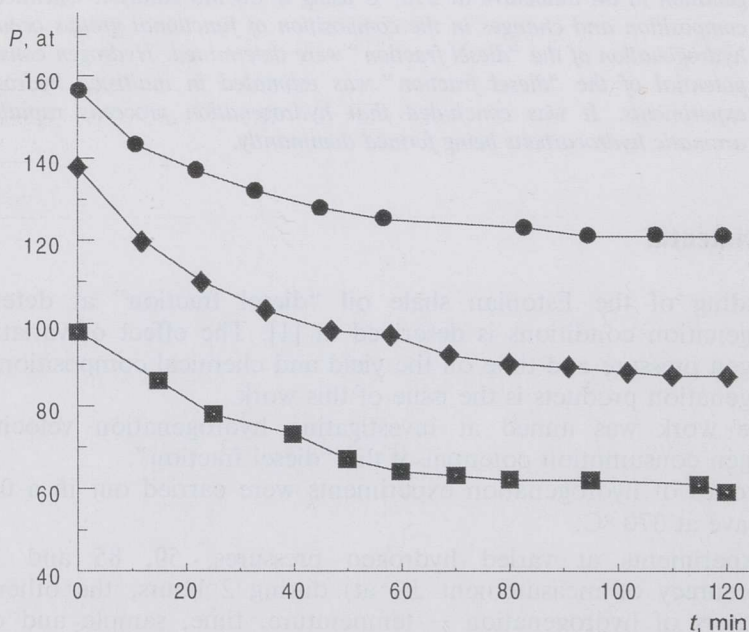


Fig. 1. Changes in the working pressure during hydrogenation of the "diesel fraction" at 50 (■), 85 (◆) and 100 (●) at.  $T = 370$  °C

**Table 1. The Yield of Hydrogenation Products of the "Diesel Fraction" at Varied Hydrogen Pressures, wt. % ( $T = 370\text{ }^{\circ}\text{C}$ ,  $t = 2\text{ h}$ )**

Initial pressure of hydrogen, at	Refined oil and its density, kg/m <sup>3</sup>	Gas	Water	Coke
50	94.9 (823)	3.8	1.3	0
85	93.9 (811)	3.8	2.3	0
100	92.0 (804)	5.3	2.7	0

hydrogenation and having some influence on the pressure characteristics. The graphs in Fig. 1 show that the reserve of hydrogen in the autoclave was sufficient in all cases and that hydrogenation of most "diesel fraction" proceeds rapidly during the first 1-1.5 hours.

The yields of hydrogenation products obtained using different initial pressures of hydrogen are presented in Table 1. One can see that the higher the initial pressure of hydrogen, the lower the yield of refined oil and its density, and the higher the yields of water and gas. This is the expected result because at higher hydrogen pressures the removal of heteroelements is more complete and their replacement with "easy" hydrogen leads to the decrease in the oil weight. Despite of great differences in hydrogen pressures, the yield of refined oil was in limits 92-95 % and no coke was formed.

The effect of hydrogenation of the "diesel fraction" on its functional group composition was investigated by infrared spectroscopy, and the results are expressed as mathematically calculated relative numerical values [2] in Table 2.

**Table 2. Characterization of Oils by Infrared Spectra**

Frequency (cm <sup>-1</sup> ) and corresponding functional group	Initial "diesel fraction"	"Diesel fraction" hydrogenated at initial pressure of hydrogen, at		
		50	85	100
Reduced optical densities				
720 (-CH <sub>2</sub> ) <sub>n</sub>	0.31	0.37	0.40	0.62
CH <sub>aromatic</sub> :				
745	0.37	0.48	0.55	0.52
770	0.66	0.67	0.64	0.52
815	0.22	0.26	0.23	0.21
880	0.16	0.13	0.14	0.18
1380 CH <sub>3</sub>	0.66	0.67	0.79	0.87
1600 (C = C) <sub>aromatic</sub>	0.22	0.17	0.28	0.11
1720 CO	0.56	0.01	0.00	0.00
2930 CH <sub>2</sub>	1.28	1.18	1.13	0.95
2960 CH <sub>3</sub>	1.28	1.13	1.12	0.95
CH <sub>aromatic</sub> :				
3020	0.52	0.30	0.46	0.67
3050	0.38	0.37	0.33	0.46
3400 OH	0.11	0.02	0.01	0.01
Ratio of optical densities				
2930/2960	1.00	1.04	1.01	1.00
3050/2930	0.30	0.31	0.29	0.48

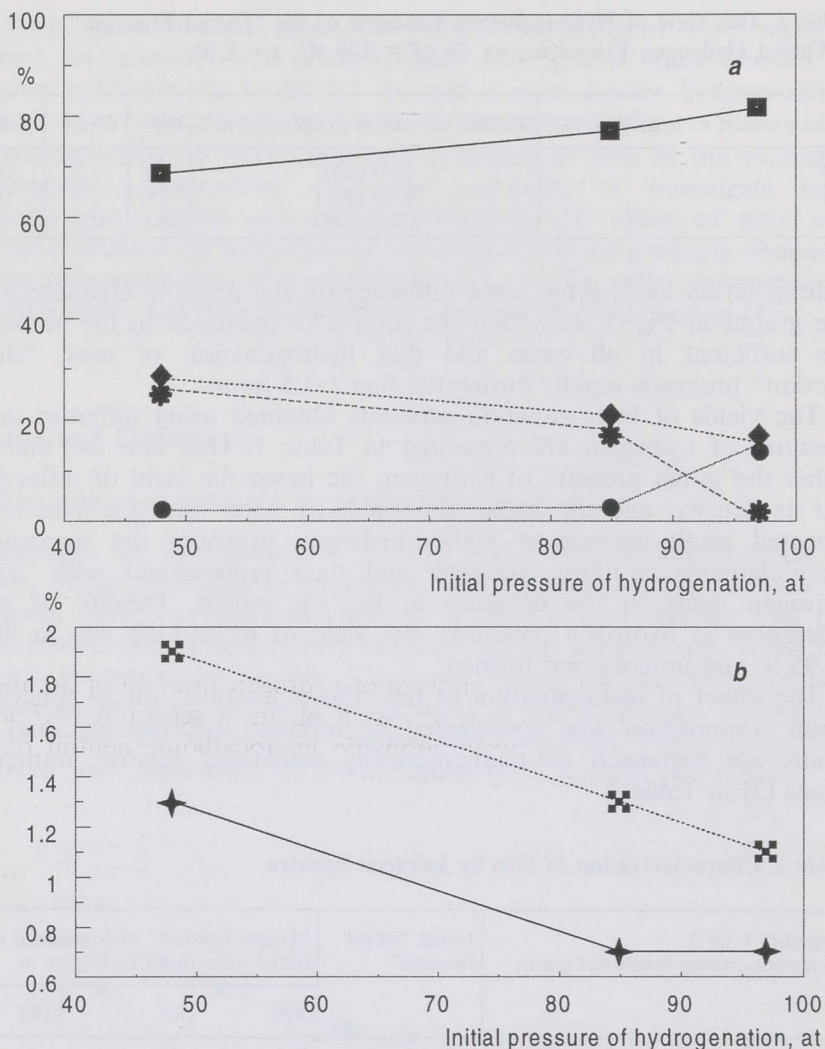


Fig. 2. The concentration of compounds separated by adsorption chromatography in oils generated at various hydrogen pressures. *a* - aliphatic hydrocarbons (■), total aromatic hydrocarbons (◆) and among them monocyclic (●) and polycyclic (\*) hydrocarbons. *b* - neutral oxygen compounds (◆) and heteroatomic compounds (⊠)

The numbers in Table 2 do not reflect the actual contents but show the tendencies of corresponding functional groups to increase or decrease just what is necessary for the comparison of resembling spectra. Data in Table 2 show that elevating the hydrogen pressure leads to the increase in the content of methylene groups in paraffinic chains (absorption at  $720\text{ cm}^{-1}$ ) and to the decrease in the content of carbonyl (absorption at  $1720\text{ cm}^{-1}$ ) and carboxyl (absorption at  $3400\text{ cm}^{-1}$ ) groups. The higher the initial pressure of hydrogen, the more significant the according increase

or decrease. Absorption at  $1380\text{ cm}^{-1}$  belongs to isolated and geminal-substituted methyl groups and its value increases with increasing the hydrogen pressure.

The ratio of absorptions at  $1380$  and  $1460\text{ cm}^{-1}$  characterizes the degree of branching in alkyl chains. Hydrogenation has no influence on that characteristic and as known branched chains are not typical for kukersite oils. Also improbable is the formation of those chains on hydrogenation. The ratio of absorptions at  $2930$  and  $2960$  is stably similar as well. Absorptions at  $745$ ,  $815$  and  $880\text{ cm}^{-1}$  belong to the aromatic compounds substituted in different positions (2-4 substitutes), absorption at  $770\text{ cm}^{-1}$  – to the naphthalene and its derivatives. Judging the stability of aromatic compounds to hydrogenation on the basis of infrared spectra only is difficult as there is no clearly expressed ebb or rise in the content of the functional groups characteristic for aromatic compounds. One may guess that the content of aromatic compounds in oils remains practically similar or has a slight tendency to decrease with increasing the hydrogen pressure. To prove it, the chemical group composition of each oil has to be determined.

The chemical group composition of oils obtained on hydrogenation at different hydrogen pressures was determined by adsorption chromatography, and the results are presented graphically in Fig. 2. One can see that with elevating the initial pressure of hydrogen from  $50$  up to  $100$  at, the content of aliphatic hydrocarbons in oil increases from  $68.7$  up to  $81.6\%$  while that of polycyclic aromatic hydrocarbons, neutral oxygen compounds and heteroatomic compounds decreases from  $26.0$ ,  $1.3$  and  $1.9$  down to  $0.4$ ,  $0.7$  and  $1.1\%$ , respectively. Elimination of oxygen and other heteroelements at  $85$  and  $100$  at is equal and more complete than at  $50$  at, but tempestuous decomposition of polycyclic aromatic hydrocarbons at  $100$  at resulting only in a slight increase in the content of aliphatic hydrocarbons and in a significant increase in the content of monocyclic hydrocarbons was unexpected.

## 2. Consecutive Stepwise Hydrogenation

The idea of multistep hydrogenation, the number of steps depending upon receptive properties of oil to hydrogen was to determine the total potential of oil to consume hydrogen, its time characteristics and the influence on oil composition depending upon consumed hydrogen. As one can see in Fig. 3, for the "diesel fraction" one-step hydrogenation during 2 hours at  $80$  at (hydrogenation 1) is enough to saturate the oil with hydrogen. By the end of the first hour, the hydrogenation of the "diesel fraction" has practically been completed. Hydrogenation of already hydrogenated oil under the same conditions (hydrogenation 2) during 2 hours is illustrated in Fig. 3 by a practically straight line of  $P$ ,  $t$ -dependence that refers to the inertness of the already hydrogenated "diesel fraction" to further hydrogen attacks. However, these conclusions had to be confirmed by quantitative and qualitative analysis of hydrogenation products. The material balance of stepwise hydrogenation products is presented in Table 3.

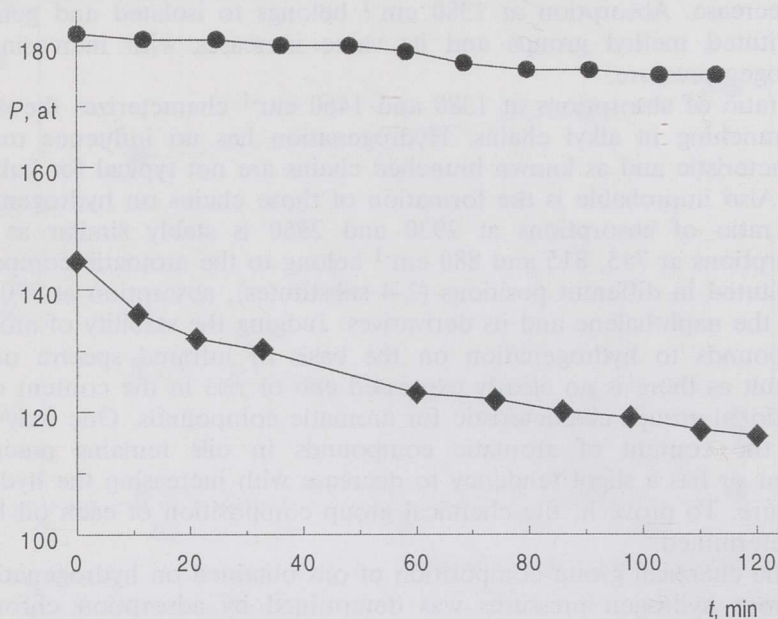


Fig. 3. Changes in the working pressure during two-step hydrogenation of the "diesel fraction".  $\blacklozenge$  - 1st step of hydrogenation  $\bullet$  - 2nd step of hydrogenation.  $T = 370^\circ\text{C}$

Table 3. The Yield of Hydrogenation Products

Product	Yield, wt.%	
	Hydrogenation 1	Hydrogenation 2
Refined oil	94.7	99.1
Gas	3.5	0.7
Water	1.3	0.0
Coke	0.5	0.2

One can see that the data in Table 3 confirm the conclusion made above – at hydrogenation of the already hydrogenated "diesel fraction" practically no typical final products of hydrogenation – gas and water – are formed. 0.9 % loss in the yield of refined oil dealt between gas and coke is negligible and probably might be caused only by thermocracking. It is known that Estonian shale oil distillates incongruently, it means that on secondary thermolysis it does not distillate completely but partly decomposes and this phenomenon is noted also on secondary thermolysis of the "diesel fraction" in autoclave in the hydrogen atmosphere as the latter is inert and has no or very slight chemical effect on oil components even when transformed into vapour phase. The composition of hydrogenisates also testifies in favour of that (see Table 4).

Table 4. The Composition of Hydrogenisates

Compounds	Yield, wt. %	
	Hydrogenation 1	Hydrogenation 2
Aliphatic hydrocarbons	71.1	90.8
Monocyclic aromatic hydrocarbons	2.8	2.5
Polycyclic aromatic hydrocarbons	18.1	5.9
Neutral oxygen compounds	0.7	0.5
High-polar heterocompounds	1.3	0.3

The main difference in the composition of hydrogenisate 2 is the increased content of aliphatic hydrocarbons and the decreased content of polycyclic aromatic compounds. We may suppose that this difference is caused by thermocracking only, without hydrogen participation in forming of these components, because it is known that in oil thermolysis processes polycyclic aromatic hydrocarbons are the main source of coke [3-4]. The coke formation on the second stage of hydrogenation and a significant decrease in the content of polycyclic aromatic compounds relatively increase the content of aliphatic hydrocarbons. At the same time splitting of long alkyl chains from asphaltenes or high-polar maltenes during shale oil thermal destruction has been noted by many authors [5-7].

## Conclusion

Hydrogenation of the so-called "diesel fraction" separated from kukersite retort oil industrially at 180-240 °C proceeds effectively during one hour at 370 °C using a Co-Mo catalyst, at the initial pressure of hydrogen 80 at.

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