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## UPGRADING OF ESTONIAN SHALE OIL DISTILLATION FRACTIONS 4. THE EFFECT OF TIME AND HYDROGEN PRESSURE ON THE YIELD AND COMPOSITION OF LIGHT MAZUTE HYDROGENATION PRODUCTS

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*Hydrogenation of the light mazute at various pressures and its consecutive stepwise hydrogenation at a constant pressure were carried out to investigate the effect of hydrogenation duration and hydrogen pressure on the yield and composition of hydrogenation products. The regularities in the composition of functional groups and compound groups were investigated. It was established that the elevation of the hydrogen initial pressure has only a small effect on the yield and distribution of hydrogenation products, but a significant effect on the composition of refined oil, while the time factor significantly influences both the distribution and composition of hydrogenation products but not the yield of refined oil.*

Upgrading of Estonian shale oil light mazute fraction boiling between 240-320 °C at determined hydrogenation conditions was described in [1]. The aim of the present work was to investigate the effect of varied hydrogen pressures and time on the yield and chemical composition of light mazute hydrogenation products.

### Experimental

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

1. Hydrogenation at varied hydrogen pressures 70, 80 and 96 at.
2. Consecutive tri-step hydrogenation at 80 at, similarly to that described in [2].

Characterization of the initial light mazute, methods and analysis scheme see in [1, 3].

## Results and Discussion

### Hydrogenation at Varied Hydrogen Pressures

The effect of hydrogen pressure on the reaction kinetics is presented in Fig. 1. One can see that the consumption of hydrogen is very intensive during the first 1-1.5 h in all cases. At the final stage, during the last 30 min the consumption of hydrogen stabilizes.

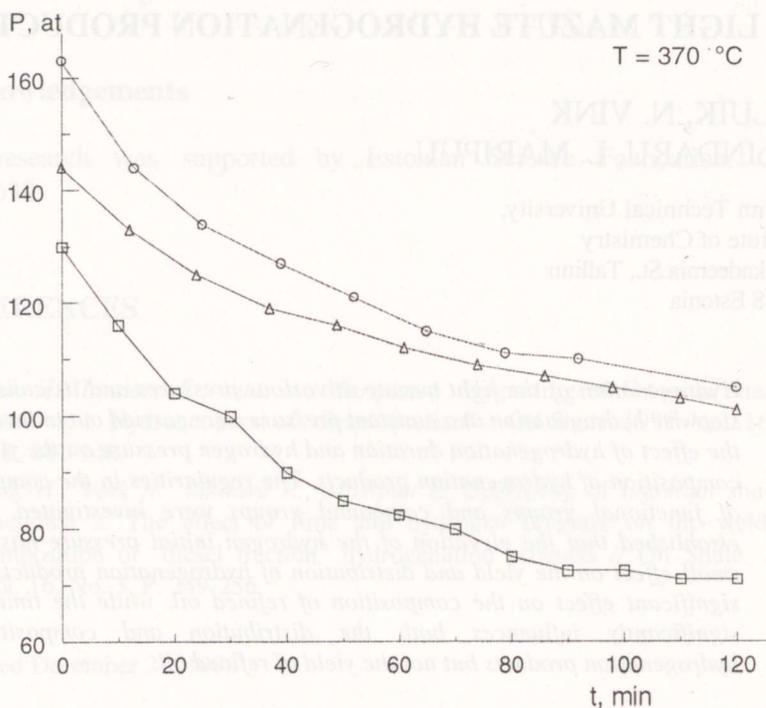


Fig. 1. Changes in the working pressure during hydrogenation of the light mazute at 70 (□), 80 (▽) and 96 (○) at

The graphs in Fig. 1 let us assume that the reserve of hydrogen in autoclave was sufficient in all cases and the primary hydrogenation of light mazute takes approximately 90 min at these conditions the initial pressure of hydrogen being 70 at. One can see that elevating the initial pressure of hydrogen up to 96 at shortens the hydrogenation time by 30 min.

The yields of hydrogenation products obtained using different initial pressures of hydrogen are presented in Table 1. Though the yields obtained are close to each other, the higher the initial pressure of hydrogen the lower the yield of refined oil and the higher the yields of water and coke, the gas content remaining constant. These regularities were observed also on the "diesel fraction" hydrogenation [2].

**Table 1. The Yield of Light Mazute Hydrogenation Products at Varied Hydrogen Pressures**

Initial pressure of hydrogen, at	The yield of hydrogenation products, wt.%			
	Refined oil	Gas	Water	Coke
70	89.6	2.9	1.7	5.8
80	89.0	2.9	2.3	5.8
96	87.8	2.8	3.1	6.1

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

Frequency (cm <sup>-1</sup> ) and corresponding functional group	Initial light mazute	Light mazute hydrogenated at initial pressure of hydrogen, at		
		70	80	96
Reduced optical densities				
720 (-CH <sub>2</sub> ) <sub>n</sub>	0.27	0.28	0.29	0.34
745	0.38	0.41	0.43	0.50
770 CH <sub>aromatic</sub>	0.27	0.36	0.41	0.52
815	0.33	0.35	0.36	0.27
880	0.18	0.21	0.16	0.18
1380 CH <sub>3</sub>	0.71	0.69	0.70	0.69
1600 (C=C) <sub>aromatic</sub>	0.50	0.40	0.37	0.30
1720 CO	0.49	0.05	0.02	0.02
2930 CH <sub>2</sub>	1.24	1.34	1.34	1.67
2960 CH <sub>3</sub>	1.27	1.37	1.39	1.69
3020 CH <sub>aromatic</sub>	0.54	0.50	0.57	0.90
3050	0.46	0.41	0.49	0.77
3400 OH	0.38	0.09	0.08	0.07
Ratios of optical densities				
2930/2960	0.97	0.97	0.98	0.97
3050/2930	0.37	0.36	0.36	0.37

The characterization of changes in the composition of functional groups of light mazute samples obtained on hydrogenation at varied pressures was issued from mathematical interpretation of infrared spectra [2]. In Table 2 one can follow the obvious regularities: with elevating the initial hydrogen pressure the content of aliphatic methylene and methyl groups increases, and the content of carbonyl and carboxyl groups decreases.

The group composition of light mazute samples hydrogenated at various hydrogen pressures was investigated by thin-layer chromatography and the results are presented in Table 3.

Elevating the hydrogenation pressure leads to an increase in the content of aliphatic hydrocarbons and decrease in the content of aromatic hydrocarbons, neutral oxygen compounds and high-polar heterocompounds.

Table 3. The Composition of Hydrogenisates

Compounds	Yield, wt.%, hydrogenation pressure, at		
	70	80	96
Aliphatic hydrocarbons	35.6	50.8	78.1
Monocyclic aromatic hydrocarbons	8.3	13.0	9.1
Polycyclic aromatic hydrocarbons	43.0	26.6	17.6
Neutral oxygen compounds	6.4	3.6	2.0
High-polar heterocompounds	6.7	6.0	3.2

### Consecutive Stepwise Hydrogenation

Tri-step hydrogenation of light mazute was proceeded to issue the effect of hydrogen availability to its consumption depending on time and also to determine the changes in the composition of refined oil. As seen in Fig. 2, the most intensive consumption of hydrogen is observed during the first phase of hydrogenation while only low consumption of hydrogen during the first hour of the second phase and practically no consumption of hydrogen during the last hour of the second phase of hydrogenation as well as during the whole period of the third hydrogenation phase takes place. Thus it could be concluded that the accomplished hydrogenation of the light mazute at 370 °C and 80 at takes in maximum no more than 3 hours.

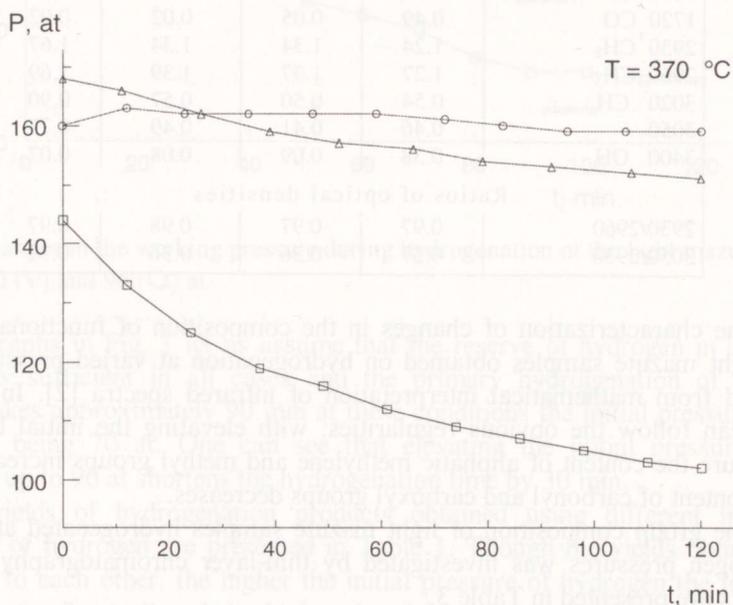


Fig. 2. Changes in the working pressure during tri-step hydrogenation of light mazute: □ - 1st step of hydrogenation, ▽ - 2nd step of hydrogenation, ○ - 3rd step of hydrogenation

Table 4. The Yield of Hydrogenation Products

Product	Yield, wt.%		
	Hydrogenation 1	Hydrogenation 2	Hydrogenation 3
Refined oil	89.0	97.9	98.9
Gas	2.9	1.4	0.9
Water	2.3	0	0
Coke	5.8	0.7	0.2

The yields of hydrogenation products obtained on the stepwise hydrogenation are presented in Table 4.

Data in Table 4 confirm the conclusion made above that an almost complete hydrogenation occurs during the first phase of hydrogenation, and as a result, oil losses including gas, water and coke are 11 %. In the second and third phases of hydrogenation no water was formed, gas and coke yields being negligible. During the last two phases of hydrogenation the loss in oil weight was only 2 % and therefore we may conclude that the influence of hydrogen on the product yield is very small.

The chemical group composition of oils obtained by stepwise hydrogenation was investigated using thin-layer chromatography and the results are presented in Table 5.

Table 5. The Composition of Hydrogenisates

Compounds	Content, wt.%		
	Hydrogenation 1	Hydrogenation 2	Hydrogenation 3
Aliphatic hydrocarbons	50.8	80.7	90.8
Aromatic hydrocarbons	39.6	15.0	8.2
monocyclic	13.0	8.9	5.9
polycyclic	26.6	6.1	2.3
Neutral oxygen compounds	3.6	2.7	0.5
High-polar heterocompounds	6.0	1.6	0.5

One can see that with lengthening the time of hydrogenisation and/or with increasing the amount of available hydrogen in autoclave the content of aromatic compounds, neutral oxygen compounds and high-polar compounds significantly decreases while the content of aliphatic compounds significantly increases. Hydrogenate 3 consists mostly of nonaromatic hydrocarbons (90.8 %) and is very poor in neutral oxygen compounds and high-polar hydrocarbons typical for the initial sample (1 and 20.9 %, respectively).

## Conclusion

- The higher the initial pressure of hydrogen on hydrogenation of light mazute, the higher the velocity of decomposition of heteroatomic compounds and the higher the content of hydrocarbons in refined oils obtained.
- Hydrogenation time (hydrogen reserve being sufficient) has only a small effect on the yield of hydrogenation products but influences significantly the composition of refined oil.
- Similar tendencies for “diesel fraction” and light mazute hydrogenation were noticed, so it seems to be expedient to perform co-hydrogenation of both Estonian shale oil fractions under the same conditions realizing it through one-step hydrogenation of the fraction boiling at 180-320 °C without its distillation into two fractions prior to hydrogenation.

## Acknowledgements

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