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UPGRADING OF ESTONIAN SHALE OIL DISTILLATION FRACTIONS. 6. THE EFFECT OF TIME AND TEMPERATURE ON THE YIELD AND COMPOSITION OF HEAVY MAZUTE HYDROGENATION PRODUCTS

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Hydrogenation of Estonian shale oil heavy mazute fraction boiling over 360 °C and characterized by high content of high-polar and heteroatomic compounds and by low content of aliphatic hydrocarbons was carried out in an autoclave at various conditions to investigate the effect of temperature and time on the yield and composition of products obtained. It was found that lengthening the hydrogenation time leads to higher yields of refined oil, which is characterized by a higher content of nonaromatic hydrocarbons and, as compared with oils obtained at elevated temperatures, by a higher content of undecomposed heteroatomic compounds.

Upgrading of Estonian shale oil heavy mazute fraction boiling over 320 °C at determined hydrogenation conditions was described in [1]. The aim of this work was to investigate the effect of temperature and time on the yield and chemical composition of heavy mazute hydrogenation products.

Experimental

Two series of hydrogenation experiments were carried out in a 0.5 dm^3 autoclave:

1. Hydrogenation at 370, 400 and 420 °C, at the initial pressure of hydrogen 100 at.

2. Consecutive three-step hydrogenation at 80 at, similarly to that described in [2]. Six-hour hydrogenation at 370 °C was carried out, the autoclave was opened after every two hours to take the oil sample for analysis and then recharged with a new quantum of pure hydrogen to continue the hydrogenation for the next two hours.

The analysis scheme of hydrogenated products see in [3].

Results and Discussion

Hydrogenation at Varied Temperatures

The interval of temperatures between 370-420 °C was tested and the curves characterizing the consumption of hydrogen are presented in Fig. 1.

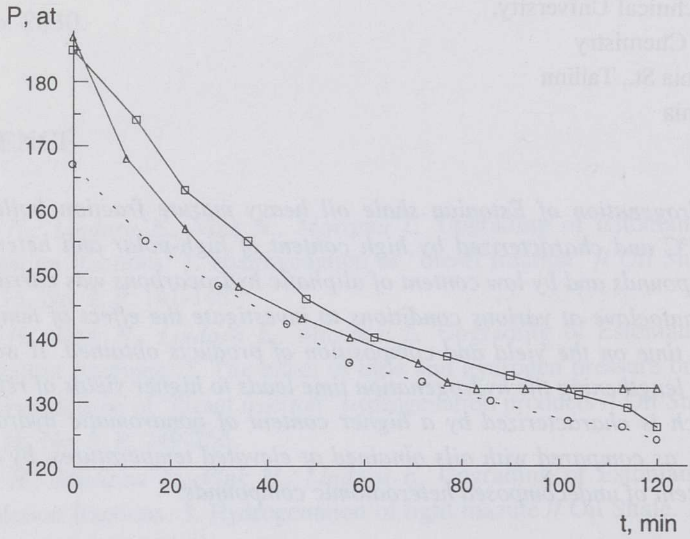

Fig. 1. Changes in the working pressure during heavy mazute hydrogenation at 400°C (□), 420°C (Δ) and 370°C (O); the initial hydrogen pressure 100 at

One can see that the consumption of hydrogen is very intensive during the first hour despite of the temperature used, but the higher the temperature the higher the velocity of hydrogen consumption. At 420 °C and after an 80-min hydrogenation hydrogen consumption practically ceases. There is an alternative to perform hydrogenation either at higher temperature and shorter time or employing lower temperature and longer time. The yields of hydrogenation products obtained at temperatures 370, 400 and 420 °C during two-hour hydrogenation at the initial pressure of hydrogen 100 at are presented in Table 1.

Table 1. **Yields of Heavy Mazute Hydrogenation Products at Varied Temperatures**

Temperature of hydrogenation, °C	The yield of hydrogenation products, wt.%			
	Refined oil	Gas	Water	Coke
370	90.2	4.9	3.6	1.3
400	88.4	5.5	4.2	1.9
420	87.2	7.8	5.1	2.9

One can see that the higher the temperature of hydrogenation the lower the yield of refined oil and the higher the yield of by-products – water, gas and coke. It is obvious that hydrogenation at higher temperatures proceeds deeper, causing elevated formation of gases and residual carbon and decrease in the yield of refined oil and its specific weight. The latter has the following values (kG/m^3): 969 (initial sample), 938 (hydrogenated at 370 °C), 918 (hydrogenated at 400 °C), and 905 (hydrogenated at 420 °C).

The group composition of compounds obtained is presented in Table 2 and these data demonstrate that the higher the temperature of hydrogenation the higher the content of hydrocarbons (particularly of the aromatic ones) and the decomposition degree of heteroatomic and high-polar compounds.

Table 2. **Chemical Composition of Hydrogenated Heavy Mazute**

Compounds	Initial dephenolated heavy mazute	Temperature of hydrogenation, °C		
		370	400	420
Nonaromatic hydrocarbons	10.4	24.0	32.4	33.2
Monocyclic aromatic hydrocarbons	4.3	9.3	23.8	30.0
Polycyclic aromatic hydrocarbons	38.7	36.3	34.2	33.2
Neutral oxygen compounds	22.6	17.8	5.6	1.7
High-polar heterocompounds	24.0	12.6	4.0	1.9

It is obvious that for heavy mazute the temperatures 400 °C and more must be applied to carry out comprehensive hydrocracking to remove most of heteroelements from oil and transform heteroatomic and high-polar compounds into low-boiling hydrocarbons. Hydrogenation at 370 °C results only in a slight decrease in the content of neutral oxygen and high-polar compounds – from 46.6 % in the initial oil down to 30.4 %, while the content of these compounds in oils obtained at 400 and 420°C is 9.6 and 3.6%, respectively.

Consecutive Stepwise Hydrogenation

To investigate the effect of time and activated hydrogen quantum on the yield and composition of hydrogenation products the consecutive three-step hydrogenation of heavy mazute was carried out. Pressure-temperature curves are presented in Fig. 2. One can see that the consumption of hydrogen is very active during the first 2 hours (1st step) continuing less actively during the next 2 hours (2nd step), and practically ending after 0.5 hours of the 3rd step.

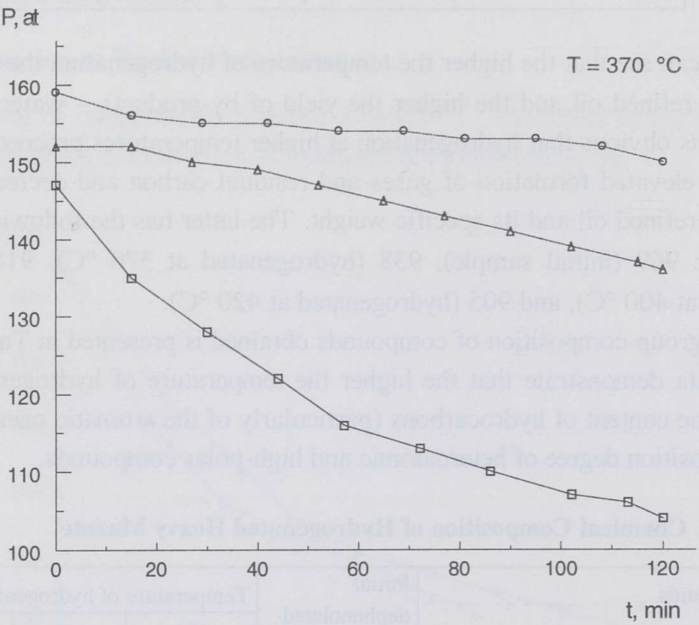

Fig. 2. Changes in the working pressure during three-step hydrogenation of heavy mazute. □ - 1st step of hydrogenation, Δ - 2nd step of hydrogenation, ○ - 3rd step of hydrogenation

The yields of hydrogenation products obtained on consecutive hydrogenation are presented in Table 3. The yield of refined oil is high – 93.9 % and, despite of significant enough consumption of hydrogen, it does not change much during the 2nd and 3rd steps of hydrogenation. Some water, gas and coke were formed during the 2nd step of hydrogenation while only gas (0.9 %) and coke (0.2 %) were formed during the 3rd step of hydrogenation.

The group composition of hydrogenisates (Table 4) shows the following expected regularities: the longer the time of hydrogenation and larger the quantity of available hydrogen the higher the yield of hydrocarbons (particularly nonaromatic ones) obtained and the lower the yield of undecomposed heteroatomic compounds.

Table 3. **Yields of Products Obtained at Consecutive Hydrogenation, wt.%**

Product	Yield, wt.%		
	Hydrogenation 1	Hydrogenation 2	Hydrogenation 3
Refined oil	93.9	98.2	98.9
Gas	2.8	0.6	0.9
Water	1.9	0.5	0.0
Coke	1.4	0.7	0.2

Table 4. **Group Composition of Hydrogenisates Obtained at Consecutive Hydrogenation**

Compounds	Yield, wt.%, at hydrogenation steps		
	1	2	3
Nonaromatic hydrocarbons	21.3	47.9	65.3
Monocyclic aromatic hydrocarbons	6.1	23.4	16.4
Polycyclic aromatic hydrocarbons	47.7	20.0	12.2
Neutral oxygen compounds	10.5	6.5	2.8
High-polar heteroatomic compounds	14.4	2.2	3.3

Conclusions

On heavy mazute hydrogenation at varied conditions the following conclusions can be drawn:

- An increase in the hydrogenation temperature leads to a decrease in refined oil yield and to larger quantities of hydrogenation by-products – gas, water and coke. Oil quality is improved due to a more complete decomposition of the heteroatomic compounds.
- Lengthening the time of hydrogenation from 2 to 6 hours the hydrogen reserve being sufficient has practically no influence on the yield of refined oil, but the longer the time of hydrogenation the higher the content of the hydrocarbons (particularly nonaromatic ones) and the lower the content of undecomposed heteroatomic compounds.
- A higher initial pressure of hydrogen on hydrogenation at constant temperature and time leads to a decrease in refined oil yield but has not significant effect on the refined oil composition.

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