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UPGRADING ESTONIAN SHALE OIL BITUMINOUS FRACTIONS

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Introduction

Hydrogenation is the main technique used in upgrading various bottom distillation and chemical separation fractions usually characterised by elevated content of heteroatomic compounds and by high viscosity.

Hydrocracking and hydropurification methods usually are catalytically activated.

As a result of hydroprocessing the chemical composition and qualities of the syncrude obtained will be moved closer to natural petroleum distillation fractions.

Research background

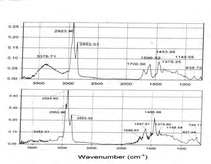
- Kukersite shale oil tail and residuum fractions 360^{0}C+, heavy mazute and thermobitumen were submitted to catalytic hydroprocessing in a batch autoclave
- Modifications occurring in the composition of refined oils were investigated
- It was presumed that differing hydrocracking conditions should be worked out to maximize upgrading of heavy liquid fractions from pyrolysis and thermal dissolution processes

Experimental

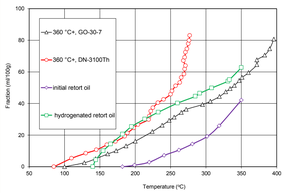
Hydroprocessing was performed in a 500 cm^3 autoclave at the following conditions:

- Weight of the initial substance: 100 g
- Initial hydrogen pressure 5-10 MPa
- Temperature: 340-420 ºC
- Duration: 40-240 minutes
- Catalysts: Shell (DN-3100Th)
  AkzoNobel (KF-848, KF-1015, KC-3210)
  Russia (KGU-950, GO-30-7)
- Solid phase (catalyst and coke formed) was separated from the hydrogenated oil by filtration through a filter paper.
- The filtrate was analized by ultimate analysis, FTIR-spectroscopic, TLC and GC-MS-methods.

FTIR-spectra of the initial TBO (above) and hydrogenated TBO (below) using Interspec FTIR-2020 spectrometer



Boiling curves of the initial and recovered product resulting from hydrogenation of oils



Conclusions

- Investigation of the upgrading possibilities of the heavy shale oil and its high-boiling fractions obtained in Estonian Kukersite oil shale retorting and thermal dissolution has revealed that more than 75% of those can be recovered as liquid fuels (mainly diesel) boiling below 360 °C.
- As a result of hydrodeoxygenation, hydrodesulfurization and hydrodenitrogenation the contents of O, S and N were decreased by 76, 89 and 45%, respectively.
- Hydrocarbon content is multipled in the refined oil obtained that can be observed as synthetic petroleum.
- For maximum upgrading thermobitumen, retorting oil and its heavy fractions differing hydroprocessing conditions should be used.

Yield of products in catalytic hydrogenation, %

Kukersite shale oil/ /Fraction	Obtainable industrial (i) or laboratory (l) yield, % on organic matter basis	Products				Hydrocarbons content	
		Raffi-nate	Coke	Water	Gas	Initial shale oil fraction	Raffinate
Total retorting oil	40 (i)	93.1	0.6	4.2	2.1	39.6	75.5
Dephenolated retorting oil	28.6 (i)	80.2	0.6	3.1	16.1	53.5	78.7
Heavy mazute 320 ºC+	24 (i)	91.1	2.1	3.4	3.4	33.9	75.1
360 ºC+ fraction	20 (i)	90.0	0.7	7.9	1.4	19.2	62.9
Thermobitumen + oil (TBO)	90 (i)	62.4	16.9	8.0	12.7	20.8	41.3

The mean need for hydrogen: 0.2 dm^3/l kg feed at normal conditions.

Elemental composition of oils (wt.%)

Oil sample	C	H	N	O	S	H/C
Total retorting oil	83.0	9.9	0.1	5.9	1.1	1.43
Hydrogenated total retorting oil	84.21	11.8	-	3.51	0.48	1.68
360 ºC+ fraction of retorting oil	84.11	8.16	0.20	6.80	0.73	1.16
Dephenolated 360 ºC+ fraction	83.66	8.42	0.21	7.07	0.64	1.21
Hydrogenated 360ºC+	86.68	9.07	0.21	3.96	0.08	1.26
Heavy mazute	84.0	9.7	-	5.48	0.82	1.37
Dephenolated heavy mazute	84.7	10.0	-	4.72	0.58	1.42
Hydrogenated dephenolated heavy mazute	85.8	11.4	-	2.51	0.29	1.59
TBO	82.6	9.1	0.3	7.7	0.29	1.32

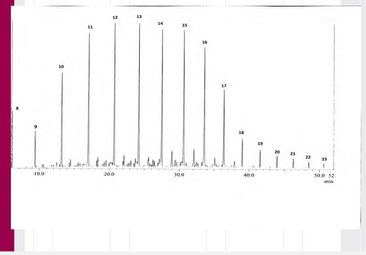
The elemental composition was examined with "Elementar Vario EL" analyzer.

Chemical group composition of initial and hydrogenated oils (%).

Component group	Retort oil		360 ºC+		Dephenolated heavy mazute		TBO	
	Initial	+ H_2 10 MPa, 370 ºC, 2 h, GO-30-7	Initial	+ H_2 7.5 MPa, 400 ºC, 1 h, DN-3100Th	Initial	+ H_2 10 MPa, 370 ºC, 2 h, KGU-950	Initial	+ H_2 3 MPa, 390 ºC, 0.7 h, KF-848
Aliphatic hydrocarbons	11.1	32.7	1.8	16.1	10.4	32.4	4.0	16.4
Monocyclic aromatic hydrocarbons	5.4	1.7	2.9	11.2	4.3	23.8	7.8	9.0
Polycyclic aromatic hydrocarbons	23.1	41.1	14.5	35.6	38.7	34.2	9.0	25.9
Neutral oxygen compounds	16.7	12.5	46.8	24.3	22.6	5.6	1.2	15.8
High-polar heterocompounds	43.7	12.0	34.0	12.8	24.0	4.0	78.0	32.9

Analysis was performed by thin-layer chromatography (TLC)

Distribution of n-alkanes C_8- C_{23} in TBO hydrogenate identified by GC-MS (Shimadzu QP 2010 Plus) apparatus.



Acknowledgement

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