LIQUEFACTION OF OIL SHALE IN SOLVENT MEDIA

HANS LUIK, LEA LUIK, GALINA SHARAYEVA, HELLA RIISALU*

Tallinn University of Technology, Laboratory of Oil Shale and Renewables Research, Ehitajate tee 5, 19086 Tallinn, ESTONIA, *Virumaa College of TUT, Järveküla tee 75, 30322 Kohtla-Järve, ESTONIA

Introduction

Liquefaction of oil shale kerogen can be realised either by pyrolysis in an open system (retorting and fast pyrolysis) or in a closed system (autoclave).
In retort pyrolysis oil is evaporated when its vapour pressure is sufficient for evacuation but in thermal dissolution process total soluble in the solvent product is separated from the solid residue.
As a result of thermobitumenization, the most part of kerogen transforms into solvent soluble thermobitumen and oil (TBO), except for gases and solid residue. The latter consists of mineral part and insoluble in the solvent organic matter (coke).

Research background

- Thermal dissolution of Estonian Kukersite and Dictyonema oil shales in series of solvents in autoclave was studied.
- It was shown that the presence of solvents significantly accelerates liquefaction of both oil shales in temperature region 340-380 °C.
- The yield of TBO formed as a result of thermal dissolution depends strongly on process variables (time, temperature, oil shale-to-solvent ratio) and solvent tested.

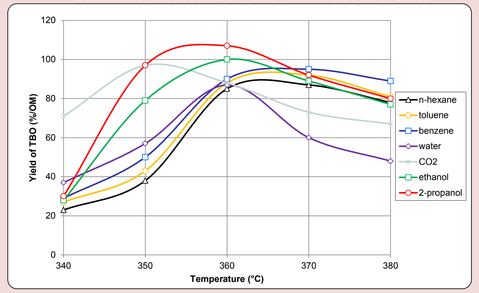
Experimental

- 20-ml micro-autoclaves were used.
- Oil shale sample mass 2 g.
- Solvent mass 6 g.
- The experiments were conducted at 340-380 °C with the residence time 1-10 hours.
- At the end of heating the autoclaves were cooled down to the room temperature, then opened and the amount of gases measured.
- The reaction products remaining in the autoclave were diluted with benzene and TBO was separated from the solid residue by filtration.
- TBO was separated into groups of compounds by preparative thin-layer chromatography.
- The individual compounds were determined by GC-MS.

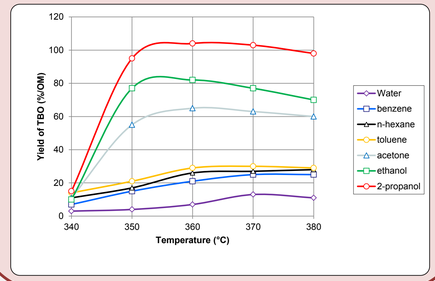
Characterisation of the feed oil shales

Characteristic	Kukersite	Dictyonema
Age	Middle Ordovician	Lower Ordovician
Analytical moisture, W^a	0.6	1.4
Ash (per dry mass), A^d	37.2	81.2
CO_2 of carbonates (per dry mass), $(CO_2)^d$	12.3	2.8
Dry organic matter, OM^d	50.5	16.0
Elemental analysis of organic part:		
C	79.32	73.02
H	9.50	9.19
N + S	0.30	2.66
O	10.88	15.13
Oil yield in Fischer assay, on OM^d basis	65.6	9.8

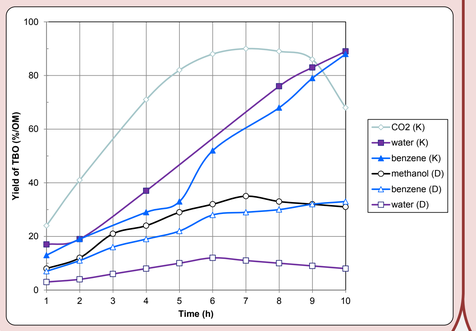
Effect of temperature on the yield of TBO during 4 hours thermal dissolution of the Kukersite oil shale with different solvents



Effect of temperature on the yield of TBO during 4 hours thermal dissolution of the Dictyonema oil shale with different solvents



Effect of time on the yield of TBO in thermal dissolution of Kukersite and Dictyonema oil shales at 340 °C

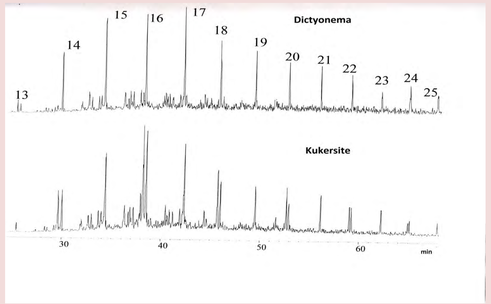


ComparableTBO yields in oil shales thermal dissolution with individual, binary and ternary solvents, %

Solvent	Kukersite	Dictyonema
Benzene	28.7	9.9
Water	35.5	5.1
Carbon dioxide	71.0	6.2
Benzene + water	46.4	7.5
Carbon dioxide + water	75.5	5.8
Benzene + water + carbon dioxide	78.9	8.7

340 °C, 4 h
Solvent weight ratios in binary and ternary systems 1 : 1 and 1 : 1 : 1

n-Alkanes C13-C25 from thermal disssolution with benzene determined by GC-MS (Shimadzu QP 2010 Plus)



Composition of TBO, %

Compound group	TBO	
	Kukersite	Dictyonema
Aliphatic hydrocarbons	6	7
Monoaromatic hydrocarbons	2	3
Polyaromatic hydrocarbons	18	28
Σ HYDROCARBONS	26	38
Neutral heteroatomic compounds	23	25
High polar and acidic compounds	51	37
Σ HETEROATOMIC COMPOUNDS	74	62

Conclusions

- The yield of benzene-soluble product, thermobitumen and oil (TBO) and its chemical composition depend on kerogen chemical composition, thermal dissolution experimental variables and solvent used.
- Maximum yields of TBO obtained from Kukersite and Dictyonema oil shales were 98 and 29% on kerogen bases, respectively, surpassing those in Fischer assay by 1.5-3 times.
- Binary solvents as benzene+water and carbon dioxide+water were demonstrated to accelerate liquefaction of the Kukersite oil shale significantly compared with benzene, water or carbon dioxide individually, whilst ternary solvents as benzene+water+carbon dioxide slightly accelerate Kukersite liquefaction compared with binary solvents.
- Extra-high TBO yields, even surpassing 100% on kerogen basis, can be achieved from both Kukersite and Dictyonema oil shales using alcohols, and ketones, those during thermobitumenization and oil formation decompose and incorporate with their fragments into TBO composition.
- TBO was characterised as slightly decomposed thermobitumen, consisting mainly of asphalthenes and high polar maltenes.

This work was financed by the Estonian Ministry of Education and Research (SF0140028s09), Estonian Research Council (ETF9331) and EU Structural Funds.