International Journal of Environmental Engineering– IJEE
Volume 2 : Issue 1 [ISSN : 2374-1724]
Publication Date: 30 April, 2015

Effect of Different Temperature-Time Combinations in Kerogen Pyrolysis to Thermobitumen and Oil

Galina Sharayeva, Lea Luik, and Hans Luik

Abstract—**Liquefaction of Kukersite and Dictyonema oil shales originating from Baltic deposits and varying by kerogen content and chemical composition were pyrolysed in a Fischer assay with the aim to maximize liquid product yield being determined as a sum of volatiles (oil) and solubles (thermobitumen). The effect of temperature in the range of 320–490 °C during 20 and 60 min residence time on the yield of thermobitumen, oil, gas, solid residue and water was studied. The chemical group and individual composition of the compounds in the liquid product such as aliphatic hydrocarbons, monoaromatic hydrocarbons, polyaromatic hydrocarbons, low-polar heteroatomic compounds and high-polar heteroatomic compounds were estimated by using TLC and GC/MS-methods. Varied temperature-time regimes used in modified Fischer assay analysis yield thermobitumen and oil in different proportions the sum of those being considerably higher compared with standard Fischer assay pyrolysis. Up to 90% of Kukersite kerogen was decomposed to the summary liquid product of thermobitumen and oil at 400 °C, 20 min or 390 °C, 60 min in a Fischer assay.**

Keywords—**modified Fischer assay pyrolysis, kerogen, thermobitumen, shale oil, yield**

Abbreviations

TB_{SS} – thermobitumen recovered as solvent soluble
O_{CV} – oil recovered as condensable volatiles
TBO – recovered as a sum of TB_{SS} and O_{CV}
SR – solid residue
OM – organic matter
FAP – Fischer assay pyrolysis
MFAP – modified Fischer assay pyrolysis
TLC – adsorption thin-layer chromatography
GC/MS – gas chromatography / mass-spectroscopy
AlHC – aliphatic hydrocarbons
MAHC – monoaromatic hydrocarbons
PAHC – polyaromatic hydrocarbons
LPHet – low-polar heteroatomic compounds
HPHet – high-polar heteroatomic compounds

I. Introduction

World reserves of conventional petroleum are finite and the oil shale in its varieties is observed as alternative source for liquid fuels and chemicals. Deposits of oil shale occur in many parts of the world. Oil shales of different deposits differ by kerogen content and chemical composition. Oil shale is commonly known as a sedimentary rock, which contains varied amounts of kerogen bound dispersedly in a mineral matrix. A complex macromolecular structure of the kerogen was formed as a result of its fossilization during hundreds millions of years. Unlike the bitumen in oil sands, the kerogen in oil shale is insoluble in conventional organic solvents [1]. However, the durable steric structure of kerogen can be pyrolytically cracked above 350 °C in special retorts. Fischer assay pyrolysis (FAP) is the standard method for evaluating the potential oil yield of an oil shale [2–4]. Total world resources of shale oil are estimated by Word Energy Council conservatively at 4.8 trillion barrels that surpassing several times the amount of crude petroleum in the world [5]. Fischer assay models industrial retorts. There are two types of retorts in industrial use. Gas heated vertical retort processes produce a large amount of harmful semicoking waste. Horizontal solid heat carrier retorts have a complicated multi-stage technological scheme. [6]. Upon heating oil shale in the retort the kerogen is initially converted to what is termed thermobitumen [7–11]. The latter being not volatile but soluble in usual solvents thermally degrades to shale oil, gas, carbonaceous residue and pyrolytic water, among which shale oil, gas and water leave (vaporize) from the shale particle matrix. Carbonaceous residue remain mixed in with the minerals, forming solid residues called semicoke. Shale oil, gas and solid residue as final products are of secondary origin being formed only after thermal decomposition of the primary thermobitumen as an intermediate.

Yields and compositions depend on pyrolysis processing conditions and diagenetic history of oil shale [12–14]. A range of pyrolysis conditions have been investigated in the pyrolysis of different oil shales to obtain maximum yield of oil. These parametres include pyrolysis temperature, time, heating rate, pyrolysis atmosphere, particle grain size, reactor type and bed geometry [15–19]. Pyrolysis temperature and heating rate were shown to have the most influence on yield and composition of the derived oil [19–22]. The pyrolysis products distribution depends on the abundance, type, distribution and size of both the mineral and organic matter contents [13]. On the basis of pyrolytic behavior of Spanish, Turkish Göynük and US Green River oil shales it was found that pyrolysis reactions can be adsorbed, catalyzed or inhibited by the mineral matrixe present in oil shale [22–28]. In [29] and [30] variations in gas and oil evolution from shales of different

---

Galina Sharayeva

Lea Luik

Hans Luik

Tallinn University of Technology, Department of Polymeric Materials,
Laboratory of Oil Shale and Renewable Research
Estonia

organic contents of various Colorado oil shales were monitored and variations registered. Effect of the pressure on pyrolysis was investigated in [13,31,32] and it was shown that vacuum pyrolysis limits the secondary decomposition reactions while oil yield was reduced as the pressure was increased in Green River oil shale. In [32] and [33] considerable differences were registered in the yields and compositions of shale oil obtained from Turkish Göynük oil shale as a result of slow pyrolysis, flash pyrolysis and extractions with super and subcritical water.

In [1] was implied that there exists an optimal retorting temperature for the maximum yield of liquid oil. The review above shows that Fischer assay yields and compositions can be modified by varying standard regime of pyrolysis. In [34–36] the modified Fischer assay pyrolysis was used for evaluating the potential liquid fuel. In [37] modified Fischer is represented as a quick and simple screening method requiring only 100 mg of sample. The same was noticed in modified Gray-King assay method (the same as Fischer but operating with 10 g of shale per assay only [38]. In [23] three kerogen types were pyrolyzed by material balance modified Fischer assay.

The yield of shale oil determined as volatiles in Fischer assay standard pyrolysis is always much lower than that of non-volatile but soluble high-molecular thermobitumen.

The goal of this work is to maximize the liquid product yield separated as a sum of volatiles and solubles from two different kerogens by modifying temperature-time conditions in Fischer assay pyrolysis.

II. Material and methods

Kukersite and Dictyonema oil shales characterized in Table 1 were crushed to less than 1 mm and homogenized for use in the Fischer assay.

TABLE I. CHARACTERISATION OF THE INITIAL OIL SHALES

Characteristic	Kukersite	Dictyonema
Age	Middle Ordovician	Lower Ordovician
Analytical moisture, W^a	0.6	1.4
Ash (per dry mass), A^d	49.5	81.2
CO_2 of carbonates (per dry mass), $(CO_2)^d$	18.2	2.8
Dry organic matter OM^d	32.3	16.0
Elemental analysis of organic part:		
C	79.32	73.02
H	9.50	9.19
N + S	0.30	2.66
O (by difference)	10.88	15.13

The samples were submitted to the pyrolysis in a Fischer assay following standard and modified regimes. Fischer assay pyrolysis (FAP) in standard conditions followed ISO 647-74: heating 50 g of oil shale in aluminium retort up to 525 °C during 90 min. Modified Fischer assay pyrolysis (MFAP) was conducted at varied temperatures in-between 320–525 °C with residence times 20 and 60 min.

As a result of pyrolysis series solvent soluble thermobitumen (TB_{SS}), oil as condensable volatiles (O_{CV}), solid residue (SR), non-condensable gas and water were quantitatively yielded. Upon cooling of the volatile matter, condensable material was collected in a round-bottomed flask. The condensate contained all the O_{CV} as well as water. The water fraction was removed by azeotropic distilliation using Dean and Stark distillation method with the use of toluene as solvent [39]. Condensable distillate at a given temperature and solubles in benzene-methanol mixture from Fischer assay dry distillation residue as O_{CV} and TB_{SS} were summarized and calculated as total liquid product (TBO).

Chemical group composition of TBO was estimated by adsorption thin-layer chromatography (TLC). For this aim, 0.5 g of the sample was taken and fractionated on the 2 mm silica gel (Fluka, 60 µm) layer on a plate 24x24 cm. n-Hexane as eluting solvent was used. The following fractions of hydrocarbons and heteroatomic compounds were separated: aliphatic hydrocarbons (AlHC), monoaromatic hydrocarbons (MAHC), polyaromatic hydrocarbons (PAHC), low-polar heteroatomic compounds (LPHet) and high-polar heteroatomic compounds (HPHet). The fractions were weighted after desorption with diethyl ether and desiccation.

The individual composition of TLC fractions was determined by GC-MS-analysis (Shimadzu QP 2010 Plus) using 30 m capillary columns ZB-5 and HP-5MS.

III. Results and discussion

As a result of conventional FAP O_{CV} in yields 65.6 and 9.8% on OM bases from Kukersite and Dictyonema oil shales, respectively, were produced as condensable volatiles. The yield of TB_{SS} separated as solubles in benzene-ethanol mixture was negligible. Recoverable O_{CV} and TB_{SS} yields as well as those of SR, gas and water obtained from both kerogens as a result of MFAP at constant residence time (20 or 60 min) and varied temperatures are represented in Fig. 1.

In the Fig. 1 one can see common features and dissimilarities between two oil shales mentioned above. The former ones are visible in SR and gas yields while the latter ones in the yields of TBO liquids. With increasing the temperature the yield of SR proportionally decreases and that of gas increases up to twice. Exception is Kukersite MFAP during 60 min where gas yield practically was not changed with temperature rise from 370 to 410 °C. Concerning regularities of TB_{SS}, O_{CV} and water formation one can notice significant differences.

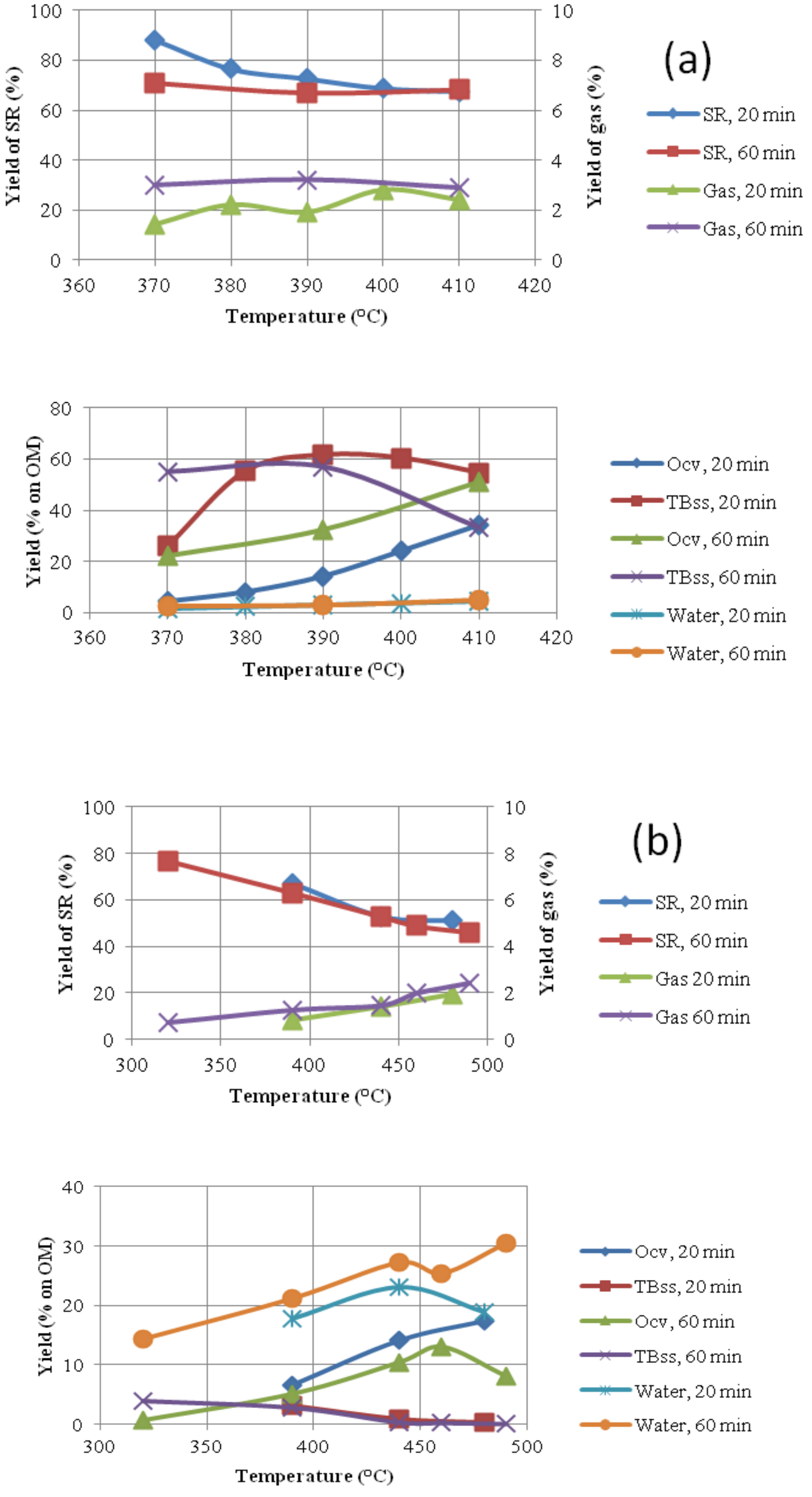

Figure 1. Yield of pyrolysis products from Kukersite (a) and Dictyonema (b) oil shales *versus* temperature.

Kukersite curves demonstrate that TB_{SS} yield abruptly increases from 25.9 to 54.7% with temperature increasing from 370 to 390 °C and then decreases with further increase of the temperature up to 410 °C (20 min). When the residence time was prolonged to 60 min, the yield of TB_{SS} was almost the same (55–57%) in the range 370–390 °C but abruptly decreases down to 33.4% with temperature reaching to 410 °C. The tendency of O_{CV} and gas formation as a result of TB_{SS} decomposition leading to decrease of TBO is observable with increasing the temperature.

Regularities of TB_{SS} formation from Dictyonema oil shale at residence times 20 and 60 min are described similarly. TB_{SS} maximum has been formed below 350 °C and at 450 °C all the TB_{SS} is decomposed to O_{CV}, gas and water. The maximum O_{CV} yield obtained in parallel with the minimum that of TB_{SS} (0.2%) was 17.67% (at 20 min and 480 °C). Dictyonema oil shale pyrolysis was accompanied with significant water formation compared with Kukersite (3–5 and 0.6–1.6% per oil shale, respectively). Water of crystallization in Dictyonema mineral part can have its role in larger water release. Twice lower kerogen content and higher that of mineral matter in Dictyonema oil shale compared with Kukersite led to considerably lower TB_{SS}, O_{CV} and finally to lower TBO as the sum.

Group composition of TBO is displayed in Fig.2 and one can see that it is different for Kukersite and Dictyonema. 60–75% of Kukersite TBO make HPHet. The content of hydrocarbons is low. In the composition of Dictyonema TBO prevail PAHC their yield amounting to 40%. HPHet, dominating in Kukersite TBO make only 20%. Among hydrocarbons PAHC are dominating in Kukersite TBO as well. It seems that the temperature has only small effect on TBO composition. With increasing the temperature slightly decreases the content of HPHet and increases that of hydrocarbons (in Dictyonema case, particularly PAHC content).

The individual composition of TLC fractions analyzed by using GC/MS-methods is represented in the Figures 3 and 4 and Table 2.

One can see that the TBO of Kukersite oil shale differs from that of Dictyonema mainly by the composition of AlHC and LPHet. Kukersite pyrolysis yielded both alkenes and alkanes C_9–C_{19} and alkanones. Longer alkanes (C_{12}–C_{31}), no alkenes and sulfur compounds in parallel to alkanones were produced in pyrolysis of Dictyonema oil shale.

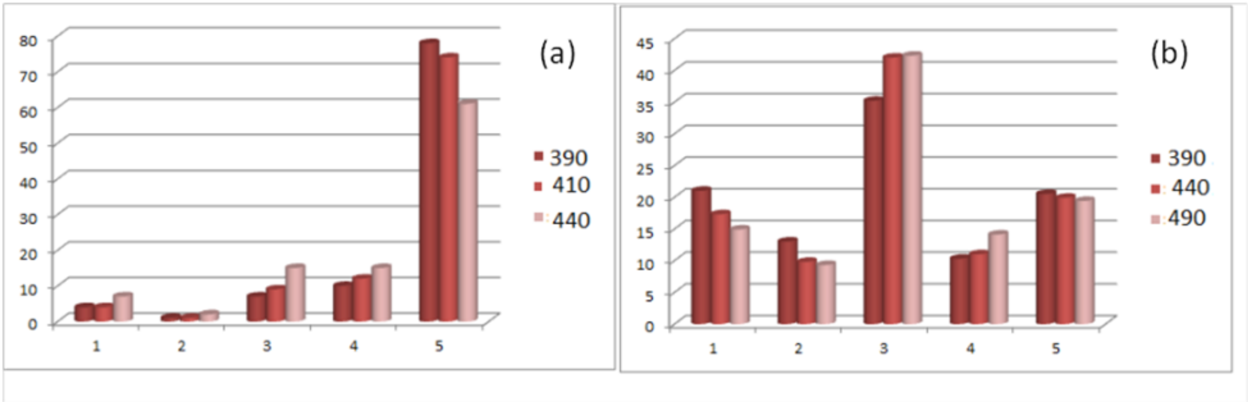

Figure 2. Group composition of TBO of Kukersite (a) and Dictyonema (b) oil shales, %. Fractions separated by TLC as follows: 1 – aliphatic hydrocarbons (AlHC), 2 – monoaromatic hydrocarbons (MAHC), 3 – polyaromatic hydrocarbons (PAHC), 4 – low-polar heteroatomic compounds (LPHet), 5 – high-polar heteroatomic compounds (HPHet).

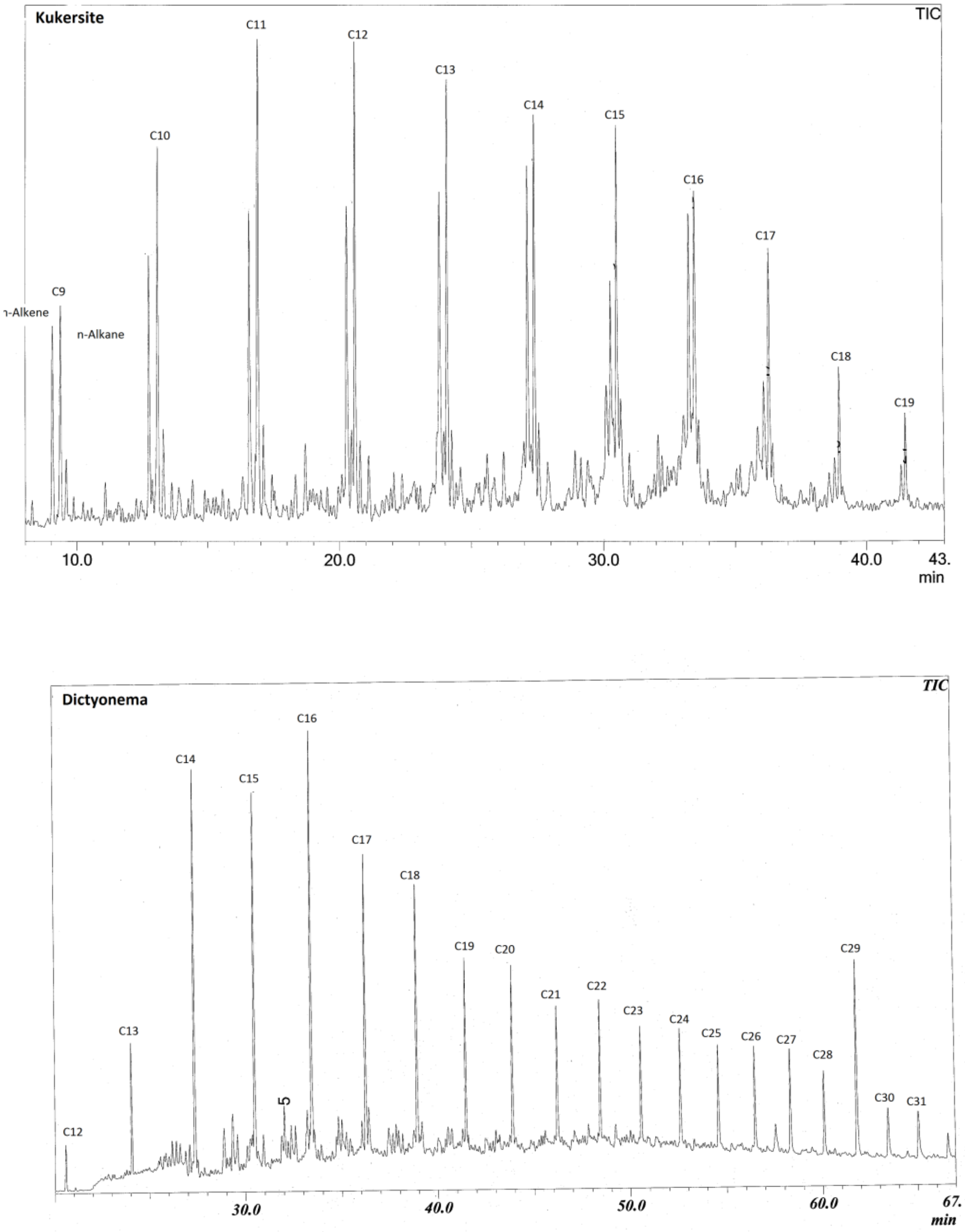

Figure 3. GC-MS-chromatograms of the aliphatic fraction showing the *n*-alkanes distribution in TBO.
The numbers C$_9$–C$_{19}$ above and C$_{12}$–C$_{31}$ below correspond to carbon atoms in the chain of *n*-alkane, shorter peaks in the chromatogram above preceding to the *n*-alkane belong to the respective *n*-alkene.

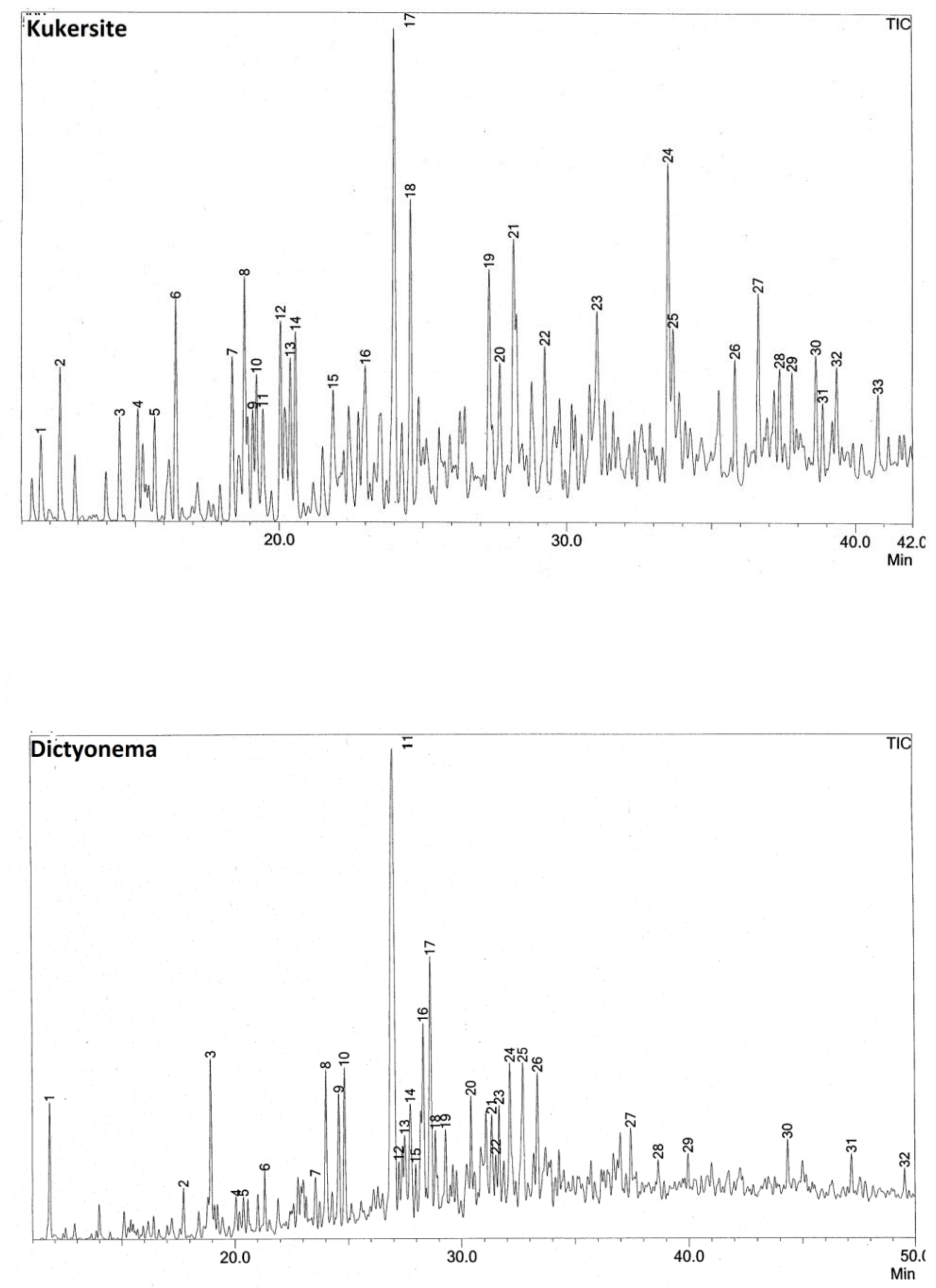

Figure 4. GC-MS-chromatograms of the polyaromatic hydrocarbons and low-polar heteroatomic compounds. The identification of the peaks marked by numbers is shown in Table 2.

TABLE II. COMPOUNDS IDENTIFIED IN TBO FRACTIONS

Peak number	Kukersite	Dictyonema
1	Isopropylbenzene	Benzenethiol
2	o-;m-;p-Ethyltoluene	1,2,3,5-tetramethylbenzene
3	Indane	1-ethyl-3,5-dimethylbenzene
4	Sec-Butylbenzene	Naphtalene
5	o-;m-;p-Propyltoluene	Benzothiophene
6	1-metylindane	Pentamethylbenzene
7	Methylindane, isomere	4,7-dimethylindane
8	Methylindane, isomere	1-methylnaphtalene
9	Pentylbenzene	2-methylnaphtalene
10	Tetralin	Cyclohexylbenzene
11	p-isobutyltoluene	Biphenyl
12	Naphtalene	Dimethylbenzothiophene
13	2-ethylindane	Dimethylnaphtalene
14	Dimethylindane, isomere	Dimethylnaphtalene
15	Etylindane, isomere	Dimethylbenzothiophene
16	Methyltetralin	Dimethylnaphtalene
17	Methyl-Naphtalene, isomere	Diphenylmetane
18	Methyl-Naphtalene, isomere	Dimethylnaphtalene
19	Ethyl-Naphtalene	
20	Dimehtyl-Naphtalene, isomere	1,1-Diphenylethane
21	Dimethyl-Naphtalene, isomere	X,y,z-trimethylnaphtalene
22	Dimethyl-Naphtalene, isomere	X,y,z-trimethylnaphtalene
23		X,y,z-trimethylnaphtalene
24	Allylnaphtalene	
25	Allylnaphtalene	
26		
27	Antracene, phenantrene derivate	1,4,5,8- tetramehylnaphtalene
28	Antracene, phenantrene derivate	Antracene, phenantrene derivate
29		Diphenyldisulphide
30		Triphenylmethane
31		Antracene, phenantrene derivate
32	Pyrene	Antracene, phenantrene derivate
33	Benz(de)antracene derivate	

IV. Conclusions

- The pyrolysis results indicate that high liquid yield can be achieved as the sum of condensable volatiles and solvent soluble with proper process conditions.
- The liquid yield and bitumen-to-oil ratio in it depend strongly on the chemical composition of the initial kerogen and pyrolysis variables in a Fischer assay.
- The maximum liquid yield from Kukersite and Dictyonema oil shales amounted at varied temperature-time regimes to 90.2 and 17.7%, respectively, surpassing those in Fischer assay by 1.4 times.
- Kukersite liquid is rich in high-polar heteroatomic compounds (60–75%) while that of the Dictyonema oil shale is characacterized by as high content as 42% of polyaromatics.
- Varying with pyrolysis temperature and time in Fischer assay it is possible to obtain higher liquefaction degree of kerogen and to modify liquid product chemical composition.

This work was financed by Estonian Research Council (SF 0140028s09, G9331) and EU Structural Funds.

References

[1] J. G. Na, C. H. Im, S. H. Chung, and K. B. Lee, “Effect of oil shale retorting temperature on shale oil yield and properties,” Fuel, vol. 95, pp. 131–135, May 2012.

[2] F. Fischer, The Conversion of Coal into Oil. New York: Van Nostrand, 1925.

[3] ISO 647. Brown Coals and Lignites - Determination of Yields of Tar, Water, Gas and Coke Residue by Low Temperature Distillation, 1st ed., 1974.

[4] P. F. V. Williams, “Oil shales and their analysis,” Fuel, vol. 62, pp. 756–771, July 1983.

[5] World Energy Council, 2010 Survey of Energy Resources, pp. 93–122. http://www.worldenergy.org/documents/ser_2010_report_1.pdf. (accessed 30.07.2014).

[6] M. Niu, S. Wang, X. Han, and X. Jiang, “Yield and characteristics of shale oil from the retorting of oil shale and fine oil-shale ash mixtures,” Appl. Energ., vol. 111, pp. 234–239, November 2013.

[7] F. P. Miknis, T. F. Turner, G. L. Berdan, and P. J. Conn, “Formation of soluble products from thermal decomposition of Colorado and Kentucky oil shales,” Energ. Fuel., vol. 1, pp. 477–483, November 1987.

[8] K. Rajeshwar, “The kinetics of the thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry,” Thermochim. Acta, vol. 45, pp. 253–263, May 1981.

[9] D. S. Thakur, and H. E. Jr. Nuttall, “Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry,” Ind. Eng. Chem. Res., vol. 26, pp. 1351–1356, July 1987.

[10] B. Horsfield, and S. J. Dueppenbecker, “The decomposition of Posidonia shale and Green River shale kerogens using microscale sealed vessel (MSSV) pyrolysis,” J. Anal. Appl. Pyrol., vol. 20, pp. 107–123, July 1991.

[11] J. W. Larsen and K. Kidena, “The sudden release of oil and bitumen from Bakken shale on heating in water,” Energ. Fuel., vol. 16, pp. 1004–1005, June 2002.

[12] A. Ekstrom, C. J. R. Fookes, H. J. Loeh, C. H. Randall, C. Rovere, J. Ellis, and P. T. Crisp, “Chemical and pyrolysis characteristics of two types of oil shale from the Condor deposit in Queensland, Australia,” Fuel, vol. 66, pp. 1133–1138, August 1987.

[13] H. Pakdel, C. Roy, and W. Kalkreuth, “Oil production by vacuum pyrolysis of Canadian oil shales and fate of the biological markers,” Fuel, vol. 78, pp. 365–375, February 1999.

[14] Y. H. Khraisha, N. A. Irqsousi, I. M. Shabig, “Spectroscopic and chromatographic analysis of oil from an oil shale flash pyrolysis unit,” Energ. Convers. Manage., vol. 44, pp. 125–134, January 2003.

[15] P. R. Solomon, R. M. Carangelo, and E. Horn, “The effects of pyrolysis conditions on Israeli oil shale properties,” Fuel, vol. 65, pp. 650–662, May 1986.

[16] H. Bar, R. Ikan, and Z. Aizenshtat, **“**Kinetic study of isothermal oil shale pyrolysis: 2. Evaluation of the organic pyroproducts distribution,” J. Anal. Appl. Pyrol., vol. 10, pp. 167–179, January 1987.

[17] D. Skala, M. Bastić, J. Jovanović, and I. Rahimian, “Pyrolysis of oil shale in a microretorting unit,” Fuel, vol. 72, pp. 829–835, June 1993.

[18] N. Salhi, C. Bennouna, H. Bitar, M. Sergent, and R. P. T. Luu, “An experimental design to optimize pyrolysis conditions of Timahdit (Morocco) oil shale,” Fuel, vol. 75, pp. 633–640, April 1996.

[19] M. Kılıç, A. E. Pütün, B. B. Uzun, and E. Pütün, “Converting of oil shale and biomass into liquid hydrocarbons via pyrolysis,” Energ. Convers. Manage., vol. 78, pp. 461–467, February 2014.

[20] P. T. Williams, and N. Ahmad, “Influence of process conditions on the pyrolysis of Pakistani oil shales**,”** Fuel, vol. 78, pp. 653–662, May 1999.

[21] P. T. Williams, and N. Ahmad, “Investigation of oil-shale pyrolysis processing conditions using thermogravimetric analysis,” Appl. Energ., vol. 66, pp. 113–133, June 2000.

[22] B. Janković, “The kinetic modeling of the non-isothermal pyrolysis of Brazilian oil shale: Application of the Weibull probability mixture model,” J. Petrol. Sci. Eng., vol. 111, pp. 25–36, November 2013.

[23] A. J. Gannon, and D. A. Henstridge, “Pyrolysis stoichiometry for three kerogen types,” Fuel, vol. 66, pp. 350–352, March 1987.

[24] A. G. Borrego, J. G. Prado, E. Fuente, M. D. Guillén, and C. G. Blanco, “Pyrolytic behaviour of Spanish oil shales and their kerogens,” J. Anal. Appl. Pyrol., vol. 56, pp. 1–21, September 2000.

[25] M. Al-Harahsheh, O. Al-Ayed, J. Robinson, S. Kingman, A. Al-Harahsheh, K. Tarawneh, A. Saeid, and R. Barranco, “Effect of demineralization and heating rate on the pyrolysis kinetics of Jordanian oil shales**,”** Fuel Process. Technol., vol. 92, pp. 1805–1811, September 2011.

[26] A. Karabakan, and Y. Yürüm, “Effect of the mineral matrix in the reactions of oil shales: 1. Pyrolysis reactions of Turkish Göynük and US Green River oil shales,” Fuel, vol. 77, pp. 1303–1309, October 1998.

[27] P. T. Williams, and H. M. Chishti, “Influence of residence time and catalyst regeneration on the pyrolysis–zeolite catalysis of oil shale,” J. Anal. Appl. Pyrol., vol. 60, pp. 187–203, August 2001.

[28] M. Sert, L. Ballice, M. Yüksel, and M. Sağlam, “Effect of mineral matter on the isothermal pyrolysis product of Şırnak asphaltite (Turkey),” Fuel, vol. 90, pp. 2767–2772, August 2011.

[29] E. W. Cook, “Green River shale-oil yields: correlation with elemental analysis,” Fuel, vol. 53, pp. 16–20, January 1974.

[30] E. B. Huss, and A. K. Burnham, “Gas evolution during pyrolysis of various Colorado oil shales,” Fuel, vol. 61, pp. 1188–1196, December 1982.

[31] R. D. Noble*, W. F. Tucker, and H. G. Harris, “Isothermal oil shale pyrolysis. 1. Oil generation and composition at various pressures,” Fuel, vol. 61, pp. 482–484, May 1982.

[32] E. M. Suuberg, J. Sherman, and W. D. Lilly, “Product evolution during rapid pyrolysis of Green River Formation oil shale,” Fuel, vol. 66, pp. 1176–1184, September 1987.

[33] J. Yanik, M. Yüksel, M. Sağlam, N. Olukçu, K. Bartle, and B. Frere,*”Characterization of the oil fractions of shale oil obtained by pyrolysis and supercritical water extraction,” Fuel, vol. 74, pp. 46–50, January 1995.

[34] T. T. Coburn, and A. M. Rubel, “Comments on the modified Fischer assay of Eastern oil shales of Kentucky,” Fuel Process. Technol., vol. 8, pp. 1–12, September 1983.

[35] N. V. Dung, “Pyrolysis behaviour of Australian oil shales in a fluidized bed reactor and in a material balance modified Fischer assay retort,” Fuel, vol. 68, pp. 1570–1579, December 1989.

[36] L. Roets, J. R. Bunt, H. W. J. P. Neomagus, and D. van Niekerk, “An evaluation of a new automated duplicate-sample Fischer Assay setup according to ISO/ASTM standards and analysis of the tar fraction,” J. Anal. Appl. Pyrol., vol. 106, pp. 190–196, March 2014.

[37] S. Sato, and A. Matsumura, “Screening method for oil shale samples for Fischer assay,” J. Jpn. Petrol. Inst., vol. 46, pp. 210–213, May 2003.

[38] N. C. Watson, “A modified Gray-King assay method for small oil shale samples,” Fuel, vol. 63, pp. 1455–1458, October 1984.

[39] ISO 1897-2, Phenol, o-Cresol, p-Cresol, Cresolic Acid and Xylenols for Indutrial Use Methods of Test. Part II. Determination of Water - Dean and Stark Method, 1st ed., 1977.