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Low Temperature Pyrolysis of Graptolite Argillite (Dictyonema Shale) in Autoclaves

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ABSTRACT

The results of the systematic experimental study obtained in this work on the effects of temperature (340–420 °C) and exposure time (0–8h) at nominal temperature on the yield of pyrolysis products from Estonian graptolite argillite (GA) generated in autoclaves without any solvent are described. The yields of solid residue (SR), gas, pyrogenetic water (W) and extractable with benzenemix ofthermobitumen and oil (TBO) were estimated. The compound groups of TBO were assessed. The highest yield of TBO, 2.18% on dry GA basis and 13.2% of organic matter (OM) was obtained at temperature of 420 °C and duration 0.5 h. The main compound groups in TBO obtained at 400 ^{o}C are polar hetero-atomic compounds and polycyclic hydrocarbons surpassing 45% and 30% of TBO. The shares of aliphatic and monocyclic hydrocarbons are below 15% of TBO. The yield of W from GA is – about 10-15% of OM. The quantity of OM left in SR after pyrolysis is high, about 65% of OM. The yield of pyrolysis products from GA and the composition of its TBO are compared with those obtained under similar conditions from different oil shales: Estonian Kukersite, US Utah Green River, and Jordanian Attarat.

Keywords-Graptolite argillite, Dictyonema shale, Low temperature pyrolysis, Autoclaves

I. INTRODUCTION

The Lower Ordovician organic-rich marine metalliferous black shale – graptolite argillite (GA) lies beneath most of Northern Estonia. Earlier it was called „Dictyonema shale“, „Dictyonema argillite“ or „alum shale“. Alum shale, as well as graptolite argillite, are distinguished by remarkably high concentrations of trace metals such as U, Mo, V and Ni, but may also be locally enriched with rare earth elements, Cd, Au, Sb, As, Pt [1].

In the study [2] all the published data concerning GA OM elemental composition and its changes during natural and artificial processes by employing vankrevelenogram were cited. The probably elemental composition of native GA OM elucidated from the study [2] is: C 75.7, H 7.8, N 2.3, O 14.2%, atomic ratios H/C 1.24 and O/C 0.16. The calorific value of GA ranges from 4.2 to 6.7 MJ/kg [1].

Pyrolysis of GA was studied in Fischer assay [2-6]. Varied temperature-time regimes used in modified Fischer assay pyrolysis yield thermobitumen and oil in different proportions, the sum of those being considerably higher compared with standard Fischer assay pyrolysis [6]. GA pyrolysis was accompanied with significant water formation (3–5 % per oil shale) whereas water of crystallization in GA mineral part could have its role in larger water release [6].

In our previous works, a systematic experimental study of slow pyrolysis in autoclaves of different shales was conducted, and the kinetics of kerogen decomposition into TBO was calculated for Estonian Kukersite [7], US Green River [8] and Jordanian Attarat[9] oil shales.

Oil yield per unit of OM can vary widely between oil shales from different deposits. On the basis of solvent swelling experiments Oja concluded [10] that oil yield is usually higher for oil shales with organic matter consisting of Type I kerogen than for those with Type II kerogen. Kerogen, which makes up most of oil shale’s organic matter, is a highly cross-linked, organic, macromolecular material [11]. Depending on the oil shale kerogen type, loosening or tightening of the kerogen structure can occur in the temperature region before an active pyrolytic volatilization of oil. Solvent swelling experiments [12] on thermally pretreated oil shales have indicated that the high oil yield kerogen (Type I) of Estonian Kukersite oil shale, which possesses softening pyrolysis behavior, shows a tendency for pre-pyrolysis structural loosening [13]. The characteristic is qualitatively similar to that of high tar yield softening coals. On the other hand, the low oil yield kerogen (Type II) of GA, which possesses non-softening pyrolysis behavior, shows a tendency for pre-pyrolysis structural tightening [14].

The goal of this study was to elucidate conditions for obtaining the maximum yield of liquid product, TBO, from GA and to compare with those from previously studied oil shales (Estonian Kukersite,US Green River and Jordanian Attarat). For this purpose, a systematic experimental study of the effects of temperature and time on the yield of pyrolysis products from GA in autoclaves without any solvent was conducted.

II. EXPERIMENTAL

A. *Characterization of the initial sample*

The conditional OM (weight loss in incineration at 550 °C) of the sample was 16.00%, ash content (weight loss in incineration at 825 °C) 80.80% and moisture 1.38%.

The elemental analysis gave: C 73.02%, H 9.19%, N+S 2.66%, O (by difference) 15.13 of OM. The yields of the pyrolysis products in Fischer assay were as follows: oil 2.96%, semicoke 91.32%, pyrogenetic water 2.61% and gas + losses 3.11% of the dry shale.

B. *Liquefaction procedure*

Pyrolysis of GA was carried out in glass test tubes placed in 58 cm3 autoclaves. In each experiment about 12 g of the air dried GA powdered to 0.04–0.1 mm were used. The samples were placed into a cold muffle oven. The constant nominal temperature varying from 340 to 420 °C was attained for the period of 60 minutes. The pyrolysis duration was measured from the time when the muffle oven reached the nominal temperature prescribed. Efficiency of the liquefaction process was evaluated by the yield of pyrolysis products: gas, total benzene solubles - bitumen, thermobitumen and oil (TBO), solid residue (SR) and pyrogenetic water (W).

C. *Analysis*

The mass of gas formed was determined by the weight loss of glass test tubes with the sample after discharging gaseous products from the open autoclave at room temperature. The liquid products consisting of TBO, W and moisture were extracted exhaustively with boiling benzene in a Soxhlet extractor. The water phase was gathered and weighted as drops on the walls of the test tube, and condenser of Soxhlet extractor after the azeotropic mixture of water and benzene was decomposed. The mass of moisture in the initial samples and SRwere weighted by drying at 105–110 °C during 2 h. The content of OM in SR was measured as weight loss in incineration at 550°Cduring 4 h.The solvents applied were removed from TBO solutions in a vacuum rotation evaporator at 60–70 °C.

The distillation residues of the TBO extracts obtained in the rotation evaporatorwere left in the open flask for evolution of the solvent traces remained. Like in the authors' earlier works, removing traces of benzene from TBO was a problematic procedure. The quantity of TBO can be underestimated due to evaporation of low-boiling destruction products or overestimated when part of the solvent, having a higher boiling temperature than the lighter fractions or being incorporated into destruction products is not removed. So, the mass of TBO was preferred to determine by subtracting the mass of gas, W and SR from the initial mass of the shale.

The compound groups of TBO were estimated by preparative thin-layer chromatography separating 500 mg samples on 24 × 24 cm plates coated with a 2 mm silica gel layer (60 mm, Fluka), and using n-hexane as the eluent. Five groups of compounds were separated and extracted from silica gel with ethyl ether: aliphatic hydrocarbons (AlHC), monocyclic hydrocarbons (MCHC), polycyclic hydrocarbons and some sulfur compounds (PCHC), neutral hetero-atomic (Nhet) and polar hetero-atomic (Phet) compounds.

III. RESULTS AND DISCUSSION

Yields of the pyrolysis products from the dry GA obtained in the test series conducted at various nominal temperatures and isothermal durations are presented in Tables 1 and 2.

The results in Table 1 show that at any temperature series the gas yield increases with time whereas the yield of TBO has a maximum and that of SR a minimum shifting with increasing temperature to shorter durations. The maximum yield of gas achieved is only 2.7%, and the maximum transformation degree of the OM is 7.4% of the dry initial shale.

The better characterization of the process can be obtained when the yields are depicted on the basis of OM. Effect of pyrolysis duration at various nominal temperatures on the yields of the main decomposition products – gas, TBO, W, and SR of OM, are presented in Table 2 and Fig. 1

The experimental data in Table 2, and in Figs. 1 and 2 prove the tendencies in Table 1. The decomposition of OM starts in the heating stage already before the nominal temperature has been achieved. The yields of gas, SR and W change with increasing both nominal temperature and pyrolysis time up to a characteristic steady state whereas the yield of TBO passes a maximum at several optimal combinations of temperature and time. The yields on OM basis achieve close values: for gas about 16%, for TBO 13.2%, and for W 15%. OM in SR after pyrolysis at most expedient pyrolysis conditions can be reduced not lower than to 58 %. Yield of the target product, TBO, obtained using the low-temperature pyrolysis procedure, s.c. TBO-technology, is not good enough.

TABLE 1.Effect of nominal temperature and isothermal duration on the yield of pyrolysis products from GA in autoclaves, % on dry GA basis

Pyrolysis conditions		**Gas**	**W**	**TBO**	**TBO+W**	**OM in SR**	**SR**
Temp. ^{o}C	**Time h**						
340	0.00	0.06	0.05	0.38	0.43	15.98	99.51
340	1.00	0.89	0.82	0.74	1.56	14.02	97.55
340	2.00	1.25	1.81	0.96	2.77	12.44	95.97
340	4.00	1.37	2.30	1.10	3.41	11.70	95.23
340	6.00	1.55	2.37	1.52	3.89	11.02	94.55
340	8.00	1.65	2.23	1.68	3.90	10.92	94.45
360	0.00	0.37	0.05	0.40	0.45	15.65	99.18
360	0.50	0.99	0.65	1.19	1.84	13.64	97.17
360	0.75	1.17	0.96	1.51	2.47	12.83	96.36
360	1.00	1.38	1.26	1.72	2.98	12.11	95.64
360	1.50	1.62	1.64	1.60	3.24	11.60	95.13
360	2.00	1.76	2.08	1.58	3.66	11.05	94.58
360	3.00	1.84	2.34	1.55	3.89	10.74	94.27
360	4.00	1.89	2.44	1.53	3.96	10.61	94.14
360	6.00	1.98	2.50	1.55	3.99	10.44	93.97
380	0.00	0.41	0.13	0.30	0.43	15.63	99.16
380	0.50	1.28	1.46	1.48	2.94	12.26	95.79
380	0.75	1.49	1.83	1.79	3.62	11.36	94.89
380	1.00	1.74	2.00	1.91	3.92	10.81	94.34
380	1.50	1.90	2.25	1.91	4.16	10.41	93.94
380	2.00	1.99	2.31	1.87	4.18	10.30	93.83
380	3.00	2.09	2.44	1.74	4.18	10.21	93.74
380	4.00	2.29	2.47	1.80	4.27	9.91	93.44
380	6.00	2.38	2.49	1.86	4.35	9.74	93.27
400	0.00	0.54	0.20	0.31	0.51	15.42	98.95
400	0.50	1.45	1.63	1.89	3.51	11.50	95.03
400	1.00	2.06	2.08	1.98	4.06	10.36	93.89
400	1.50	2.16	2.22	2.05	4.27	10.04	93.57
400	2.00	2.27	2.42	1.86	4.28	9.93	93.46
400	4.00	2.27	2.40	1.93	4.33	9.87	93.40
420	0.00	0.64	0.36	0.20	0.57	15.26	98.79
420	0.50	1.97	2.18	2.18	4.36	10.14	93.67
420	1.00	2.34	2.42	1.90	4.32	9.81	93.34
420	1.50	2.53	2.49	1.82	4.31	9.63	93.16
420	2.00	2.55	2.55	1.75	4.30	9.61	93.14
420	3.00	2.66	2.56	1.66	4.22	9.59	93.12

TABLE 2. Effect of nominal temperature and isothermal duration on the yield of pyrolysis products from GA in autoclaves, % on OM basis

Pyrolysis conditions		**Gas**	**W**	**TBO**	**TBO+ W**	**OM in SR**	**Conversion degree**
Temp °C	**Time h**						
340	0.00	0.38	0.29	2.31	2.60	97.02	2.98
340	1.00	5.39	5.00	4.50	9.50	85.11	14.89
340	2.00	7.60	11.00	5.84	16.84	75.56	24.44
340	4.00	8.29	13.99	6.71	20.69	71.02	28.98
340	6.00	9.44	14.41	9.22	23.64	66.93	33.07
340	8.00	10.01	13.52	10.18	23.70	66.30	33.70
360	0.00	2.24	0.31	2.45	2.75	95.00	5.00
360	0.50	6.00	3.94	7.22	11.16	82.84	17.16
360	0.75	7.13	5.80	9.18	14.98	77.89	22.11
360	1.00	8.38	7.64	10.47	18.11	73.51	26.49
360	1.50	9.84	9.97	9.73	19.70	70.46	29.54
360	2.00	10.70	12.65	9.58	22.23	67.07	32.93
360	3.00	11.19	14.20	9.39	23.59	65.22	34.78
360	4.00	11.49	14.80	9.26	24.06	64.45	35.55
360	6.00	12.04	15.15	9.40	24.20	63.41	36.59
380	0.00	2.48	0.78	1.82	2.60	94.92	5.08
380	0.50	7.75	8.85	8.99	17.84	74.41	25.59
380	0.75	9.05	11.12	10.87	21.99	68.96	31.04
380	1.00	10.55	12.17	11.63	23.80	65.66	34.34
380	1.50	11.51	13.67	11.60	25.27	63.22	36.78
380	2.00	12.09	14.03	11.33	25.36	62.55	37.45
380	3.00	12.67	14.80	10.57	25.37	61.96	38.04
380	4.00	13.90	14.99	10.96	25.94	60.16	39.84
380	6.00	14.44	15.12	11.32	26.44	59.12	40.88
400	0.00	3.27	1.22	1.86	3.08	93.65	6.35
400	0.50	8.83	9.88	11.45	21.33	69.84	30.16
400	1.00	12.48	12.61	12.02	24.63	62.89	37.11
400	1.50	13.11	13.47	12.45	25.92	60.97	39.03
400	2.00	13.76	14.67	11.30	25.97	60.27	39.73
400	4.00	13.79	14.60	11.70	26.30	59.91	40.09
420	0.00	3.90	2.21	1.24	3.45	92.65	7.35
420	0.50	11.98	13.25	13.21	26.46	61.56	38.44
420	1.00	14.21	14.70	11.55	26.25	59.54	40.46
420	1.50	15.34	15.10	11.08	26.18	58.48	41.52
420	2.00	15.51	15.48	10.65	26.13	58.36	41.64
420	3.00	16.16	15.55	10.08	25.63	58.21	41.79

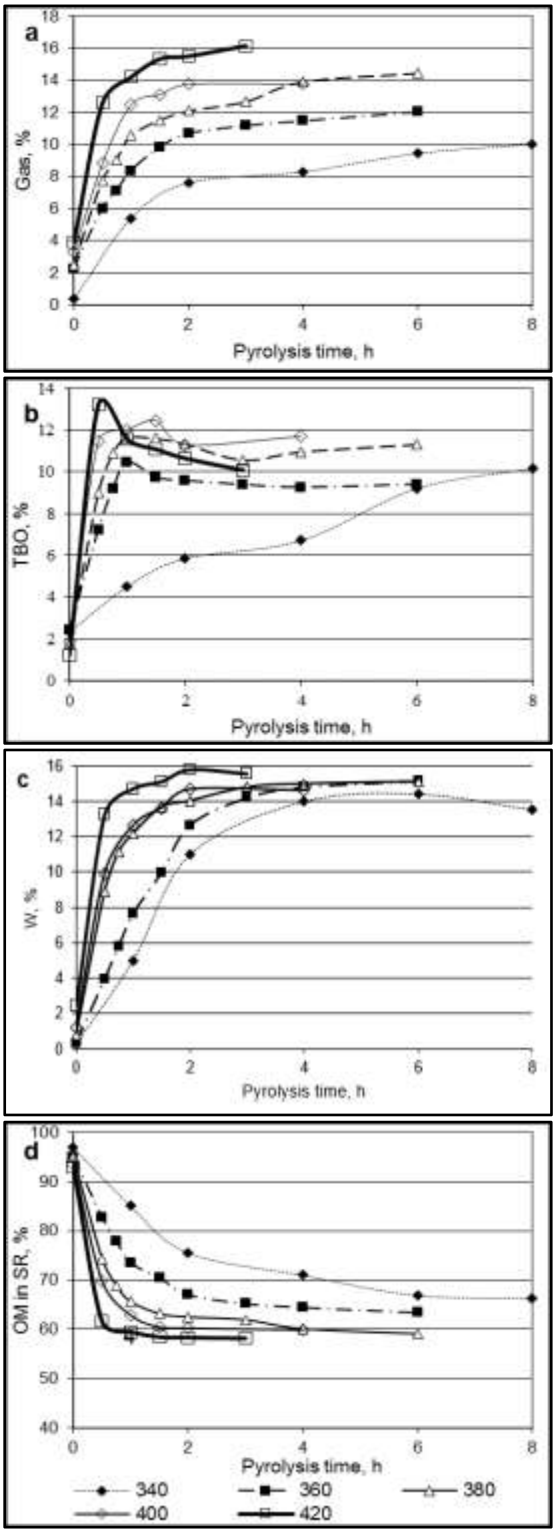

Fig. 1. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of gas (a), TBO (b), pyrogenetic water (c) and solid residue (d), % on OM basis at different pyrolysis temperature: 340, 360, 380, 400, 420°C.

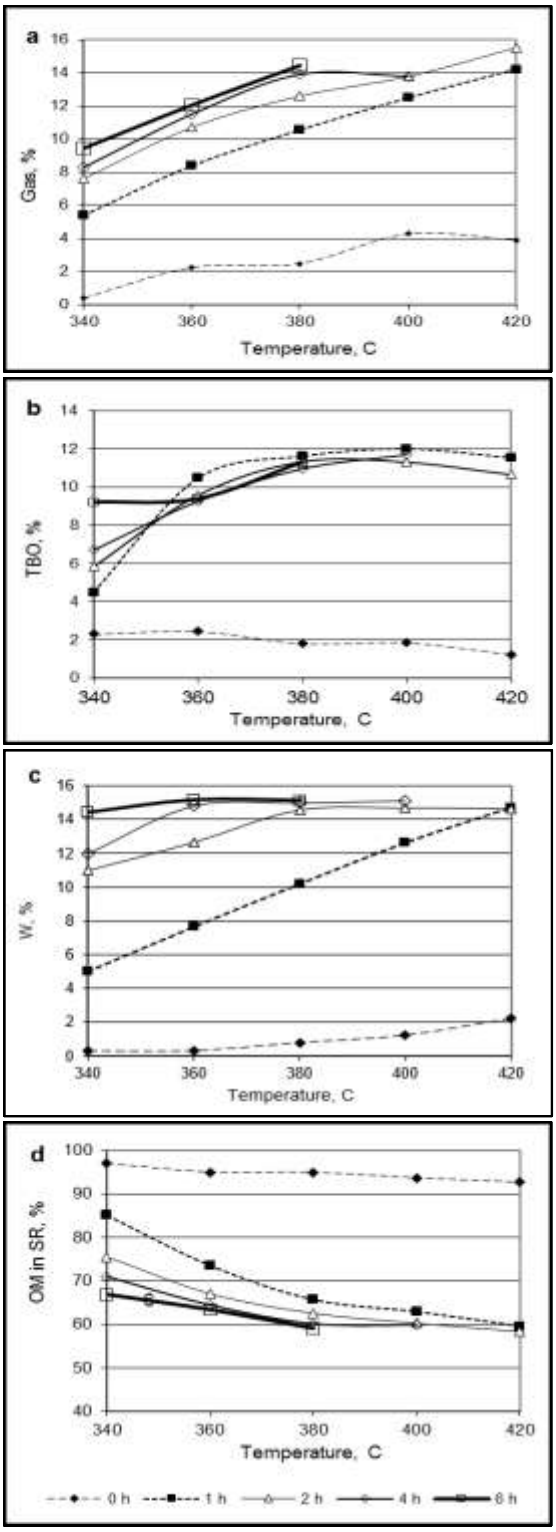

Fig. 2. Effect of nominal temperature in autoclavic pyrolysis on the yield of gas (a), TBO (b), pyrogenetic water (c) and solid residue (d), % on OM basis at different isothermal duration: nominal temperature achieving, 1h, 2h, 4h, 6h.

IV. COMPARISON OF YIELDS AND GROUP COMPOSITIONS OF THE PYROLYSIS PRODUCTS FROM DIFFERENT OIL SHALES

The yields of pyrolysis products from GA obtained in this work for the first time, were compared with our earlier results obtained using the TBO-technology on oil shales from different deposits: Estonian Kukersite (31% OM) [7], US Utah Green River (13.6% OM) [8], and Jordanian Attarat (21.4% OM) [9]. Also, the group composition of their TBO were compared.

The yields of pyrolysis products from the oil shales obtained in autoclaves at the identical conditions are given in Fig. 3.

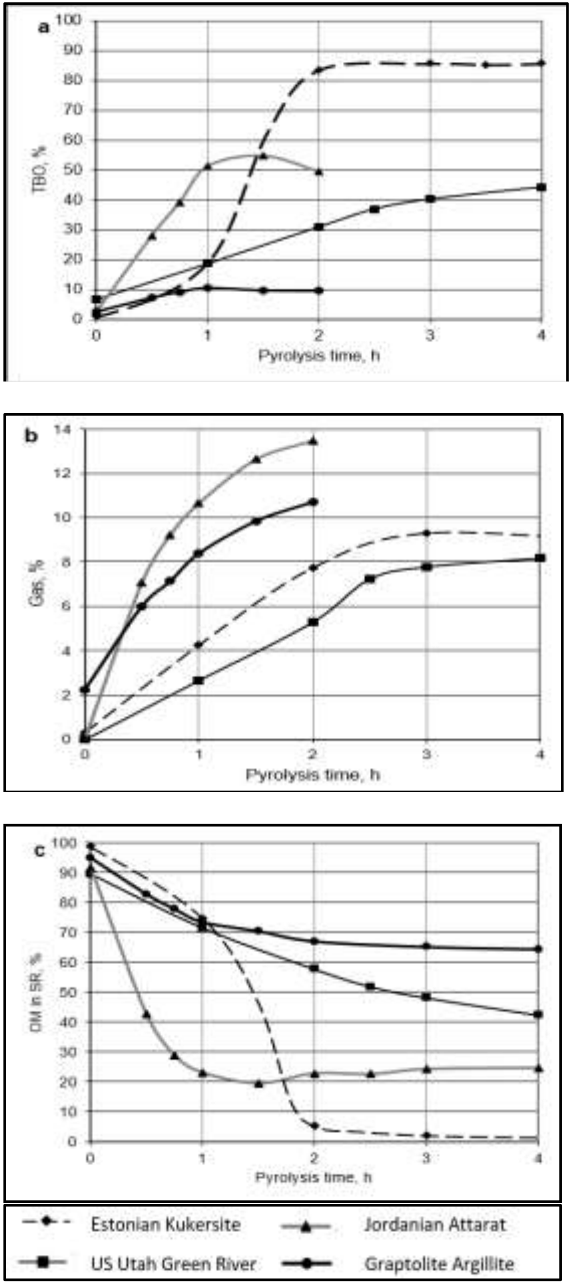

Fig. 3. Comparison yieldsof pyrolysis products (360°C) from different oil shales.

The optimum durations at 360 °C and maximum yields of TBO in their OM basis depicted in Fig. 3a are very different: for Estonian Kukersite about 2 h, 85%, for Jordanian oil shale 1.5 h, 55%, for US Utah Green River 4h and 45%, and for Estonian GA –1h and 10-12% only.At higher temperature the maximum is achieved at shorter time. The angle of inclination gives the possibility to compare the speed of TBO formation. Kinetics of destruction of Estonian Kukersite, US and Jordanian oil shales was described in [7,8,9].

The yield of gas from different oil shales (Fig. 3b) increases steadily with temperature and time increasing. The gas yield is higher for Jordanian oil shale and GA (more than 11-13%) and compared withKukersite and US shales (8-9%).

The pyrolysis time for minimum quantity of OM left in SR after pyrolysis using TBO technology (Fig. 3c) corresponds with the conditions for the maximum yield of TBO. About 65% of OM is left in the residue of GA, 40% of US, and 20-25% of Jordanian oil shale. The organic residue of Kukersite oil shale is 2-5% of OM only.

TABLE 3. Group composition of TBO, % of TBO

Compound group	Estonian		US	Jordanian
	GA 400°C,1.5 h	Kukersite 360°C, 3h	Green River 380°C, 2h	Attarat 380°C, 1h
AlHC	10.5	14.4	24.4	8.2
MCHC	14.3	2.3	5.5	8.4
PCHC	30.5	20.9	11.6	32.9
Nhet	16.2	14.3	10.0	13.2
Phet	28.5	48.1	48.5	37.3

The group composition of TBO obtained at pyrolysis conditions with maximum TBO yield from compared shales is given in Table 3. According to Table 3, the main compound groups in TBO obtained in the slow pyrolysis from GA in an autoclave without any solvent are polycyclic hydrocarbons (about 30%) and polar hetero-atomic compounds making totally 59% of TBO. The quantity of latter is close of that from in Green River oil shale and less than in Jordanian and Kukersite oil shales (69-70%). The yields of desired aliphatic and monocyclic hydrocarbons in TBO of GA is below 25%, what is less than in US shale and exceeding that of Kukersite and Jordanian shales.

V. CONCLUSIONS

A systematic experimental study of the effects of temperature and time on the yield of pyrolysis products from Estonian graptolite argillite (GA) in autoclaves was conducted.

In the low-temperature (340–420 °C) pyrolysis of GA in autoclaves during the exposure time of 0–8 h at nominal temperature, the gas yield increases with time and temperature. In the optimum combinations of temperature and duration the yield of benzene extract, consisting of natural bitumen, a pyrolysis intermediate product thermobitumen and oil (TBO), passes a maximum, and the yield of solid residue (SR) a minimum.

The highest yield of TBO, 2.18% of dry GA and 13.2% of organic matter (OM),was obtained at the temperature of 420 °C and duration 0.5 h. The yields of pyrogenetic water from GA is high – about 10-15% of OM. At optimal pyrolysis conditions not less than 58.5% of OM was left in SR.

The main compound groups in TBO obtained from GA in pyrolysis at 400 °C are polycyclic hydrocarbons (about 30%) and polar hetero-atomic compounds surpassing totally 45% of TBO.

The yield of pyrolysis products from GA and group composition of their TBO were compared with those from different deposits of oil shales (Estonian Kukersite, US Utah Green River, Jordanian Attarat). The share of desired aliphatic and monocyclic hydrocarbons in TBO of GA was below 25%, what is less than in US Green River oil shale and exceeding that of Kukersite and Jordanian shales.

VI. ACKNOWLEDGEMENTS

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REFERENCES

[1] Hade, S., Soesoo, A. Estonian graptolite argillites revisited: A future resource? *Oil Shale* 31 (1), 2014, 4-18.

[2] Veski, R., Palu, V. Investigation of Dictyonema oil shale and its natural and artificial transformation products by a vankrevelenogram. *Oil Shale*, 20(3), 2003, 265–281.

[3] Oil Shale Formations.- Tallinn, 1973 [in Russian]

[4] Lippmaa, E., Maremäe, E. Uranium production from the local Dictyonema shale in North-East Estonia. *Oil Shale*, 17(4), 2000, 387–394.

[5] Siirde, A. Some new data about Dictyonemashale.*Proc. Tallinn Polytech. Inst.* 1956. Vol. A, No. 73. 3-22 [in Russian].

[6] Sharayeva, G.; Luik, H.; Luik, L. (2015). Effect of Different Temperature-Time Combinations in Kerogen Pyrolysis to Thermobitumen and Oil. *International Journal of Environmental Engineering*, 2(1), 174 - 181.

[7] Johannes, I., Tiikma, L., Zaidentsal, A., Comparison of the thermobituminizationkinetics of Baltic oil shale in open retorts and autoclaves. *Oil Shale*, 27, 2010, 17-25.

[8] Johannes, I., Tiikma, L., Luik, H., Sharajeva, G. Thermal extraction of oil from Utah Green River (USA) oil shale in autoclaves. *International Journal of Engineering and Applied Sciences*, 6 (5), 2015, 23-35.

[9] Tiikma, L., Johannes, I., Luik, H., Lepp. A., Sharayeva, G. Extraction of oil from Jordanian Attarat oil shale. *Oil Shale*, 32 (3), 2015, 218–239.

[10] Oja, V. Vaporization parameters of primary pyrolysis oil from kukersite oil shale. *Oil Shale*, 32 (2), 2015, 124–133.

[11] Lille, Ü. Behavior of Estonian kukersite kerogen in molecular mechanical force field. *Oil Shale*, 21(2), 2004, 99–114.

[12] Savest, N., Oja, V., Kaevand, T., Lille, Ü. Interaction of Estonian kukersite with organic solvents: A volumetric swelling and molecular simulation study. *Fuel*, 86(1–2), 2007, 17–21.

[13] Savest, N., Hruljova, J., Oja, V. Characterization of thermally pretreatedkukersite oil shale using the solvent-swelling technique. *Energ. Fuel*, 23(12), 2009, 5972–5977.

[14] Kilk, K., Savest, N., Yanchilin, A., Kellogg, D. S., Oja, V. Solvent swelling of Dictyonema oil shale: Low temperature heat-treatment caused changes in swelling extent. *J. Anal. Appl. Pyrol.*, 89(2), 2010, 261–264.