FORMATION OF DECOMPOSITION PRODUCTS FROM DICTYONEMA SHALE DURING THE LAST STAGES OF SEMICOKING

I. BLYAKHINA
K. UROV

Institute of Chemistry
Tallinn, Estonia

It has been established that maximum oil yield (on kerogen basis) is achieved at 430 °C for Dictyonema shale from Estonia. Further heating improves neither quantity nor quality of the oil obtained, but energy requirements grow noticeably; therefore, it is not desirable to process this shale at higher temperatures. As a result, prospects of co-processing kukersite and Dictyonema shale are not encouraging: the optimum final temperature of heating is different for each of these shales.

In our previous studies, we noted a considerable role for the secondary reactions on the final stages of semicoking (in the temperature region 400-520 °C) when processing two Lower Eocene oil shales from Uzbekistan [1, 2] and Middle Ordovician shale, so-called kukersite, of Estonia [3]. In the present work, Lower Ordovician Dictyonema shale of Estonia has been investigated for the same effect. Though deposits of kukersite and Dictyonema shale are next to each other, even overlapping partially, their age also being close, these shales are formed in rather different conditions and represent two extremes as to their characteristics [4, 5]. Therefore it seemed justified to look more closely into the thermal processing of this shale in similar conditions to those used in the afore-mentioned shale research.

The proximate analysis of the investigated shale was as follows (wt.-%): analytical moisture 1.3, ash A^d 83.8, mineral carbon dioxide $(CO_2)^a$ - absent, organic matter OM^d (OM^d = 100 - A^d) 16.2, total sulfur S^d_t 3.3. The ultimate analysis of kerogen was as follows (wt.-%): C 61.8, H 6.8, atomic H/C ratio 1.32. Considering low hydrogen content and H/C ratio in kerogen of this shale a relatively low yield of oil (on kerogen basis) is anticipated.

Experimental

An electrically heated Fischer retort has been used for stepwise thermolysis experiments. The shale was heated at the rate of 5 °C/min up to the final temperatures of 400, 430, 460, 490 and 520 °C and then isothermally for 20 minutes. The oils obtained were dephenolized by a 10 % aqueous solution of potassium hydroxide. The phenol-free oils were subsequently separated into individual chemical compounds by thin layer chromatography (TLC) on silica gel with *n*-hexane as an eluent. Oil fractions and gaseous products were analyzed by gas chromatography. A Specord 75IR1 spectrometer has been used for obtaining infrared spectra.

Results and Discussion

Data on the yield of thermal decomposition products are given in Table 1. Based on the data for chemical composition of the produced oils (Table 2) and gaseous products (Table 3), the yield of principal products and their components are calculated on organic matter basis (Fig. 1).

Table 1. **Yield of Thermolysis Products (wt.-%)**

Product	Final temperature of heating (°C)				
	400	430	460	490	520
Dry shale basis:					
Shale oil	2.4	3.6	3.3	3.7	3.6
Pyrolytic water	0.8	1.1	1.6	1.3	1.3
Solid residue	94.2	93.6	93.3	91.5	90.8
Gas and losses					
(by difference)	2.6	1.7	1.8	3.5	4.3
Kerogen basis:					
Shale oil	14.8	22.2	20.4	22.8	22.2
Pyrolytic water	4.9	6.8	9.9	8.0	8.0
Solid residue	64.2	60.5	58.6	47.5	43.2
Gas and losses					
(by difference)	16.1	10.5	11.1	21.7	26.6

It is evident from the presented data that, unlike the case of the previously investigated shales [1-3], heating of Dictyonema shale up to the final temperature of only 430 °C results in a maximum oil yield (22 %, organic matter basis), and processing the shale at higher temperatures does not lead to a higher yield of oil. Of course, this cannot be interpreted as an indication that oil generation ceases altogether above 430 °C.

Table 2. **Characteristics of Shale Oils**

Indices	Final temperature of heating (°C)				
	400	430	460	490	520
Density ρ^{20}_{20}	0.9773	0.9646	0.9593	0.9523	0.9381
Sulphur S^T_t, wt.-%	4.6	4.5	4.4	4.1	4.3
Chemical group composition, wt.-%:					
Hydrocarbons:					
Aliphatic and naphthenic	19.6	16.3	16.1	16.1	14.9
Monocyclic aromatic	7.9	6.6	6.1	8.2	6.5
Bi- and polycyclic aromatic	22.6	30.7	32.7	31.5	35.7
Heteroatomic compounds:					
Neutral basic	45.7	42.5	40.6	40.7	39.0
Acidic	4.2	3.9	4.5	3.5	3.9
Concentration ratios:					
Hydrocarbons : heteroatomic compounds	1.004	1.155	1.217	1.262	1.331
Aromatic hydrocompounds : non-aromatic hydrocompounds	1.56	2.29	2.41	2.47	2.83
Aliphatic isoprenoids : n-alkenes (C_{13}-C_{20})	0.287	0.164	0.131	0.149	0.129
Naphthalene : methyl-naphthalenes	0.56	1.12	1.19	1.18	1.12
n-Dipentylketone : n-diheptylketone	0.46	0.60	0.81	0.60	1.53

Oil formation continues into the temperature region 430-520 °C, but at the same time, the processes for its degradation into gas, pyrolytic water and solid residue are intensified to such an extent that oil generation and its decomposition are nearly balanced.

Table 3. **Composition of Thermolysis Gases (vol.-%, air-free basis)**

Compound	Final temperature of heating (°C)				
	400	430	460	490	520
H_2S	16.6	34.5	31.5	32.5	48.6
CO_2	40.5	19.7	16.7	13.5	11.0
CO	11.6	8.5	7.6	7.1	3.5
H_2	8.1	10.6	11.4	12.1	8.2
CH_4	12.2	14.5	16.9	19.5	14.3
C_2H_6	4.7	5.1	7.0	6.4	6.2
C_2H_4	1.5	1.6	2.1	1.6	1.6
C_3H_8	1.8	2.1	2.3	3.1	2.6
C_3H_6	1.8	1.9	2.6	2.3	2.3
C_4H_{10}	0.5	0.9	1.1	1.0	0.9
C_4H_8	0.7	0.6	0.8	0.9	0.8
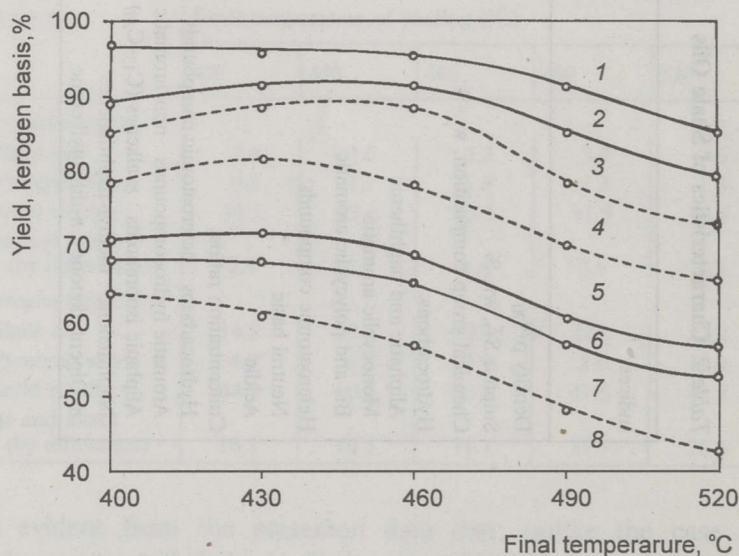
Fig. 1. Formation dynamics of the Dictyonema shale thermolysis products on the final stages of semicoking: *1-3* - gas (*1* - H_2S, *2* - CO_2 + CO, *3* - hydrocarbons); *4* - pyrolytic water; *5-7* - shale oil (*5* - hetero-atomic compounds, *6* - non-aromatic hydrocarbons, *7* - aromatic hydrocarbons); *8* - non-volatile residue

At the same time, typical alterations are taking place in the chemical composition of oils. An increase in the final temperature of heating leads to a decrease in the content of thermally-unstable heteroatomic compounds and non-aromatic hydrocarbons but there is an increase in aromatic hydrocarbons (Table 2). This is in keeping with a presumed important role for secondary cracking reactions at higher temperatures.
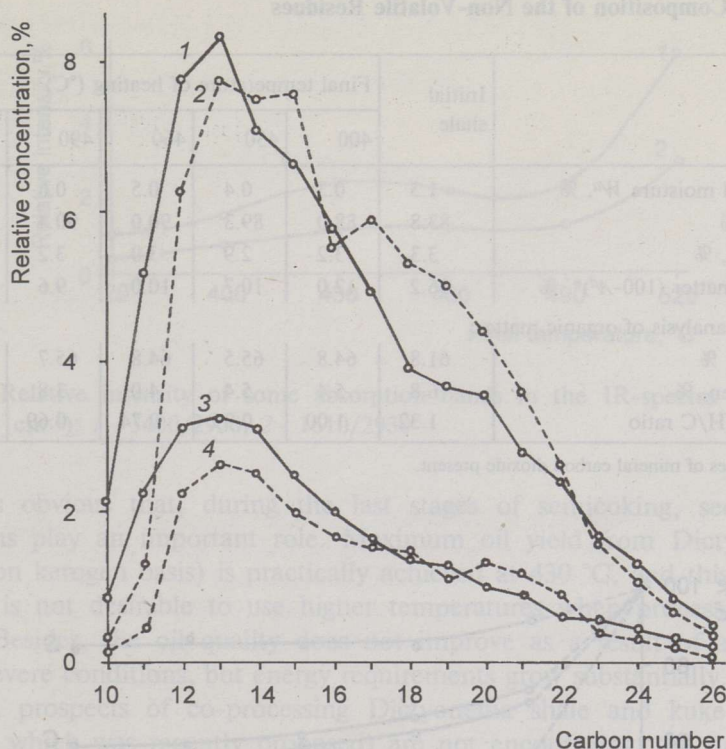

Fig. 2. Distribution of the shale oils aliphatic hydrocarbons according to the chain length in the TLC fractions: *1* and *2* - *n*-alkanes; *3* and *4* - *n*-1-alkenes; *1* and *3* - 520 °C; *2* and *4* - 400 °C

At the same time, more low-boiling products are formed during the last stages of semicoking (Table 2; Fig. 2). Thus, the concentration ratios "*n*-dipentylketone (C_{11}) : *n*-diheptylketone (C_{15})" and "naphthalene : : methylnaphthalenes" have a tendency to grow with increases in the final temperature of treatment. It is also typical that the ratio of isoprenoic and straight chain hydrocarbons drops at higher temperatures the former being thermally less stable.

Of all the decomposition products, only the yield of gaseous compounds increases above 460 °C (from 11.1 %, kerogen basis, at 460 °C to 26.6 % at 520 °C), and that is primarily a result of the occurrence of hydrogen sulfide (Table 3; Fig. 1). Earlier we suggested that hydrogen

sulfide is generated at the expense of pyritic sulfur during the thermal processing of oil shale. That is is a result of pyrite interaction with the kerogen decomposition products, including water [2]. Indeed, the pyrolytic water yield (on organic matter basis) drops from 9.9 % at the final temperature of 460 °C to 8.0 % at 520 °C (Table 1).

Table 4. **Composition of the Non-Volatile Residues**

Indices	Initial shale	Final temperature of heating (°C)				
		400	430	460	490	520
Analytical moisture W^a, %	1.3	0.3	0.4	0.5	0.6	0.7
Ash A^d, %	83.8	88.0	89.3	90.0	90.4	91.0
Sulfur S^d_t, %	3.3	3.2	2.9	3.0	3.2	3.0
Organic matter $(100-A^d)^*$, %	16.2	12.0	10.7	10.0	9.6	9.0
Ultimate analysis of organic matter:						
Carbon, %	61.8	64.8	65.5	64.8	65.7	71.4
Hydrogen, %	6.8	5.4	5.4	4.0	3.8	3.4
Atomic H/C ratio	1.32	1.00	0.99	0.74	0.69	0.57

* Only traces of mineral carbon dioxide present.
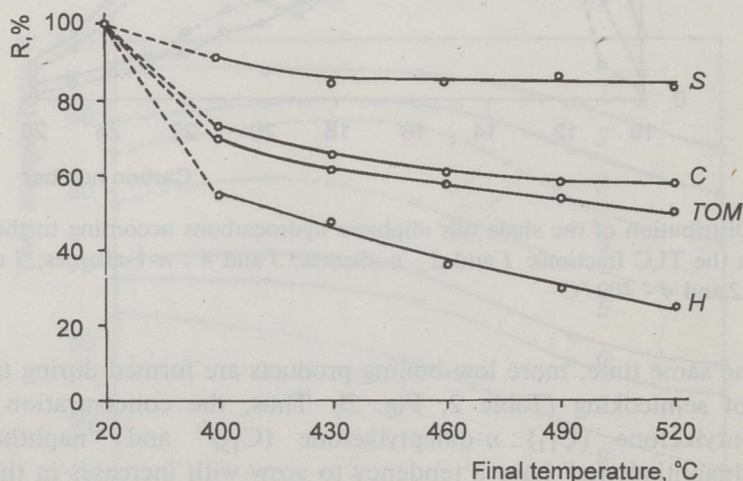
Fig. 3. Content of sulfur, organic carbon, total organic matter (TOM) and organic hydrogen in the non-volatile residues, % of their content in the initial shale (R)

As to the solid residues of the shale processing, their atomic ratio of H/C steadily decreases with increasing the temperature of treatment (Table 4), primarily at the expense of hydrogen (Fig. 3). Aromaticity of

organic residue (relative intensity of the bands at 1610 and 2930 cm⁻¹ in the infrared spectra) starts to grow substantially only at the temperature of 490 °C (Fig 4). It is interesting to note that in the same region a remarkable rise is observed for the intensity of the 3400 cm⁻¹ band. That may be connected with formation of phenolic hydroxyl groups from other oxygen containing structures, for example, ether bridges.
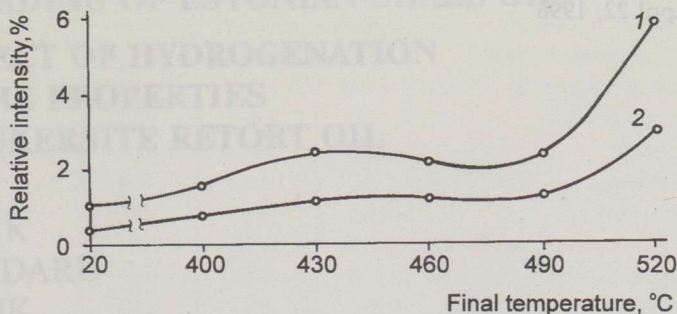

Fig. 4. Relative intensity of some absorption bands in the IR-spectra of solid residues (cm⁻¹): *1* - 3400/2930; *2* - 1610/2930

It is obvious that, during the last stages of semicoking, secondary reactions play an important role. Maximum oil yield from Dictyonema shale (on kerogen basis) is practically achieved at 430 °C, and this means that it is not desirable to use higher temperatures when processing this shale. Besides, the oil quality does not improve as a result of applying more severe conditions, but energy requirements grow substantially. In this respect, prospects of co-processing Dictyonema shale and kukersite (a process which was recently proposed) are not encouraging: the optimum final temperature of heating is quite different for these individual shales.

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