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THERMAL DECOMPOSITION OF OIL SHALES IN THE TEMPERATURE REGION 520-800 °C

I. BLYAKHINA
K. UROV

Tallinn Technical University,
Institute of Chemistry
15 Akadeemia Rd., Tallinn
12618 Estonia

In this work the temperature range for stepwise thermal decomposition of kukersite and Dictyonema shale has been extended to 800 °C for elucidating the nature of secondary reactions taking place during the last stages of pyrolysis. It has been established that in the temperature region of 520 – 800 °C the shale oil yield, organic matter basis, decreases and oil quality does not improve. Gas yield is higher mainly on account of CO₂ and H₂S. Considering also the growth of energy requirements for heating a shale to higher temperatures, it is not expedient to surpass the optimum processing temperature (430 °C and 460 - 470 °C for Dictyonema shale and kukersite, respectively), even locally.

Introduction

In our previous investigations [1-4] we tried to elucidate the trend and extent of secondary reactions taking place during last stages of semicoking (up to 520 °C) by stepwise thermal decomposition of oil shales (kukersite and Dictyonema shale of Estonia and Dzhami shale of Uzbekistan). In this work we extended the temperature region investigated up to 800 °C that is beyond the semicoking range (up to 500-520 °C) with the aim to specify the nature of secondary reactions occurring at higher temperatures as in the case of industrial processing of shales the actual temperatures often exceed 500 °C.

In [5] data are given on the yield and properties of pyrolysis products obtained from the Kotsebinsk deposit (Russia, Saratov district) oil shale at final temperatures of heating 300, 400 and 500 °C. Stepwise thermal decomposition of Green River oil shale has also been performed in the temperature region 300-500 °C [6].

Experimental

Characteristics of Middle Ordovician kukersite and Lower Ordovician Dictyonema shale used in this work were as follows, %:

- Analytical moisture W^a 1.6 and 1.1
- Ash A^d 33.1 and 83.5
- Mineral carbon dioxide $(CO_2)_M^d$ 5.0 and traces
- Organic matter, dry shale basis $[100 - A^d - (CO_2)_M^d]$, 61.9 and 16.5, respectively.

Thermolysis of the shale was performed in a specially constructed retort, similar to Fischer retort, but made of steel instead of low-melting aluminium. The temperature in the retort was programmed at 5 °C/min to the final level of 520, 610, 670, 725, and 800 °C for kukersite, and 520, 600, 670, 730, and 800 °C for Dictyonema shale followed by isothermal exposure for 20 min.

Acidic compounds (principally phenols) were separated from the shale oil obtained by a 10 % aqueous solution of potassium hydroxide. The dephenolized oils were thereupon separated into chemical group compounds by thin layer chromatography on silica gel with *n*-hexane as eluent. Oil fractions obtained as well as gaseous products were analyzed by gas chromatography using the columns of different polarity.

Results and Discussion

Data on the yield of pyrolysis products, dry shale (Table 1) and organic matter (Fig. 1) basis, obtained at the final temperatures used indicate that with surpassing the semicoking region shale oil yield has a tendency to decrease, especially in the case of Dictyonema shale (23.1 % rel.; 2.4 % rel. for kukersite). The same goes for the solid residue organic part, at the same time its carbon content grows but hydrogen content decreases. For the Dictyonema shale organic residue atomic H/C ratio drops from 0.43 at 600 °C to 0.08 at 800 °C. On the contrary, the gas yield increases with the temperature rise (in the region 520-800 °C by 59 and 50 % rel. for kukersite and Dictyonema shale, respectively). According to Campbell et al. [7], the carbon lost by oil as a result of its degradation largely appears as gas (mainly CH₄). The raise in the pyrogenetic water yield can be stated only for Dictyonema shale.

All above-mentioned is in keeping with intensification of secondary cracking reactions at higher temperatures.

Chemical group composition of the oils produced changes surprisingly little in the temperature region 520-800 °C evidently being determined in the first place by the chemical nature of kerogens (Table 2; Fig. 2). In the case of kukersite the rise in the yield of the neutral oxygen compounds is accompanied by decrease in the yield of phenols and is probably caused by degradation of thermally unstable alkylresorcinols, specific for kukersite oil, into neutral products.

Table 1. Dependence of the Yield of Thermolysis Products (Dry Shale Basis) on the Final Temperature of Processing, wt. %

Product	Kukersite					Dictyonema						
	Final temperature, °C											
	520	610	670	725	770	800	800	520	600	670	730	800
	Sample number											
	1	2	3	4	5	6	7	8	9	10	11	
Shale oil	37.0	37.6	37.3	36.4	36.9	36.1	3.9	3.7	2.9	3.2	3.0	
Pyrogenetic water	3.8	2.8	3.0	3.6	3.5	3.6	0.7	1.2	2.1	1.7	1.9	
Solid residue	47.5	45.1	42.7	41.4	41.0	41.7	93.4	92.6	91.4	91.5	91.1	
Gas and losses (by difference)	11.7	14.5	17.0	18.6	18.6	18.6	2.0	2.5	3.6	3.6	4.0	

Table 2. Chemical Group Composition of the Oils Obtained, wt. %

Group of compounds	Kukersite					Dictyonema						
	Sample number according to Table 1											
	1	2	3	4	5	6	7	8	9	10	11	
Hydrocarbons:												
Aliphatic and naphthenic	16.5	15.0	16.5	15.8	17.0	14.9	24.3	26.6	23.2	19.8	17.4	
Aromatic	25.4	27.4	27.3	27.5	26.9	28.1	37.0	36.3	37.0	37.0	38.4	
Heteroatomic compounds:												
Neutral and basic	45.1	45.3	44.4	44.5	44.7	49.7	33.0	30.1	32.1	30.9	32.1	
Acidic	13.0	12.3	11.8	12.2	11.4	7.3	5.7	7.0	7.7	12.3	12.1	

Table 3. Composition of Pyrolysis Gases (Air-Free Basis), vol. %

Compound	Kukersite											Dictionema										
	Sample number according to Table 1											Sample number according to Table 1										
	1	2	3	4	5	6	7	8	9	10	11	1	2	3	4	5	6	7	8	9	10	11
CO ₂	23.6	27.1	31.5	37.0	40.0	39.2	2.1	13.0	16.6	16.2	15.1	23.6	27.1	31.5	37.0	40.0	39.2	2.1	13.0	16.6	16.2	15.1
CO	8.3	12.2	11.8	13.3	12.6	14.8	2.8	4.3	3.7	2.7	6.7	8.3	12.2	11.8	13.3	12.6	14.8	2.8	4.3	3.7	2.7	6.7
H ₂ S	20.1	15.4	12.7	11.7	11.9	9.9	62.0	43.8	42.3	49.0	36.1	20.1	15.4	12.7	11.7	11.9	9.9	62.0	43.8	42.3	49.0	36.1
H ₂	4.6	5.0	6.9	6.7	6.1	7.3	5.3	10.3	11.1	8.4	12.1	4.6	5.0	6.9	6.7	6.1	7.3	5.3	10.3	11.1	8.4	12.1
CH ₄	19.6	17.8	17.9	15.1	12.6	15.3	8.9	14.3	15.8	13.5	23.3	19.6	17.8	17.9	15.1	12.6	15.3	8.9	14.3	15.8	13.5	23.3
C ₂ H ₆	8.6	8.6	6.9	5.8	5.6	5.2	8.2	5.0	4.6	4.5	3.0	8.6	8.6	6.9	5.8	5.6	5.2	8.2	5.0	4.6	4.5	3.0
C ₂ H ₄	2.7	2.2	2.6	1.4	1.5	1.2	2.3	3.7	1.3	1.2	0.5	2.7	2.2	2.6	1.4	1.5	1.2	2.3	3.7	1.3	1.2	0.5
C ₃ H ₈	3.8	3.6	2.8	2.7	2.8	2.3	2.9	1.8	1.6	1.5	1.2	3.8	3.6	2.8	2.7	2.8	2.3	2.9	1.8	1.6	1.5	1.2
C ₃ H ₆	4.4	3.5	3.0	2.5	2.8	2.0	2.9	1.9	1.6	1.5	1.0	4.4	3.5	3.0	2.5	2.8	2.0	2.9	1.9	1.6	1.5	1.0
C ₄ H ₁₀	1.5	1.6	1.5	1.3	1.5	0.9	1.0	0.7	0.6	0.6	0.4	1.5	1.6	1.5	1.3	1.5	0.9	1.0	0.7	0.6	0.6	0.4
C ₄ H ₈	1.3	1.5	1.0	1.1	1.1	0.8	1.0	0.7	0.5	0.5	0.3	1.3	1.5	1.0	1.1	1.1	0.8	1.0	0.7	0.5	0.5	0.3
C ₅ H ₁₂	1.0	0.9	0.8	0.9	0.9	0.6	0.4	0.3	0.2	0.3	0.2	1.0	0.9	0.8	0.9	0.9	0.6	0.4	0.3	0.2	0.3	0.2
C ₅ H ₁₀	0.5	0.6	0.6	0.5	0.6	0.5	0.2	0.2	0.1	0.1	0.1	0.5	0.6	0.6	0.5	0.6	0.5	0.2	0.2	0.1	0.1	0.1

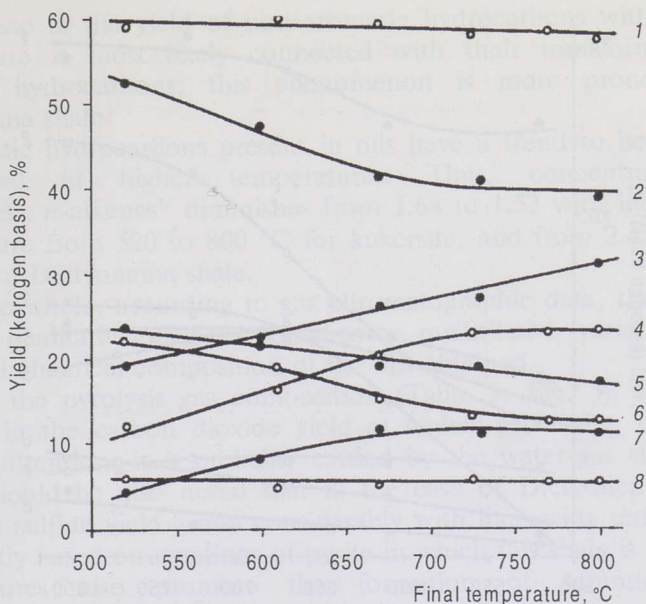


Fig. 1. Dependence of the yield of thermal decomposition products on the final temperature of processing: 1 and 5 - shale oil; 2 and 6 - organic matter of solid residue; 3 and 4 - gas; 7 and 8 - pyrogenetic water. Oil shales: 1, 4, 6 and 8 - kukersite; 2, 3, 5 and 7 - Dictyonema shale

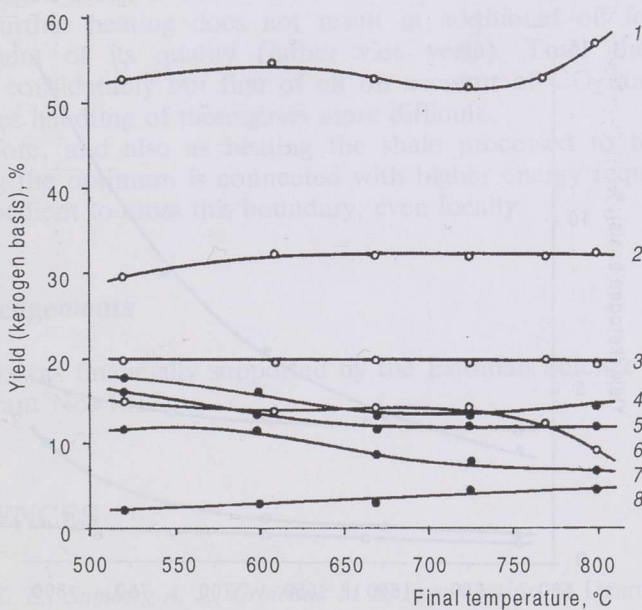


Fig. 2. Influence of the processing final temperature on the yield of the oils chemical group compounds: 1 and 5 - neutral heteroatomic compounds; 2 and 4 - aromatic hydrocarbons; 3 and 7 - nonaromatic compounds; 6 and 8 - phenols. Oil shales: 1, 2, 3 and 6 - kukersite; 4, 5, 7 and 8 - Dictyonema shale

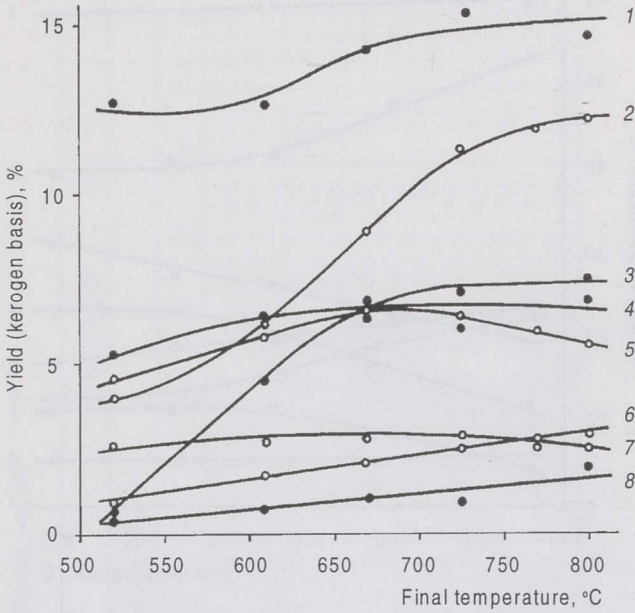


Fig. 3. Dependence of the yield of pyrolysis gaseous compounds (wt.%, kerogen basis) on the final temperature of processing: 1 and 7 - H_2S ; 2 and 3 - CO_2 ; 4 and 5 - hydrocarbons; 6 and 8 - CO . Oil shales: 1, 3, 4 and 8 - Dictyonema shale; 2, 5, 6 and 7 - kukersite

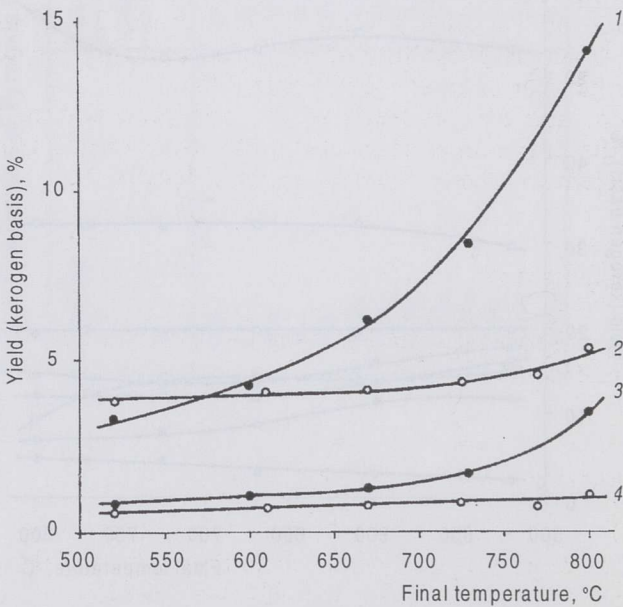


Fig. 4. Characteristics of hydrocarbons present in thermolysis gases: 1 and 2 - volume ratio alkanes : alkenes; 3 and 4 - volume ratio CH_4 : ($\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8 + \text{C}_4\text{H}_{10} + \text{C}_5\text{H}_{12}$). Oil shales: 1 and 3 - Dictyonema shale; 2 and 4 - kukersite

Decrease in the yield of non-aromatic hydrocarbons with increasing temperature is most likely connected with their transformation into aromatic hydrocarbons; this phenomenon is more pronounced for Dictyonema shale.

Aliphatic hydrocarbons present in oils have a trend to become more unsaturated at higher temperatures. Thus, concentration ratio "*n*-alkanes : *n*-alkenes" diminishes from 1.68 to 1.52 with increasing the temperature from 520 to 800 °C for kukersite, and from 2.42 to 2.29 in the case of Dictyonema shale.

On the whole, according to gas chromatographic data, there were no essential qualitative changes, only some quantitative variations in the individual chemical composition of the oils obtained.

As to the pyrolysis gas composition (Table 3; Fig. 3), a substantial increase in the carbon dioxide yield at higher processing temperatures deserves attention; it is probably caused by the water-gas shift reaction [8]. It should be also noted that in the case of Dictyonema shale the hydrogen sulfide yield grows considerably with increasing temperature; it is evidently based on reactions of pyrite in which this shale is rich. Higher temperatures also promote the formation of saturated gaseous hydrocarbons, especially methane (Fig. 4).

Results of this work confirm the assumption that the highest yield of shale oil, organic matter basis, is connected with the semicoking region but not necessarily with its highest temperature (500-520 °C), it is different for various shales. Thus, for Dictyonema shale the maximum oil yield, kerogen basis, is observed at 430 °C, for kukersite at 460-470 °C [3, 4]. Further heating does not result in additional oil formation or improvement of its quality (rather vice versa). True, the gas yield increases considerably but first of all on account of CO₂ and H₂S that only makes handling of these gases more difficult.

Therefore, and also as heating the shale processed to temperatures surpassing the optimum is connected with higher energy requirements, it is not expedient to cross this boundary, even locally.

Acknowledgements

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