Oil Shale, Vol. 15, No. 1
pp. 31-36

ISSN 0208-189X

https://doi.org/10.3176/oil.1998.1.03

DEPENDENCE OF THE YIELD AND COMPOSITION OF SEMICOKING PRODUCTS ON THE MOISTURE CONTENT OF SHALE

V. VYSOTSKAYA
I. BLYAKHINA
K. UROV

Institute of Chemistry
15 Akadeemia St., Tallinn
EE 0026 Estonia

Influence of the initial shale moisture content on the yield and composition of semicoking products has been studied on examples of kukersite and Dictyonema shale of Estonia. It has been established that water does influence the organic matter distribution between semicoking products and their composition. Thus, oil yield (kerogen basis) from the kukersite shale is in the case of the raw material 1.1 % moisture content about 20 % higher than at using absolutely dry shale. Regulation of the moisture content of the initial shale as a handy and cheap means of influencing the thermolysis process is worth special notice.

Introduction

There are some indications as to the connection between the moisture content of processed kukersite and the yield and composition of its semicoking (under normal pressure) products as well as to inadvisability of a too thorough drying of raw material before retorting [1, 2]. It has also been established that when semicoking is carried out in the steam stream the shale oil yield, phenols among this, increases [3-5]. Nevertheless, up to now the problem has not been studied systematically, though a possible regulation of the shale pyrolysis process by such a simple procedure as their moisture content variations is attractive.

Data on heat treatment of solid fossil fuels with water under elevated pressures (in an autoclave) have been presented in numerous investigations [6-11 a. o.].

In this work an attempt has been made to elucidate the influence of the raw material moisture content on the yield and composition of semicoking products on an example of two oil shales of Estonia: Middle Ordovician kukersite and Lower Ordovician Dictyonema shale.

Experimental

Characteristics of kukersite and Dictyonema shale (in parenthesis) used in the work were as follows, %: analytical moisture W^a 1.6 (1.3), ash A^d 32.4 (80.4), mineral carbon dioxide $(CO_2)^d_M$ 5.1 (traces), organic matter [100 - A^d - $(CO_2)^d_M$] 62.5 (19.6), total sulfur S^d_t 1.7 (3.3). In the mixtures prepared for retorting the moisture content varied within the ranges of 0-20 % (Table).

Chemical Group Composition of the Shale Oils Obtained, %

Chemical group compounds	Kukersite						Dictyonema shale					
	Moisture content of the samples used, %											
	0.0	1.1	3.0	5.0	10.0	20.0	0.0	1.0	3.0	5.0	10.0	20.0
Hydrocarbons:												
Aliphatic and naphthenic	14.9	17.9	13.7	14.0	17.8	16.9	13.0	9.5	13.2	16.7	14.2	9.6
Aromatic	28.6	26.2	28.2	26.5	26.1	26.7	38.7	45.5	41.8	36.8	32.1	36.0
Heteroatomic compounds:												
Neutral and basic	47.9	48.0	49.2	48.4	46.7	47.8	37.9	39.5	36.0	35.6	40.8	45.6
Acidic	8.6	7.9	8.9	11.1	9.4	8.6	10.4	5.5	9.0	10.9	12.9	8.8

Semicoking of the initial mixtures was performed in a Fischer retort using standard procedure. Acid compounds (principally phenols) were separated from the shale oils 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 an eluent. The oil fractions and gaseous products of pyrolysis were analyzed by gas chromatography in columns of different polarity.

Results and Discussion

One can observe from the curves of shale oil, gas, pyrolytic water and semicoke yield (organic matter basis), depending on the moisture content of the shale processed (Fig. 1) that the influence of water is most pronounced in the region of its content of 0-5 %. At that, the highest yield of oil from the kukersite kerogen is observed at the shale water content of 1.1 %; it exceeds the oil yield from absolutely dry shale by 23 % rel. A less conspicuous loss of oil yield (14 % rel.) as a result of excessive drying has been observed also for Dictyonema shale, maximum oil yield, kerogen basis, being at the moisture content of the starting material of about 3 %.

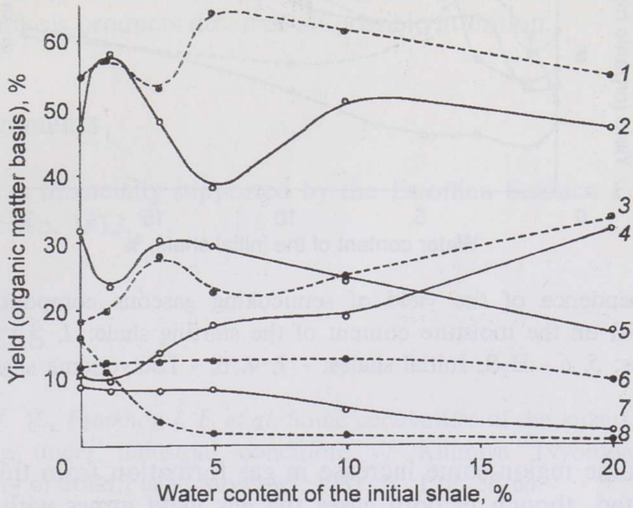

Fig. 1. Dependence of the yield of semicoking products (kerogen basis) on the moisture content of the starting shale: *2, 6* - shale oil; *3, 4* - gas; *1, 5* - semicoke; *7, 8* - pyrogenetic water. Initial shales: *1, 3, 6, 7* - Dictyonema shale; *2, 4, 5, 8* - kukersite

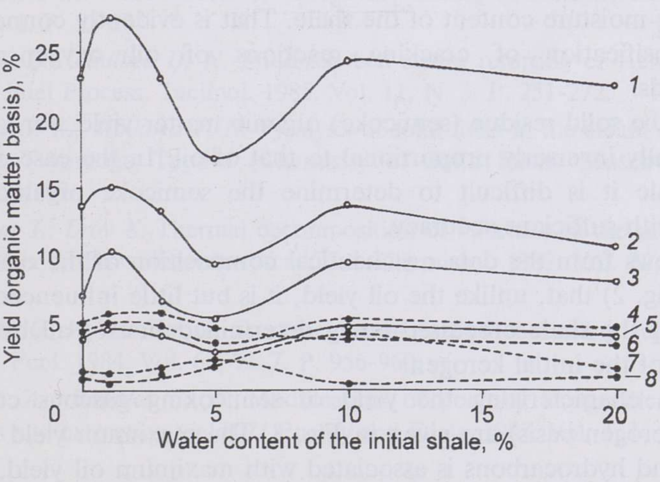

Fig. 2. Dependence of the yield of oil chemical group compounds (kerogen basis) on the moisture content of the starting shale: *1, 4* - neutral heteroatomic compounds; *2, 6* - aromatic hydrocarbons; *3, 8* - nonaromatic hydrocarbons; *5, 7* - acidic compounds. Initial shales: - *4, 6, 7, 8* - Dictyonema shale; *1, 2, 3, 5* - kukersite

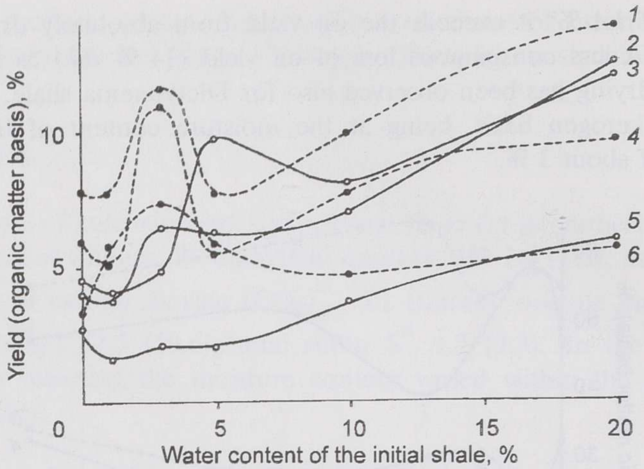

Fig. 3. Dependence of the yield of semicoking gaseous compounds (wt. %, kerogen basis) on the moisture content of the starting shale: *1, 3* - CO_2; *2, 4* - hydrocarbons; *5, 6* - H_2S. Initial shales: - *1, 4, 6,* - Dictyonema shale; *2, 3, 5* - kukersite

In the same region some increase in gas formation from this shale has been detected, though in both cases the gas yield grows with increasing moisture content of the material processed (up to 20 %), probably due to water-gas shift reaction ($C + H_2O \rightarrow CO_2 + H_2$) [12] that takes place with hydrocarbons even at temperatures below 300 °C.

The yield of water generated as a result of thermal decomposition reactions (so-called pyrogenetic water) has a tendency to grow with increasing moisture content of the shale. That is evidently connected with the intensification of cracking reactions of oil oxygen-containing compounds.

As to the solid residue (semicoke) organic matter yield, for kukersite it is practically inverserly proportional to that of oil. In the case of Dictyonema shale it is difficult to determine the semicoke organic material content with sufficient accuracy.

It follows from the data on chemical composition of the oils obtained (Table, Fig. 2) that, unlike the oil yield, it is but little influenced by water content of the shale processed being determined first of all by chemical structure of the initial kerogen.

Curves characterizing the yield of semicoking gaseous compounds (wt. %, kerogen basis) are given in Fig. 3. The maximum yield of carbon dioxide and hydrocarbons is associated with maximum oil yield, the yield of hydrogen disulfide tends to grow with increasing moisture content of the shale, in all likelyhood as a result of pyrite reaction with water [13].

Thus, moisture content of the starting shale does influence noticeably the organic matter distribution between semicoking products though at present we cannot definitely attribute this phenomenon to supressing secondary cracking reactions, or to steam distillation of volatile products, or to changes in the mixture thermal conductivity, or to water playing a role of a hydrogen donor (the last is supported by results obtained in [6]).

In any case, regulation of the raw material moisture content as a very simple and cheap method for influencing the yield and composition of shales thermolysis products deserves all possible attention.

Acknowledgements

This work was financially supported by the Estonian Science Foundation under Grant No. 1812.

REFERENCES

1. *Jefimov V. M., Petukhov J. F. et al.* Some pecularities of the kukersite thermal processing under industrial conditions // Khimiya Tvyordogo Topliva (Chemistry of Solid Fuels, Moscow). 1981. N. 1. P. 56-64.
2. *Jefimov V. M., Kundel H. A., Purre N. A.* Influence of the shale quality and processing conditions in various plants on the yields of phenols / Problems of efficacy and quality in the oil shale processing industry. TsNIITENeftekhim, Moscow. 1984. P. 15-25.
3. *Kundel H. A., Khalevina T. A., Peredkova N. M.* Thermal decomposition of kukersite in the steam stream // Goryuchie slantsy (Oil Shale)/EstNIINTI. 1983. N. 1. P. 15-20.
4. *Carter S. D., Taulbee D. N.* Fluidized bed steam retorting of Kentucky oil shale // Fuel Process. Technol. 1985. Vol. 11, N. 3. P. 251-272.
5. *Angelova G. K., Minkova V. N.* Pyrolysis of solid fuels in the steam stream // Khimiya Tvyordogo Topliva (Chemistry of Solid Fuels, Moscow). 1986. N. 3. P. 94-99.
6. *Netchayev I., Urov K.* Thermal decomposition of kukersite in the presence of heavy water // Proc. Estonian Acad. Sci. Chemistry. 1983. Vol. 32, N. 2. P. 98-102.
7. *Despande G. V., Halder G. D. et al.* Extraction of coal using supercritical water // Fuel. 1984. Vol. 63, N. 7. P. 956-960.
8. *Graff R. A., Brandes S. D.* Modification of coal by supercritical steam: pyrolysis and extraction yields // Energy and Fuels. 1987. Vol. 1, N. 1. P. 84-88.
9. *Tanaka T., Tsutsumi A., Yoshida K.* Coal liquefaction using supercritical water / Intern. Conf. Sci., Tokyo, Oct. 23-37, 1989: Proc. Vol. 2. San Jose (Calif.), 1989. P. 671-674.

10. *Missal P., Canel M.* Veredlung von Braunkohlen mit Wasser und mit Wasser-Tetralin-Gemischen in unter- und überkritischer Phase // Chem. Techn. (DDR). 1991. Vol. 43, N. 8. P. 295-303.

11. *Michels R., Landais P.* Artificial coalification: comparison of confined pyrolysis and hydrous pyrolysis // Fuel. 1994. Vol. 73, N. 11. P. 1691-1696.

12. *Kayembe N., Pulsifer A. H.* Kinetics and catalysis of the reactions of coal char and steam // Fuel. 1976. Vol. 55, N. 3. P. 211-216.

13. *Blyakhina I., Urov K.* Stepwise thermal decomposition of kukersite // Oil Shale. 1993. Vol. 10, N. 2-3. P. 187-194.

Received May 27, 1997