

A REVIEW ON BASIC METHODS OF EXTRACTION OF NEUTRAL OXYGEN COMPOUNDS FROM SHALE OIL, THEIR COMPOSITION AND PROPERTIES

L. KEKISHEVA^{*1}, N. KRAINYUKOVA^{*2}
Yu. ZHIRJAKOV^{*2}, J. SOONE^{*2}

Tallinn University of Technology,
Oil Shale Research Institute
35 Järveküla St., Kohtla-Järve 30328, Estonia

Generalized data on the properties and chemical composition of neutral oxygen compounds are given, including basic methods of their extraction from shale oil.

The oil produced by retorting kukersite oil shale is characterized by high concentration of oxygen (7–8%) [1].

According to elemental analysis and molecular weight, average content of oxygen compounds in this type of shale oil is as high as 60–70% which excludes the use of conventional petroleum refining methods for its processing. The oxygen compounds of shale oil are usually divided into two different groups: phenols reacting with NaOH in aqueous solution and neutral oxygen compounds. The most thoroughly studied aspect of these groups is the structure of phenols, particularly alkyl phenols and alkyl resorcinols. The neutral oxygen compounds are studied to a much lesser extent, although their content in the oil is as high as 20–30%.

The first studies on determining the character of neutral oxygen compounds were performed by Hüsse [2], the presence of hydroxyl, carbonyl and ester groups was shown in dephenolized fractions of shale oil produced by retorting. Pronina [3] studied the presence of ketones in shale oil as semicarbazones, but no data were given on individual compounds.

Neutral oxygen compounds were studied in some more detail by Semyonov and Gurevich [4] who identified hydroxyl-containing compounds, ethers, aldehydes and ketones by determining the group

^{*1} Corresponding author: e-mail expertfield1@hotmail.com

^{*2} E-mail expertfield1@hotmail.com

^{*3} E-mail jyri.soone@ttu.ee

chemical composition. The ketones identified were methyl-*n*-amylketone, methyl-*n*-hexylketone, methyl-*n*-septylketone, methyl-*n*-octylketone, 2,4-dimethylcyclohexanone and 4-methyl-1-hydrindone. In addition the presence of nonyl- and decylketones and *meta*-methylacetophenone was shown.

Eisen [5] studied the effect of magnesium organic compounds on the oxygen compounds present in heavy oil produced in tunnel ovens. He separated and identified 28 ketones, including cyclopentanone, cyclohexanone, benzophenone, acetophenone, hexen-5-one-2, penten-3-one-2. Besides ketones Eisen [6] identified dibenzofuran, oxibenzofuran, thiophene and its derivatives; he succeeded also in identifying hydroxyl-containing compounds – seven alcohols (C₃–C₅) of the saturated and *iso*-homologous series.

Vasilyev *et al.* [7] combined the methods of UV-, IR-, NMR H and ¹³C spectroscopy and showed that in shale oil fraction 300–320 °C aromatic ketones are not prevalent, and ketones are represented mostly by alicyclic ketones and alkanones. NMR ¹³C spectroscopy showed that higher members of homologous series of cyclopentanones, esters of carboxylic acids (lactones), higher derivatives of 2-alkanols, cyclohexanols and other secondary and tertiary alcohols are present in neutral oxygen compounds.

The above data evidence the presence of neutral oxygen compounds with hydroxyl and carbonyl functions in shale oil. The presence of ketones has been confirmed with certainty. Data obtained on the content of aldehyde functional groups are controversial, and the structure of hydroxyl-containing compounds is not conclusively described. We are of the opinion that alkyl phenols with lower acidity cannot be excluded from the composition of neutral oxygen compounds. This conclusion was made by Lille [8, 9] in the studies on neutral oxygen compounds of the shale oil fraction 300–360 °C.

It is known that oil treatment with aqueous alkali solutions is one of the methods for extraction of phenols. Being weak acids they are in a state of hydrolytic equilibrium with phenolates, and therefore a portion of phenols remains in the treated oil. Some authors explain indifference of phenols in respect to alkali solution with formation of intramolecular hydrogen bonds. The alkali method has a number of substantial disadvantages, because NaOH is a catalyst for oxidation reactions and condensation of phenols with neutral oxygen compounds. High reactivity and thermal instability of neutral oxygen compounds is one of the basic problems arising in studies on their composition and structure.

The most important trends in thermal transformation of carbonyl compounds and esters are the reactions of hydration of esters, dehydrative condensation, aldol and ester condensations, and also desoxydation. The studies on thermal transformation of neutral oxygen compounds of the fraction 180–325 °C showed that at 200 °C water evolves [10], while at 250 °C simultaneous processes of desoxydation and dehydration take place. At 350 °C decomposition of neutral oxygen compounds is accompanied by substantial evolution of water, gas and even 0.5% of solids.

Another known method of extracting neutral oxygen compounds and phenols from shale oil fractions is the so-called metasolvan method with methanol as extragent. The use of this method of successive extraction (by treatment with alcohol concentrations of 60, 65, 70 and 75%) enabled to obtain maximum yield of phenols. From the summary phenols extracted by successive extraction, neutral oxygen compounds were separated with 60% aqueous solution of methanol.

Semyonov and Gurevich [11] proposed two methods of extraction of neutral oxygen compounds: the first – extraction of both neutral oxygen compounds and phenols with successive dilution of methanol to the concentration at which only the phenols remain dissolved; the second – preliminarily dephenolization of the oil fraction by alkali solution and extraction of the neutral oxygen compounds from the dephenolized fraction by concentrated methanol which is a good solvent for neutral oxygen compounds and not for hydrocarbons, the latter are only partly carried away with the mixture of neutral oxygen compounds and alcohol.

The above authors extracted neutral oxygen compounds from shale oil fraction 200–300 °C and determined the following group composition, %:

Hydroxyl-containing compounds	21.5
Carbonyl-containing compounds	49.7
Aldehydes (according to Pondorf)	21.0
Ethers (by saponification)	11.2

The results of extraction of the diesel fraction (215–335 °C) with methyl alcohol deserve attention [12]. For extraction 95% methyl alcohol was used at 20 °C and at a fraction to alcohol ratio 1 : 1.

Table 1. Extraction of Shale Oil Diesel Fraction with Methyl Alcohol

Product	Yield, vol. %	Density at 20 °C	Phenols, wt. %	Neutral oxygen compounds, vol. %	Cetan number
Raw diesel fraction (dephenolized)	–	0.8821	14.99*	25.0	39.5
Solvent-free raffinate	47.5	0.8639	None	6.8	59.0
Solvent-free extract	52.5	0.9751	27.6	45.46	20.8
Solvent-free and dephenolized extract	38.0	0.9207	–	60.20	29.6

* The content of phenols is calculated on the non-dephenolized fraction.

It has been found that methyl alcohol is the most efficient solvent for non-dephenolized fractions, but fractions 360 °C+ are not easily separated because the densities of the raffinate and the extract are very close. The fractions with end point below 360 °C are rapidly and accurately separated. The results of semi-commercial experiments of methanol extraction in a counter-current column [13, 14] at a ratio of diesel fraction to methanol 1 : 1.5 are given in Table 2.

The above data demonstrate that methyl alcohol is the most suitable solvent for shale oil distillates. Besides, some other alcohols may be used. Their selectivity can be explained by the formation of associates of alcohol + phenols. For dephenolized fractions the mixture of alcohol and acetone proved sufficiently efficient.

Table 2. Properties of the Extract and the Raffinate Produced by Methanol Separation of Shale Oil Diesel Fraction in a Semi-Commercial Unit, %

Properties	Raffinate	Extract
Yield	50	50
Density	0.86	0.98
Content of phenols	0.5	30.5
Content of neutral oxygen compounds	13.7	66.0
Residual methanol	2.0	2.0

Besides the experiments with methyl alcohol sufficiently detailed studies have been made on the use of sulphur anhydride and furfurool as selective solvents for refining shale-oil-derived diesel fuel. Solvent refining using these reagents is possible regarding only dephenolized fractions. Practical use of these reagents is not efficient due to big losses on the account of condensation with oil components.

Conclusions

From neutral oxygen compounds making up of 20–30% of the shale oil, those present in light and middle oil fractions have been studied most completely. In these fractions they are represented by aliphatic saturated and unsaturated ketones, cycloketones, aromatic ketones, alkyl benzofurans, alkyl benzothiophenes, etc. Shale oil has to be regarded as a complex physical-and-chemical system of oxygen-containing compounds linked together with hydrogen bonds. At the same time, this aspect has been investigated in limited extent. The composition of shale oil high-boiling fractions has been studied insufficiently.

Solutions of methyl and ethyl alcohols are considered the most suitable solvents for extraction of neutral oxygen compounds from shale oil diesel fraction. The method of selective separation of shale oil fractions represents a most attractive way for dividing those into three basic components: phenols – neutral oxygen compounds – hydrocarbons. Probably, in practice dephenolization by methanol will be used, while the alkali method remains for analytical use only.

Efficient results can be obtained treating the oil simultaneously or successively with several solvents of different physical-and-chemical nature. Thus, the treatment with hydrocarbon solvent enables not only to improve

the separation of phenol water, mechanical impurities and unstable high-molecular components present in the raw shale oil, but also to dissolve a considerable portion of shale oil.

Thanks to separation of chemically valuable components directly from the solution, the technology of separation is markedly simplified, because of the destruction of hydrogen bonds and weakening of polar interaction between shale oil components. Since neutral oxygen compounds are thermolabile, it is preferable to separate them from the shale oil, not from its distillate fractions. At shale oil distillation oil components of different nature have close boiling points, and as a result azeotropic mixtures are formed. Distillation of separate individual groups of components (phenols, neutral oxygen compounds) enables to obtain high yields of target products.

REFERENCES

1. *Purre, T., Vasiljev, V.* Processing of low-temperature shale oil produced by retorting Baltic oil shale // Environmentally Acceptable Utilization of Lean Fuels / A. Aslanyan (ed). Moscow, 1990. P. 136–145 [in Russian].
2. *Hüsse, J.* Zusammensetzung und Eigenschaften der höheren Fraktionen des estländischen Brennschiefer-Rohöls und seine Ausnutzungsmöglichkeiten als Schieferöl. – Tartu, 1930.
3. *Lanin, V., Pronina, M., Murzayeva, A.* About neutral oxygen compounds present in middle fraction of oils from Baltic oil shales // Proc. Inst. of Fossil Fuels, Ac. Sci. SSSR. 1954. Vol. 3. P. 95 [in Russian].
4. *Semyonov, S., Gurevich, B.* Studies on neutral oxygen compounds of shale oil middle fractions // Proc. VNIIPS. Vol. 11. 1954. P. 57 [in Russian].
5. *Eisen, O.* Investigation of Chemical Composition of Shale Oil Heavy Fraction : Dissertation / Tallinn Technical University, 1954 [in Russian].
6. *Eisen, O.* Analytical Methods for Oils Produced by Processing Solid Fuels. Chemical Composition of Estonian Shale Oil : Thesis for D. Chem. – Tallinn, 1967. P. 50 [in Russian].
7. *Vasiljev, V., Mets, V., Dmitriyev, V.* A study of the structure of neutral oxygen compounds of shale oil // Liquid Products of Oil Shale Processing as a Chemical Raw Material : Collect. of papers. Moscow, 1986. P. 57–70 [in Russian].
8. *Lille, Ü.* Research on Alkyl Resorcinols : Thesis for D. Chem.– Tallinn, 1973 [in Russian].
9. *Lille, Ü., Vysotskaja, V., Kaidash, N., Soo, M., Pehk, T.* Properties of neutral oxygen compounds of shale oil fraction 300–360 °C // Chemistry and Technology of Oil Shale : Collect. of papers of Oil Shale Research Institute. Tallinn, 1973. Vol. 19. P. 78–87 [in Russian].
10. *Zelenin, N., Tchernyshova, K.* Primary processes of thermal conversion of the main components of shale oil middle fractions // Chemistry and Technology of Oil Shales and Products of Their Processing : Collect. of papers of VNIIPS. Leningrad : Gostoptekhizdat, 1956. Vol. 5. P. 237–252 [in Russian].

11. *Semyonov, S., Gurevich, B.* Separation of neutral oxygen compounds of oil shale middle fractions // *Ibid.* 1954. Vol. 2. P. 49 [in Russian].
12. *Zelenin, N., Semyonov, S.* Oil-shale-derived diesel fuel // *Ibid.* 1948. Vol. 1. P. 94–108 [in Russian].
13. *Semyonov, S.* Selective separation of middle fractions of oils produced at retorting Baltic oil shales // *Ibid.* 1959. Vol. 8. P. 163 [in Russian].
14. *Zelenin, N., Fainberg, V., Tchernyshova, K.* Chemistry and Technology of Oil Shale. – Leningrad : *Khimiya*, 1968. P. 250–255 [in Russian].

Presented by T. Purre

Received March 12, 2003