Available online at www.sciencedirect.com

ScienceDirect

*Mendeleev Commun.*, 2022, **32**, 139–141

Mendeleev Communications

# Composition of petroleum asphaltenes derived from ruthenium-catalyzed oxidation

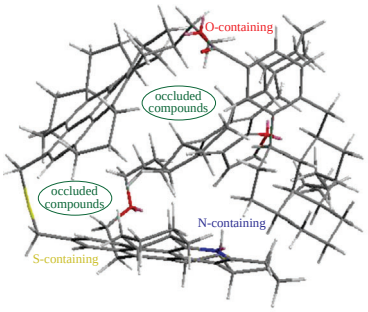
**Tatiana V. Cheshkova,*[a] Elena Yu. Kovalenko,[a] Tatiana A. Sagachenko,[a] Raisa S. Min[a] and Eugenia B. Golushkova[b]**

[a] *Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, 634055 Tomsk, Russian Federation. E-mail: chtv12@mail.ru*

[b] *Tomsk Polytechnic University, 634050 Tomsk, Russian Federation. E-mail: egol74@mail.ru*

DOI: 10.1016/j.mencom.2022.01.045

**Ruthenium ion-catalyzed oxidation of methanonaphthene oil (Krapivinskoye oilfield) revealed that its high molecular asphaltenes contain aromatic–aliphatic bridges and non-covalently bound (occluded) compounds. Covalently bound fragments are represented by $C_5$–$C_{18}$ *n*-alkanes, aromatic biphenyl-type structures, and naphthalenes located in the peripheral part of asphaltene molecules. Typical biological markers, *i.e.* terpanes, steranes, and *n*-alkanes have been identified among the occluded compounds.**




*Keywords*: asphaltenes, oxidation, ruthenium ions, catalysis, esters, phthalic anhydride, mass spectrometry, alkylarenes, arylalkanes.

Interest in the characterization of the molecular structure of petroleum asphaltenes is mainly due to the fact that their composition and structure largely determine the efficiency of the processes of extraction, transportation, and refining of liquid hydrocarbons. The study of asphaltenes is difficult since they are the most high-molecular and complex formations of oil dispersed systems. For the description of the chemical structure of asphaltenes, methods comprising targeted splitting these macromolecules into fragments (moieties) are becoming more recognized. These moieties are capable of storing information on the initial structure, and in some cases, on the bonding type. Selective chemical destruction of asphaltenes[1] allows for detecting C–S, C–O, and aromatic–aliphatic bridge bonds as well as determining the qualitative composition of 'bound' moieties.[1–4] The results of such studies are important for explication of the molecular structure of asphaltene components and prediction of the composition of products of liquid hydrocarbon processing.

The purpose of this work was to study the composition of structural elements bound in asphaltene molecules through the aromatic–aliphatic bridges. To break these bonds, we used ruthenium ion-catalyzed oxidation (RICO).† This method provides highly selective oxidation of carbon atoms of aromatic rings to $CO_2$ and/or carboxyl groups without destruction of aliphatic and naphthenic structural fragments. The structure of thus formed acids provides information on the distribution of alkyl groups attached to the aromatic cores of asphaltene molecules, the distribution of polymethylene bridges connecting two aromatic blocks, as well as the nature of fusing aromatic rings.[5–10] In addition, information on the composition of compounds captured by hollow cells of asphaltenes at the early stages of the formation of oil systems can be obtained.[1,10]

The object of study is high molecular asphaltenes of methanonaphthenic oil from the Krapivinskoye oilfield, which constitute the bulk (87.9% rel. mass) of its asphaltene components.[3] According to GC–MS analysis, the RICO products of high molecular asphaltenes are the mixtures of oxidized and nonoxidized compounds. The main oxidation products are monocarboxylic aliphatic acids and mono- and dicarboxylic aromatic acids. The formation of *n*-alkanoic acids identified in

† To break the $C_{ar}$–C bonds, water (30 ml), sodium metaperiodate (3.4 g), and ruthenium(III) chloride (10 mg) were added to a weighed portion of asphaltenes (0.3 g) dissolved in a mixture of tetrachloromethane (20 ml) and acetonitrile (20 ml), and this was magnetically stirred at room temperature for 24 h. At the end of the reaction, the organic and aqueous phases were separated using a separatory funnel, and the aqueous phase was extracted with tetrachloromethane until the colour of the dissolved compounds completely disappeared. The extract was combined with the organic phase; the resulted solution was washed with water and dried with sodium sulfate. The solvent was distilled off (*cf.* refs. 5, 6). The residue was methylated with an excess of 12% $BF_3$ solution in MeOH as described.[11] After adding the methylating agent (4 ml), the mixture was stirred at room temperature for 12 h, then water (5 ml) and zinc powder were added to scavenge iodine released from the organic phase. Unreacted zinc was separated by filtration, the organic layer was washed with brine (3 × 20 ml), dried with $Na_2SO_4$, and the excess of solvent was removed using a rotary evaporator.

The composition of methylation products was determined by GC–MS on a Hewlett Packard 6890/5973 spectrometer, quartz capillary column (30 × 0.25 mm), HP-1-MS stationary phase, helium as the carrier gas. Temperature programming: 100 °C (3 min), then heating to 310 °C at 3 deg $min^{-1}$ rate, and final 30 min keeping at this temperature. Mass fragmentograms of characteristic ions were reconstructed on the basis of the total ion current chromatogram. The literature data and the computer library of mass spectra of the National Institute of Standards and Technology (NIST) were used to identify the compounds.

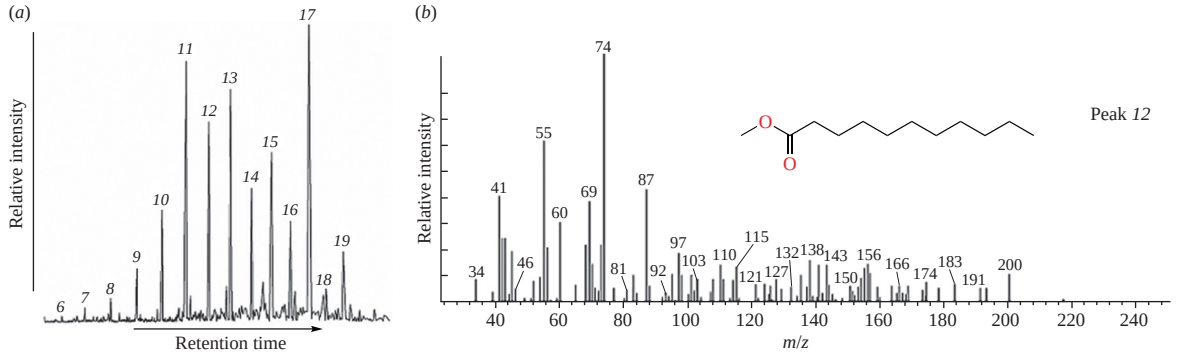
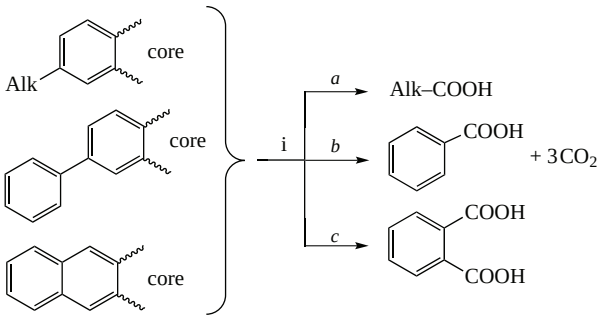



**Figure 1** (*a*) Mass-chromatogram of *m/z* 74 ion of methyl $C_6$–$C_{19}$ carboxylates for products of cleavage of $C_{ar}$–C bonds in high molecular asphaltenes; (*b*) mass spectrum of undecanoic acid methyl ester (peak *12*).

the form of their $C_6$–$C_{19}$ methyl esters [Figure 1(*a*)] suggests the presence of alkyl groups in the structure of the asphaltenes under study whose normal alkyl groups from $C_5$ to $C_{18}$ are directly attached to the aromatic core (Scheme 1, pathway *a*).

In the oxidation products, aromatic acids are present in free form rather than as their methyl esters, which may be due to the peculiarities of the methylating agent used. According to published data,[11] the esterification reactivity of the $BF_3$/MeOH solution with respect to aromatic acids is lower than with respect to fatty acids. Monocarboxylic aromatic acids are presented by benzoic and 3-methylbenzoic acids. Their formation suggests the presence of aromatic fragments of biphenyl type in the molecular structure of asphaltenes under study (see Scheme 1, pathway *b*).[13,14]




**Scheme 1** *Reagents and conditions*: i, $NaIO_4$, $RuCl_3$, MeCN, $H_2O$, 22 °C, 24 h.

Dicarboxylic aromatic acids are represented by phthalic acid and its methyl and dimethyl derivatives. These compounds are detected as their cyclic anhydrides, namely, phthalic anhydride (isobenzofuran-1,3-dione) and methyl- and dimethyl-substituted isobenzofuran-1,3-diones (Figure 2). Phthalic acids are usually considered as the main product of oxidation of naphthalene (see Scheme 1, pathway *c*).[9,10,14] Their presence in the oxidized RICO products as anhydrides is apparently due to dehydration in the injector in the course of GC–MS analysis.[14,15]

Saturated hydrocarbons represented by $C_{14}$–$C_{37}$ *n*-alkanes (*m/z* 71), $C_{27}$–$C_{30}$ steranes (*m/z* 217), and $C_{27}$, $C_{29}$–$C_{33}$ terpanes (*m/z* 191) prevailed among the unoxidized RICO products. The identified hydrocarbons were not covalently bound moieties in the macromolecular structure of asphaltenes, but they were trapped in free spaces inside their skeletons. The skeletons resulted from the twisting of long branched aliphatic chains framing the naphthene aromatic core of asphaltene molecules or their folding into a complex three-dimensional structure.[16] The

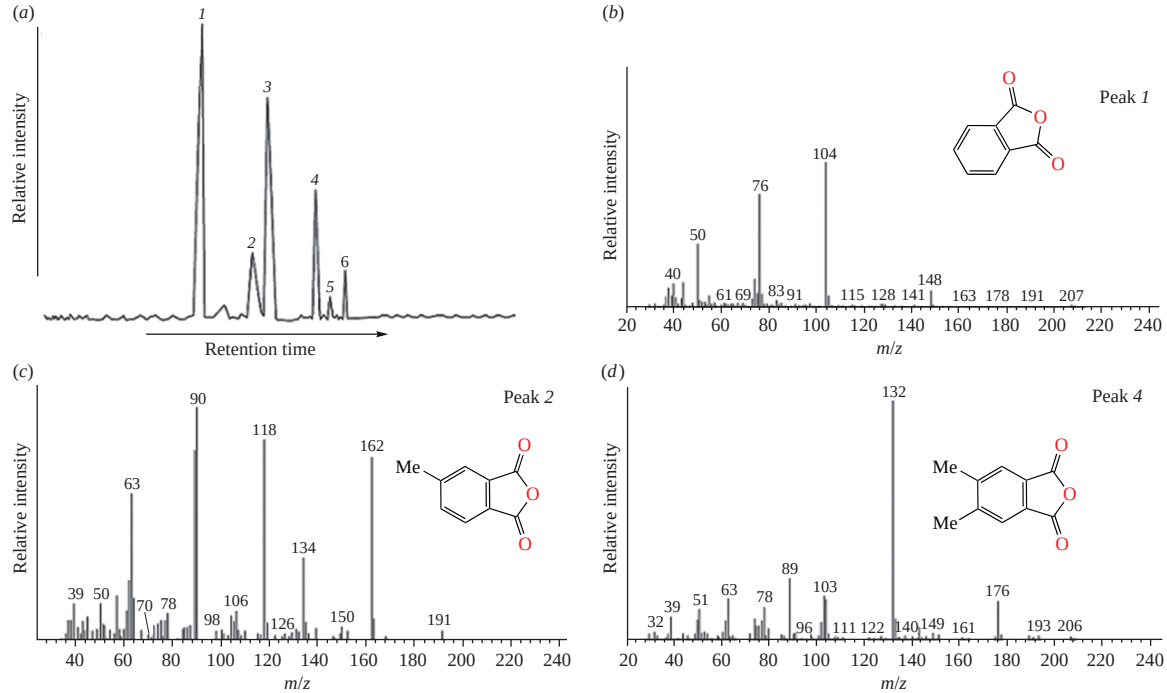



**Figure 2** (*a*) Mass-chromatogram of *m/z* 104, 118 and 132 ions for the products of $C_{ar}$–C bond cleavage in macromolecules of high molecular asphaltenes. Peaks: *1*, phthalic anhydride; *2*, 4-methylisobenzofuran-1,3-dione; *3*, 5-methylisobenzofuran-1,3-dione; *4*, 5,6-dimethylisobenzofuran-1,3-dione; *5*, 4,5-dimethylisobenzofuran-1,3-dione; *6*, 4,7-dimethylisobenzofuran-1,3-dione. Mass-spectra of (*b*) phthalic anhydride (peak *1*); (*c*) 4-methylisobenzofuran-1,3-dione (peak *2*); (*d*) 5,6-dimethylisobenzofuran-1,3-dione (peak *4*).

oxidation promotes the release of occluded compounds.[1,16] Blocked molecules are protected from the influence of catalytic, microbial, and chemical processes occurring in the oil system.[17] Hence, the study of their composition is important for obtaining data on the beginning of generation of hydrocarbons in the field of postdiagenetic transformations of sediments.[18] The presence of such biological markers as terpanes, steranes, and *n*-alkanes was observed among the occluded components of the geomacromolecules of kerogens, oils, and bitumen.[10,16,19–21]

In summary, the employment of RICO made it possible to establish that the composition of high molecular asphaltenes of oil from Krapivinskoe oilfield includes *n*-alkyl groups directly connected to the aromatic cores of their molecules, while aromatic parts of biphenyl and naphthalene types are located at the periphery of molecules. Free *n*-alkanes, steranes and terpanes were occluded inside the asphaltene macromolecule. The information obtained expands the understanding of the structure of asphaltenes. Hence, it may be used to construct a hypothetical model of their molecules.

This study was supported by the Ministry of Science and Higher Education of the Russian Federation (Registration no. 121031200185-6).

## References

1 L. R. Snowdon, J. K. Volkman, Z. R. Zhang, G. L. Tao and P. Liu, *Org. Geochem*., 2016, **91**, 3.
2 P. Peng, A. Morales-Izquierdo, A. Hogg and O. P. Strausz, *Energy Fuels*, 1997, **11**, 1171.
3 T. V. Cheshkova, V. P. Sergun, E. Y. Kovalenko, N. N. Gerasimova, T. A. Sagachenko and R. S. Min, *Energy Fuels*, 2019, **33**, 7971.
4 C. Li, P. Peng, G. Y. Sheng and J. M. Fu, *Org. Geochem*., 2004, **35**, 531.
5 T. W. Mojelsky, D. S. Montgomery and O. P. Strausz, *AOSTRA J. Res*., 1985, **2**, 131.
6 T. W. Mojelsky, T. M. Ignasiak, Z. Frakman, D. D. McIntyre, E. M. Lown, D. S. Montgomery and O. P. Strausz, *Energy Fuels*, 1992, **6**, 83.
7 Q. Shi, J. W. Wang, X. Zhou, C. Xu, S. Zhao and K. H. Chung, in *Structure and Modeling of Complex Petroleum Mixtures*, eds. C. Xu and Q. Shi (*Structure and Bonding*, ed. D. M. P. Mingos, vol. 168), Springer, 2016, pp. 71–92.
8 Z. G. Zhang, S. Guo, S. Zhao, G. Yan, L. Song and L. Chen, *Energy Fuels*, 2009, **23**, 374.
9 O. P. Strausz, T. W. Mojelsky, F. Faraji, E. M. Lown and P. Peng, *Energy Fuels*, 1999, **13**, 207.
10 O. P. Strausz, T. W. Mojelsky, E. M. Lown, I. Kowalewski and F. Behar, *Energy Fuels*, 1999, **13**, 228.
11 P. Peng, A. Morales-Izquierdo, E. M. Lown and O. P. Strausz, *Energy Fuels*, 1999, **13**, 248.
12 P. Peng, J. M. Fu, G. Y. Sheng, A. Morales-Izquierdo, E. M. Lown and O. P. Strausz, *Energy Fuels*, 1999, **13**, 266.
13 E. Nowicka, T. J. Clarke, M. Sankar, R. L. Jenkins, D. W. Knight, S. Golunski, G. J. Hutchings, D. J. Willock, M. Francisco and S. H. Taylor, *Chem. – Eur. J*., 2018, **24**, 655.
14 M. A. G. Teixeira, M. L. A. Gonçalves and R. C. L. Pereira, *Prepr. Pap. – Am. Chem. Soc., Div. Fuel Chem*., 2002, **47**, 183.
15 F. Benoit, J. L. Holmes and N. S. Isaacs, *Org. Mass Spectrom*., 1969, **2**, 591.
16 B. Cheng, J. Zhao, C. Yang, Y. Tian and Z. Liao, *Energy Fuels*, 2017, **31**, 8823.
17 B. Cheng, J. Du, Y. Tian, H. Liu and Z. Liao, *Energy Fuels*, 2016, **30**, 4529.
18 V. A. Kashirtsev, *Russ. Geol. Geophys*., 2018, **59**, 975 (*Geol. Geofiz.*, 2018, **59**, 1211).
19 Y. Tian, J. Zhao, C. Yang, Z. Liao, L. Zhang and H. Zhang, *J. Asian Earth Sci.*, 2012, **54**–**55**, 174.
20 B. Cheng, Z. Liao, T. Wang, H. Liu, Y. Tian and S. Yang, *J. Pet. Sci. Eng*., 2015, **127**, 359.
21 Z. Liao, A. Geng, A. Graciaa, P. Creux, A. Chrostowska and Y. Zhang, *Org. Geochem*., 2006, **37**, 291.

*Received: 22nd June 2021; Com. 21/6592*