# RADIATION CHEMICAL CONVERSION OF OIL DERIVED FROM OIL-BITUMEN ROCK

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**Abstract.** The results of research in the radiation processing of synthetic oil derived from oil–bitumen rock of the Balakhany deposit in Azerbaijan are presented. The study has been conducted on a $^{60}$Co gamma-source at a dose rate of $P$ = 0.5 Gy/s and various absorbed doses of $D$ = 43–216 kGy. Samples of synthetic oil from natural bitumen rocks have been analyzed by chromatography, gas chromatography–mass spectrometry, and IR-spectroscopy, and their radiation resistance has been evaluated. The results of the study allow for both assessment of the feasibility of manufacturing petrochemicals for various applications by radiation processing and use of these materials for isolating radioactive sources to preclude their impact on the environment.

**Keywords:** oil–bitumen rock, synthetic oil, oxygen, hydrocarbon gases, radiation.

## Introduction

Oil–bitumen rock (OBR) is a natural material formed from crude oil in the upper layers of the Earth crust as a result of the slow evaporation of light fractions from the oil, natural oil deasphalting, and the processes of interaction of its components with oxygen and sulfur. According to United Nations estimates, the world's geological reserves of OBR amount to ~360 billion tons on the hydrocarbon (HC) basis and are an alternative source of HC feedstock [1].

Large OBR accumulations were found in Canada, the United States, and the CIS countries. The reserves in Azerbaijan make 200 million tons in 11 deposits [2, 3].

In Russia there are 400 OBR deposits with total reserves of 7.2 billion tons. The total world production of oil from OBR is about 84 mb/d (million barrels per day). In Canada, there are plants for oil extraction from oil sands, one of which has a daily output of more than 140 thousand barrels of oil [4].

## Experimental

The object of investigation was the synthetic oil derived from OBR of the Balakhany field of Azerbaijan. Experiments were carried out on an MRKh γ-30 $^{60}$Co gamma-ray source at a dose rate of 0.5 Gy/s. By distillation in a Retort Heating Jacket apparatus at a temperature of 950 F (510°C), 50 mL of synthetic crude was obtained from 375 g. The rock composition (%) was as follows: oil 22, water 6, sand 72.

Samples of synthetic oil were irradiated to different absorbed doses in the range of 43–216 kGy in air or vacuum to follow the kinetics of the processes and to reveal the role of oxygen in the radiation resistance of the OBR. The samples of the synthetic oil intended for chromatographic analysis were dried with anhydrous sodium sulfate ($Na_2SO_4$) and diluted with dichloromethane ($CH_2Cl_2$); mass chromatograms in the $m/z$ range of 35–400 ($m/z$ is the ion mass to charge ratio) were recorded on a GCMS Trace DSQ instrument (Thermo Electron, Finnigan USA, 2005).

The sample notation was as follows: 12169, the initial synthetic oil; 12170, the synthetic oil irradiated for 96 h in air; and 12171, the synthetic oil irradiated for 96 h in a vacuum.

IR spectra of the samples were recorded on an M-80 spectrophotometer in the wave number range of 700–4000 $cm^{-1}$. The gaseous products were analyzed by gas chromatography.

## Results and discussion

The components identified in the unirradiated synthetic oil are shown in Table 1.

The unirradiated oil samples predominately contain relatively light hydrocarbons, such as undecane, dodecane, tridecane, tetradecane, and hexadecane. After irradiation, an increase of the peak heights of heavier hydrocarbons, such as eicosane, allopregnane, and octadecane, is observed. This is due to the occurrence of complex radiation induced processes of polycondensation and rearrangement in the molecular structure of the synthetic oil.

The effect of γ -radiation on the structural group composition of the samples of synthetic bituminous oil was investigated.

*Table 1*

**Liquid full scan.**

| No. | Component elution time, min | Identified components of initial synthetic oil | Formula |
|---|---|---|---|
| 1 | 4.17 | Toluene | $C_7H_8$ |
| 2 | 7.37 | p-Xylene | $C_8H_{10}$ |
| 3 | 7.79 | cis-2-Nonene | $C_9H_{18}$ |
| 4 | 8.02 | Nonane | $C_9H_{20}$ |
| 5 | 9 | Octane, 2,6-dimethyl- | $C_{10}H_{22}$ |
| 6 | 9.65 | 1-Octyn-3-ol, 4-ethyl- | $C_{10}H_{18}O$ |
| 7 | 10.09 | Benzene, 1-ethyl-3-methyl- | $C_9H_{12}$ |
| 8 | 10.56 | Benzene, (1-methylethyl)- | $C_9H_{12}$ |
| 9 | 10.74 | 1-Decene | $C_{10}H_{20}$ |
| 10 | 10.92 | Decane | $C_{10}H_{22}$ |
| 11 | 11.31 | 1-Octanol, 2-methyl- | $C_9H_{20}O$ |
| 12 | 11.75 | Benzene, 1-ethyl-4-methyl- | $C_9H_{12}$ |
| 13 | 13.3 | 1-Undecanol | $C_{11}H_{24}O$ |
| 14 | 13.46 | Undecane | $C_{11}H_{24}$ |
| 15 | 14.67 | Undecane, 6-methyl- | $C_{12}H_{26}$ |
| 16 | 14.93 | Benzene, 1,2,4,5-tetramethyl- | $C_{10}H_{14}$ |
| 17 | 15.58 | Cyclopropane, nonyl- | $C_{12}H_{24}$ |
| 18 | 15.73 | Dodecane | $C_{12}H_{26}$ |
| 19 | 15.97 | Undecane, 2,6-dimethyl- | $C_{13}H_{28}$ |
| 20 | 17.67 | 1-Tridecene | $C_{13}H_{26}$ |
| 21 | 17.8 | Tridecane | $C_{13}H_{28}$ |
| 22 | 18.81 | 1-Pentadecanol | $C_{15}H_{32}O$ |
| 23 | 18.92 | Cyclohexanol, 5-methyl-2-(1-methylethyl)-, [1R-(1à,2á,5à)]- | $C_{10}H_{20}O$ |
| 24 | 19.64 | 1-Tetradecene | $C_{14}H_{28}$ |
| 25 | 19.75 | Tetradecane | $C_{14}H_{30}$ |
| 26 | 20.73 | Naphthalene, 2,7-dimethyl- | $C_{12}H_{12}$ |
| 27 | 20.81 | Tetradecane, 2,6,10-trimethyl- | $C_{17}H_{36}$ |
| 28 | 21.45 | 2,6-Dodecadien-1-ol, 3,7,11-trimethyl-, (E,E)- | $C_{15}H_{28}O$ |
| 29 | 21.58 | Pentadecane | $C_{15}H_{32}$ |
| 30 | 21.92 | 1H-Indene, 2,3,3a,4,7,7a-hexahydro-2,2,4,4,7,7-hexamethyl | $C_{15}H_{26}$ |
| 31 | 22.64 | Naphthalene, 1,6,7-trimethyl- | $C_{13}H_{14}$ |
| 32 | 23.19 | 1-Hexadecanol | $C_{16}H_{34}O$ |
| 33 | 23.29 | Hexadecane | $C_{16}H_{34}$ |
| 34 | 24.84 | 1-Heptadecanol | $C_{17}H_{36}O$ |
| 35 | 24.92 | Heptadecane | $C_{17}H_{36}$ |
| 36 | 26.4 | 8-Heptadecene | $C_{17}H_{34}$ |
| 37 | 26.47 | Octadecane | $C_{18}H_{38}$ |
| 38 | 27.95 | Nonadecane | $C_{19}H_{40}$ |
| 39 | 29.37 | Eicosane | $C_{20}H_{42}$ |
| 40 | 30.49 | Octadecane, 3-methyl- | $C_{19}H_{40}$ |
| 41 | 30.72 | Heneicosane | $C_{21}H_{44}$ |
| 42 | 32.74 | Allopregnane | $C_{21}H_{36}$ |
| 43 | 33.26 | Octadecane, 3-ethyl-5-(2-ethylbutyl)- | $C_{26}H_{54}$ |

The IR spectrum of the synthetic oil (initial) displayed an absorption band at 740 $cm^{-1}$ due to rocking vibration of the $–CH_2$ group and the 1380 $cm^{-1}$ bending and 2860 and 2960 $cm^{-1}$ stretching bands characteristic of the methyl group $CH_3$. The spectrum also contains bands characteristic of the $=CH_2$ group and the C=C bond of unsaturated hydrocarbons, corresponding to out-of-plane bending vibrations of the substituted benzene ring. The absorption band at 1720 $cm^{-1}$ corresponds to the carbonyl group C=O. In addition, there are absorption bands in the region of 1020–1160 $cm^{-1}$ with maxima at 1025, 1070, 1120, and 1160 $cm^{-1}$ corresponding to oxygen containing groups (C–O–, C–O–O, O–H). Owing to the long-term occurrence in the environment, the bitumen rock has a high concentration of oxygenated compounds.

The presence of these reactive groups determines a higher adhesive strength of the binding components with the rock (adhesive properties) as compared with manmade compositions based on petroleum refining products; however, they are easily cleaved by irradiation. Irradiation reduces the concentration of oxygen containing groups as a result of their transfer to the heavier fractions.

The IR spectra of the synthetic oil derived from the bitumen rock are given in Figure 1. A comparison of the IR spectra of the samples (irradiated in air for 72 and 120 h) with the spectrum of the initial material shows that the intensities of the absorption bands of paraffinic, unsaturated, and aromatic hydrocarbons and oxygenated compounds are significantly reduced in the following order: unirradiated oil > oil irradiated in air for 72 h > oil irradiated in air for 120 h. As the absorbed dose increases, the optical density at the absorption bands of functional groups in the samples also decreases. The spectroscopic analysis data are presented in Figure 2.

To study the radiation resistance of BR, the samples of the synthetic oil were irradiated with absorbed doses of 43–216 kGy at a $^{60}$Co γ-ray dose rate of $P$ = 0.5 Gy/s. The rate curves of gas buildup during the γ-radiolysis of synthetic oil recovered from natural oil–bitumen rocks are given below in Figure 3.

For all the gases, oxygen enhances the radiation-chemical degradation of the synthetic oil, an effect that is associated with oxidative degradation reactions involving radiolytic radicals. This oil is characterized by a high concentration of cyclic structures, particularly aromatics, concentrated in middle distillates.

The average values of the radiation-chemical yield (molecule/100 eV) of gases from the synthetic bituminous oil are listed in Table 2.

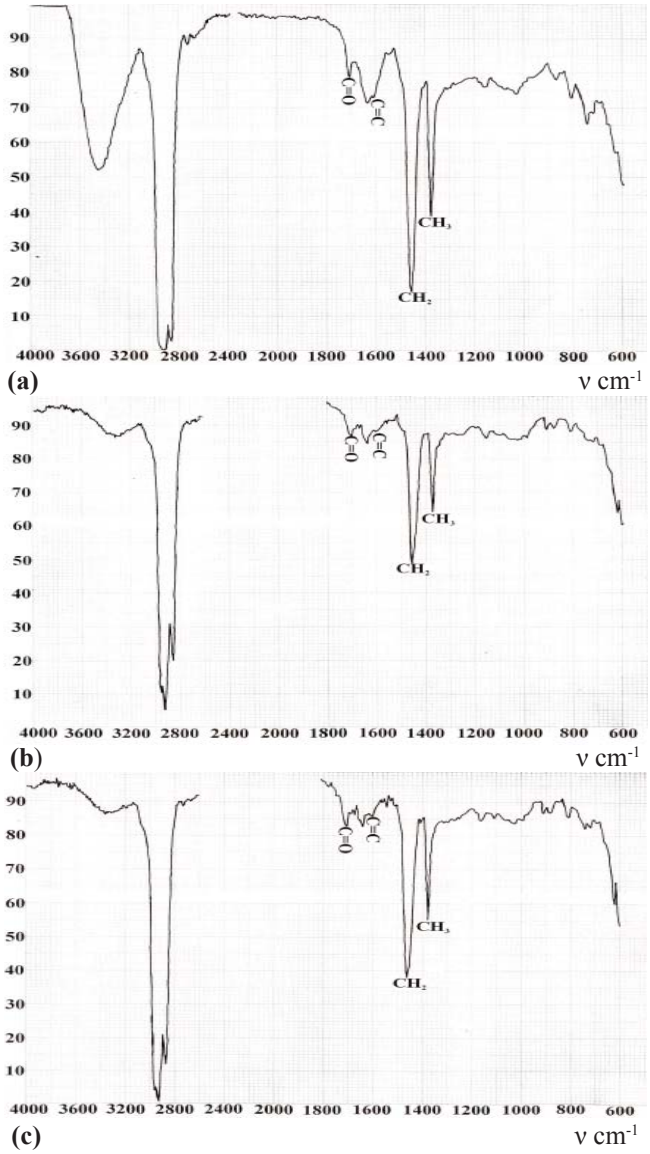
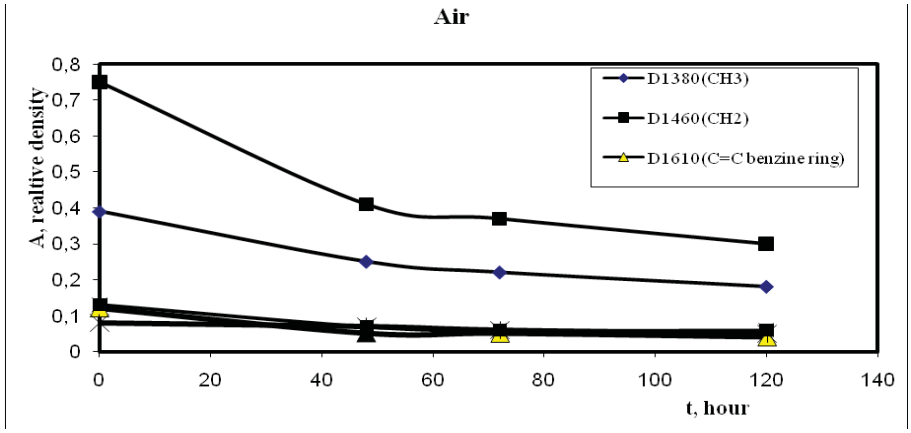
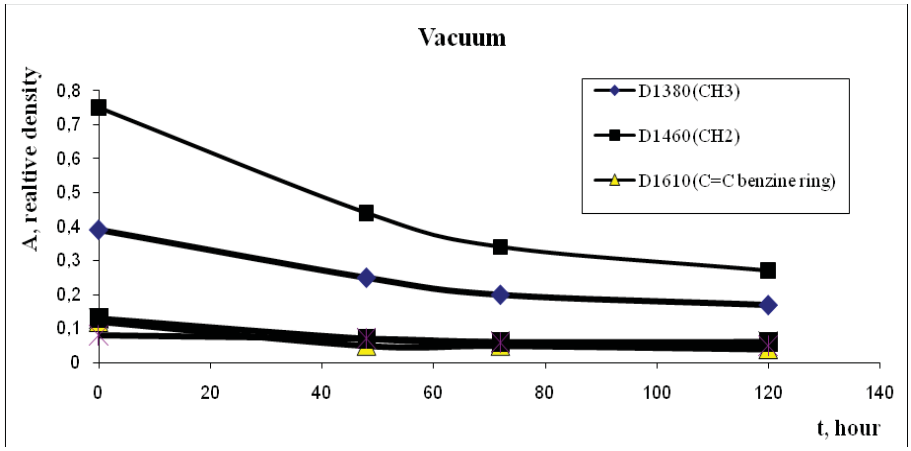



**Figure 1. IR spectra of synthetic oil recovered from the bituminous rock: (a) the initial synthetic oil; and (b, c) the synthetic oil irradiated in air for 72 and 120 h, respectively.**




(a)




(b)

**Figure 2. Dependence of the absorbance of samples of the synthetic oil recovered from the bituminous rock on the absorbed dose in (a) air and (b) vacuum.**

*Table 2*

**Average values of the radiation-chemical yield (molecule/100 eV) of gases from synthetic bituminous oil.**

| Average radiation-chemical yield of gas from BR synthetic oil (molecule/100 eV) | $H_2$ | CO | $CO_2$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| air | 0.31 | 0.85 | 0.66 | 0.06 | 0.05 | 0.024 | 0.13 | 0.33 | 0.32 | 0.16 | 0.04 |
| vacuum | 0.37 | 0.26 | 0.67 | 0.03 | 0.02 | 0.005 | 0.014 | 0.022 | 0.176 | 0.13 | 0.06 |

It should be noted that paraffinic and polycyclic aromatic hydrocarbons exhibit a relatively high stability against radiation. However, functional groups (especially, oxygen containing groups) and olefins have a low radiation resistance. The stability of these organic compounds towards radiation depends on their excitation and ionization potentials. In the presence of polyconjugated aromatic structures, the none of the vibrational degrees of freedom gets a sufficient energy for breaking chemical bonds. The energy can also be dissipated before the decomposition of the molecule [5]. The irradiation of these samples in an air medium leads to slight enhancement of the degradation process, but the product yields remain relatively low. In order to increase the radiation chemical yield of gases and ensure the chain mechanism of degradation of hydrocarbons in such systems, it is necessary to apply a high temperature. At elevated temperatures, the substrate degradation processes proceed effectively owing to abstraction reactions involving radiolytic hydrocarbon radicals. In the case of joint heat and radiation treatment, in order to preclude the recombination processes of chain termination, it is necessary to choose appropriate temperature and dose rate at which the radiation effect is maximal [6].

**Conclusions**

The relatively high radiation resistance of the synthetic oil, recovered from the OBR, in vacuum and air below 50°C is associated with the presence of paraffins, polynuclear aromatic hydrocarbons, and resin asphaltene substances in its composition. This makes it possible to use the synthetic oil as a feedstock for manufacturing a waterproof material applicable in radiation fields, including the disposal of radioactive waste. The organic matter of the OBR may serve as a promising source material for manufacturing various fuels, lubricating oils, coke, and asphalt. Hydrogen, hydrocarbon gases, and olefin hydrocarbons can be produced from the synthetic oil by the joint ionizing radiation and heat treatment at consistent values of the temperature and the dose rate.

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