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Effect of Ozonation on Component Composition and Flotation Properties of Kerosene

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Abstract

Petrochemicals are traditionally used as reagents during flotation enrichment of coal. In order to improve flotation efficiency, oxidative modification of apolar hydrocarbon reagents is used. This paper uses ozone as an oxidative agent and kerosene fraction – as an apolar one. The effect of ozonation on component composition and process properties of kerosene was explored. It was demonstrated that the relative content of aliphatic CH₂ bonds in the α -position to the aromatic ring was decreased in kerosene composition resulting from ozonolytic treatment. Furthermore, the fraction of methyl, methoxyl, alkyl ether, and alicyclic compounds increases; one of polycyclic and monocyclic arenes decreases and the content of aliphatic carboxylic acids, linear and cyclic ethers and esters, lactones and anhydrides rises. Owing to an increased fraction of heteropolar oxygen-containing compounds in composition of ozonized kerosene, floatation reagents with complex properties of foaming and collecting agents may be produced on its basis, which facilitates increasing the efficiency of coal sludge flotation.

Keywords: kerosene, ozonation, oxygen-containing groups, flotation, coal

INTRODUCTION

Products from crude oil refining and gas condensate processing (kerosene, thermal cracking gas oil, mineral oils, diesel fuel, *etc.*) are used during flotation enrichment of fine fractions of high-ash and hard-cleaning coal as the main collectors (collecting agents) [1, 2]. In order to enhance flotation efficiency, pulp additives made of frothers with polar functionalities, such as aliphatic (C₆–C₉), cyclic (cyclohexanol) and terpene (Flotol-7,9 agent) alcohols, mixtures of organooxygen compounds, distillation residues of the production of butanol (still bottoms of butyl alcohols), propylene glycol (polypropylene glycol monobutyl ether frother), styrene (styrene distillation residue), and dime-

thyldioxane (flotation agent-oxal T-92), *etc.*, are used in practice [2-4].

In order to produce integrated reagents that simultaneously have foaming and gathering properties, oxidative modification of oil hydrocarbons and their mixtures is used [5, 6]. To increase flotation efficiency, reagents of comprehensive effect should have a hydrocarbon radical with the optimum length and a polar oxygen atom, or a functional group (OH, C=O, COOH, *etc.*) that provide molecules with an opportunity to gain a foothold on the energetically inhomogeneous surface of coal due to specific forces of intermolecular interaction (hydrogen, coordination, or donor-acceptor bonds) [7, 8].

Among oxidation methods for modification of hydrocarbons, ozonation stands out. Unlike traditional oxidizing agents (mineral acids, hydrogen peroxide, potassium permanganate, molecular oxygen, *etc.*) used in chemistry and chemical technology, ozone has a number of advantages, such as high reactivity and selectivity towards certain types of bonds and heteroatoms; mild conditions of the process (there is no need in catalysts, and also high temperature and pressure), *etc.* [9, 10].

Some of the widely used flotation reagents include kerosenes, *i.e.* an oil fraction with a boiling point of 150–300 °C containing 20–60 % of aliphatic, 20–50% of naphthenic, 5–25% of bicyclic aromatic, and up to 2% of unsaturated hydrocarbons.

The purpose of the research was to investigate the effect of ozonation on the chemical composition of the resulting products and flotation properties of kerosene.

EXPERIMENTAL

The basic flotation agent based on kerosene fraction from one of Kuzbass processing plants (kerosene TS-1) was used as the research object. It had the following characteristics: density of 775 kg/m³ at 20 °C, the kinematic viscosity of 1.25 mm²/s at 20 °C, the mass fraction of total sulphur of 0.25 %, the acidity of 0.5 mg of KOH/100 g. Water content in kerosene before and after ozonation was not determined, as the use of flotation reagents presumes the presence of water in a technological process.

Ozonation of a sample of kerosene ($V = 50$ mL) was carried out at room temperature and air pressure in a bubbling reactor with a continuous supply of ozone/oxygen mixture (ozone content of 35–40 mg/L). Ozone concentration was determined by a UV gas analyzer (ozone absorption in the ultraviolet region of the spectrum at a wavelength near 250 nm). Table 1 gives the characteristics of the initial and ozonized kerosene.

Elemental analysis was carried out using ThermoFlash2000 CHNS/O analyzer.

The infrared (IR) spectra were recorded on the Fourier spectrometer INFRALUM FT-801 in the 400–4000 cm⁻¹ range. The optical density of absorption bands was normalized according to the band at 1460 cm⁻¹ (absorption of C–H bonds, a measure of the organic matter). The oxidation level (K_o) of samples was computed against the total intensity (the sum of integral optical densities, D) of the absorption bands of oxygen-containing hydroxyl (3200 cm⁻¹) and carboxyl (1730 cm⁻¹) groups to the sum of optical densities of aliphatic CH_x (2920 cm⁻¹) and aromatic CH (3040 cm⁻¹) moieties:

$$K_o = (D_{3200} + D_{1730}) / (D_{2920} + D_{3040})$$

The ¹H and ¹³C NMR spectra of the products were acquired using Bruker Avance AV 300 spectrometer; deuterated toluene was used as a solvent. The decoding and quantitative interpretation of spectra were carried out using the known techniques [11, 12].

Flotation activity of kerosene was assessed according to the enrichment of coal fines (a fraction less than 0.2 mm), ash content (A^d) of 16.0 %, KS grade (coal coke weakly sintering) from the Kuznetsk Basin. Experiments were carried out in a laboratory flotation machine at a constant flow rate of the collector with a 70 g/L solid content in the flotation feed. Ozonized kerosene, and also kerosene with the addition of polypropylene glycol monobutyl ether frother and Ekofol containing free hydroxyl groups and ether bonds were used as reference samples. The flow rates of kerosene, polypropylene glycol monobutyl ether frother, and Ekofol were 0.7 kg/t and 0.1–0.2 kg/t, respectively. Experimental results were assessed according to the yields of the concentrate (γ_c) and waste (γ_w), the ash content of the concentrate (A_c^d) and wastes (A_w^d), combustible matter recovery into the concentrate (E_c), and process selectivity (K_{sel}). Flotation foam characteristics (foam volume, V_f and resistance, R_f) and the solid content (C_c) in the foam product were also considered. They have effects on the efficiency of concentrate subsequent pumping and dehydration.

TABLE 1

Chemical composition and properties of initial and ozonized kerosene samples

Sample	Ozonation time, h	Amount of ozone absorbed, g/kg	Yield of resinous products, mass %	Acid index, mg KOH/100 g	Oxidation index K_o , r. u.
Initial	–	–	–	0.46	0.01
Ozonized	1	7.3	0.5	2.04	0.06
Ozonized	2	14.3	1.7	4.72	0.16

RESULTS AND DISCUSSION

Kerosene fraction ozonation is accompanied with the formation of oxygenated low-molecular-mass products (peroxides, aldehydes, acids, ketones, etc.), and also insoluble high-molecular compounds (resins), alongside with oxidation of hydrocarbons in various classes [10, 13]. Resin products begin to be generated in the reaction volume when the flow rate of ozone reaches ≈ 3 g/kg. The acid number of kerosene increases by 10 times for 2 h of ozonation. Ozone assimilation by kerosene is ~ 14 g/kg, whereas the yield of resin products reaches 1.7 % (Table 1). The formation of resins may be related to the flowing of synthesis side reactions of high-molecular-mass oxygenated compounds due to the interaction of primary oxidation products with ozone and among themselves [13].

There is a reduction in the intensity of absorption of aliphatic CH bonds ($2980, 2950\text{ cm}^{-1}$) with increasing herewith the fraction of methoxyl ($\text{CH}_3\text{-O}$) and alkyl ether ($\text{CH}_2\text{-O}$) ($2880, 2850\text{ cm}^{-1}$), methyl (1380 cm^{-1}), and acyclic ($3050\text{-}3100, 800\text{-}1060\text{ cm}^{-1}$) moieties in IR spectra of ozonized samples (Fig. 1) [11]. An increase in the fraction of C=C groups conjugated with the C=O group ($1600, 1560\text{ cm}^{-1}$), and also arenes with disubstitution (changes in the nature of the spectrum in the $900\text{-}680\text{ cm}^{-1}$ range) is typical for aromatic hydrocarbons. This may be related to the formation of dicarboxylic acids (e.g. phthalic acid) [13]. There is an increase in the intensity of absorption bands of oxygenated moieties, such as O-H (3200 cm^{-1}) and C=O ($1730, 1710\text{ cm}^{-1}$) of carboxylic acids bound by hydrogen bonds, C=O of esters, lactones, and anhydrides (1790 cm^{-1}), aromatic ketones (1690 cm^{-1}), C-O of linear and

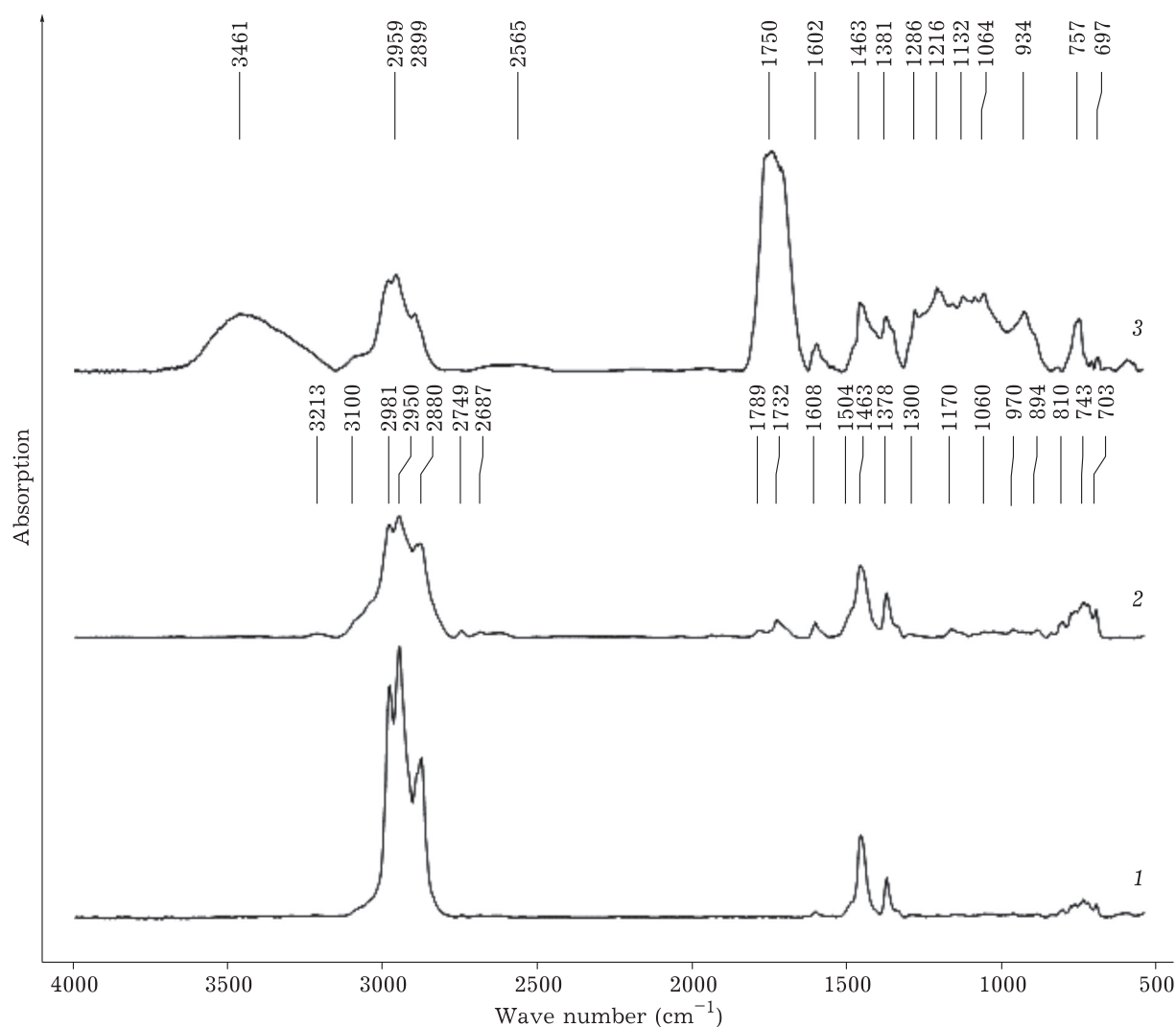


Fig. 1. IR spectra of initial (1) and ozonized (2) samples of kerosene, and also ozonized resins (3).

cyclic ethers and esters (1170, 1060 cm^{-1}). The oxidation level (K_o) computed from the ratio of absorption band intensities of oxygenated groups of acid nature (OH + COOH) and hydrocarbon moieties are increased by 16 times in the course of ozone assimilation by kerosene, according to IR spectroscopic data (see Table 1).

As demonstrated by analysis of ^{13}C and ^1H NMR spectra of kerosene, the prevalent components therein are aliphatic and naphthenic hydrocarbons with chemical shifts in the ranges of 0–60 ppm and 0–2.3 ppm in the carbon and proton spectra, respectively. According to ^1H NMR spectroscopic data, the values of normalized integral intensities of protons of the main types in kerosene components were determined. Proceeding from quantitative ^1H NMR data (Table 2), hydrogen fraction in the composition of aliphatic and alicyclic compounds is more than 90 rel. %. Monocyclic arenes are prevailing among aromatic compounds presented in the ^{13}C and ^1H NMR spectra within 93–171 ppm and 6–8.6 ppm ranges, correspondingly. Resulting from ozonation, the portion of the hydrogen in CH and CH_2 groups in the α -position to the aromatic ring is decreased. Furthermore, the percentage of hydrogen in methyl groups of saturated species, and also CH and CH_2 moieties of naphthenes and cycloalkanes are increased, which is in agreement with IR spectroscopic data (see Table 2). Among other moieties present in kerosene in less significant amounts (1–4 %), there is a reduction in the composition of olefinic and polycyclic aromatic compounds. The acquired data are interrelated with ozone reaction characteristics. Higher rates of interaction on C=C bonds of unsaturated ($k = (2-5) \cdot 10^5 \text{ L}/(\text{mol} \cdot \text{s})$), polyaro-

matic ($k = 20-500 \text{ L}/(\text{mol} \cdot \text{s})$) hydrocarbons, and C–C bonds in the α -position to the aromatic ring ($k = 0.2-10 \text{ L}/(\text{mol} \cdot \text{s})$) compared to C=C bonds of benzene ($k = 0.06 \text{ L}/(\text{mol} \cdot \text{s})$) and C–C bonds of alkanes and cyclanes ($k = 0.02-0.20 \text{ L}/(\text{mol} \cdot \text{s})$) are among them [13].

Furthermore, high-molecular-mass resin products were subjected to integrated analysis. According to elemental analysis data, ozonized resins have the following composition, mass %: C 67.1, H 6.7, S 0.6, O 25.6; H/C 1.19; O/C 0.29. Analysis of ^{13}C , ^1H NMR, and IR spectra (see Fig. 1) suggests that resin products obtained during kerosene ozonation include oxygenated compounds of mainly aliphatic or alicyclic composition, which is proven by the H/C atomic ratio, the values of which are more than 1. This is indicated by the presence of the three most intense bands of CH_2 groups (5–40 ppm (^{13}C NMR), 1.1–1.8 ppm (^1H NMR), 2850–3100, 1460, 930, 720 cm^{-1} (IR)) and CH_3 moieties (5–35 ppm (^{13}C NMR), 0.8–1.2 ppm (^1H NMR), and 1380 cm^{-1} (IR)) [11]. The occurrence of less intense bands corresponding to the C_{ar} , CH_{ar} (110–150 ppm (^{13}C NMR)), HC_{ar} (6.5–7.5 ppm (^1H NMR)), and also CH_{ar} (3040 cm^{-1}) and $\text{C}=\text{C}_{\text{ar}}$ (1600, 1550 cm^{-1}) in NMR and IR spectra prove the presence of a minor fraction of aromatic compounds. Oxygenated compounds are presented by linear aliphatic and cyclic ethers (30, 52, 96–99 ppm (^{13}C NMR), 3–6 ppm (^1H NMR), and 1100–1300 cm^{-1} (IR)); ketones (207 ppm (^{13}C NMR), 2–3.6 ppm (^1H NMR), and 1650–1770 cm^{-1} (IR)); carboxylic acids (168–172, and 176 ppm (^{13}C NMR), 10.2 ppm (^1H NMR), 2500–2700, and 3200–3500 cm^{-1} (IR)) of aliphatic (5–50 ppm (^{13}C NMR), 2–2.6 ppm (^1H NMR), and 1715 cm^{-1} (IR)), and

TABLE 2
Fragmentary composition based on ^1H NMR spectra of kerosene samples

Chemical shift range (ppm)	Proton assignments	Proton distribution among kerosene structural groups, rel. %	
		Initial	Ozonized
0.0–1.0	CH_3 groups of saturated compounds and in γ -position and further positions to aromatic ring	34.21	35.54
1.0–2.0	CH_2 groups of paraffinic chains and cyclanes and CH_3 groups in β -position to aromatic ring	55.32	56.24
2.0–2.25	CH groups of paraffinic and naphthenic moieties	3.25	3.40
2.25–2.8	CH_3 group in α -position to aromatic fragments	1.89	1.99
2.8–4.5	CH and CH_2 groups in α -position to aromatic moieties	0.68	0.18
4.5–6.0	H atoms in olefinic fragments	0.97	0.71
6.0–7.3	hydrogen atoms in monoaromatic compounds	3.03	3.24
7.3–8.0	hydrogen atoms polycyclic and heteroatomic	0.28	0.28
8.0–8.6	hydrogen atoms polycyclic and heteroatomic aromatic rings	0.46	0.38

TABLE 3

Results of laboratory flotation of KS coal (kerosene collector)

Number of experiment	Frother		Concentrate						A_w^d , %	K_{sel}^{**}
	Class	Rate, kg/t	γ_c , %	A_c^d	E_c , %	V_f , mL	R_f , %	C_c , g/L		
1	–	–	57.4	10.5	61.1	130	22.3	84	23.4	0.15
2*	–	–	73.9	8.4	80.5	245	24.5	134	37.5	0.35
3	Ekofol	0.10	70.6	8.7	76.6	235	25.1	116	33.4	0.29
4	same	0.15	73.9	9.1	79.9	260	26.2	119	35.5	0.31
5	same	0.20	75.3	9.5	81.1	280	26.8	120	35.8	0.31
6	PGMBE	0.10	69.9	8.8	75.8	220	25.0	111	32.6	0.28
7	same	0.15	73.6	9.5	79.2	255	25.5	114	34.1	0.29
8	same	0.20	74.8	9.6	80.5	270	25.9	125	35.0	0.30

* Ozonized kerosene as a collecting agent.

** $K_{sel} = (A_w^d - A_c^d) / (100 - A^d)$ where A_w^d , A_c^d , and A^d are ash contents of waste, concentrate and initial coal, respectively.

*** PGMBE is polypropylene glycol monobutyl ether frother.

aromatic (120–150 ppm (^{13}C NMR), 7.5–8 ppm (^1H NMR), and 1695 cm^{-1} (IR)) composition, esters, lactones, and anhydrides (160–165 ppm (^{13}C NMR), 2–2.5 ppm, 7.5–8 ppm (^1H NMR), 1780–1730, and $1300\text{--}980\text{ cm}^{-1}$ (IR)). Sulphur detected by elemental analysis may be a part of sulphones and sulphoxides (146, 51–53, and 33–37 ppm (^{13}C NMR), 2.5 ppm (^1H NMR), 1300, 1150, and 1050 cm^{-1} (IR)) [11].

Analysis of the chemical and fragmentary composition of ozonized resins testifies the presence of high contents of acidic compounds ($K_o = 2.2$), which suggests that these gums may be used to produce polyester paint and anti-corrosion protective coatings [14].

Kerosene and derivatives based therefrom were assessed as reagents during flotation of KS coal fines with ash content of 16.0 %. Sludge flotation using the unmodified paraffin facilitates the preparation of a concentrate with ash content (A_c^d) of 10.5 % in the amount (γ_c) of 57.4 % (Table 3). This testifies the low efficiency of the collecting agent without another addition of modifiers and foamers. The use of ozonized kerosene as the main agent of ozonized kerosene allowed increasing the concentrate yield by 16.5 %, whereas waste ash content (A_w^d) – by 14.1 %. Herewith, the selectivity coefficient of the process increased more than twice compared to the initial kerosene. Apparently, the appearance of heteropolar oxygenated compounds in its composition resulting from ozonation that are able to form hydrogen bonds with hydrophilic groups on coal surface facilitates increased flotation activity of kerosene, which contributes to the fastening of the reagent and hydrophobization of the surface of coal grains [15].

Experiments with the addition of commercial alcohol-based frothers, such as polypropylene glycol monobutyl ether frother and Ekofol, have demonstrated similar results. Flotation activity of kerosene is increased during their introduction, whereas at high concentrations (0.2 kg/t), the yield of pure coal products becomes higher than that during flotation with ozonized kerosene. However, the concentrate ash content is significantly higher, which has an effect on an increase in coal losses with flotation waste and testifies weak selectivity of the reagents. Apart from that, the addition of polypropylene glycol monobutyl ether frother or Ekofol, the cost of which is 3–5 times higher than the value of kerosene, to the latter results in a significant increase in the cost of coal products.

The use of ozonolytic modification facilitates the transformation of an apolar reagent that is kerosene collector, into a reagent with comprehensive effects that has collecting and foam forming properties, as demonstrated by flotation results. Flotation foam parameters (V_f and R_f) for ozonized kerosene are not only highly competitive with frothers, such as polypropylene glycol monobutyl ether frother and Ekofol (see Table 3), but are also significantly superior to them according to properties. Thus, foam formed during flotation is less water-flooded (C_c) and easier decomposable (R_f). In such a manner, there is the technical and economic feasibility for the use of ozonized kerosene as a more selective and efficient reagent during flotation of coking coal sludges.

CONCLUSION

Resulting from ozonation, there are transformation and redistribution of kerosene component

composition with increasing the fraction of heteropolar oxygenated compounds. In the hydrocarbon composition of kerosene, the relative content of aliphatic CH₂-bonds in the α -position to the aromatic ring is decreased with increasing here-with the fraction of methyl, methoxyl, alkyl ether, and alicyclic compounds. The portion of polycyclic arenes herein is decreased, whereas that of monocyclic arenes is increased; the contents of aliphatic carboxylic acids, linear and cyclic ethers and esters, lactones and anhydrides, and also aromatic ketones are elevated.

Kerosene modification with ozone facilitates the preparation of flotation reagents of the comprehensive effect that combine properties of collector and frother almost not to be inferior in properties to combined reagents based on apolar hydrocarbon and alcohol-based reagents.

Oxygenated resins generated resulting from kerosene ozonation may be used during the production of polyester resins and paint insulating coatings.

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