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Comparing the Efficiency of Various Oxidizers for Diesel Fraction Sulphur-Containing Compounds in Two-Stage Desulphurization Process Combining Oxidation and Adsorption

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Abstract

A comparative analysis was performed concerning the oxidation efficiency for sulphur-containing compounds of diesel fraction employing various oxidizers (ozone, peroxides) in a two-stage desulphurization process (the combination of oxidation and adsorption). The oxidation level of the diesel fraction sulphur-containing compounds has been studied depending on the amount an oxidizer used and on the conditions of the process. Changes in the group composition of saturated and aromatic hydrocarbons, sulphur-containing compounds of saturated and aromatic nature due to sample oxidation and the subsequent adsorption purification of the products obtained have been analyzed.

Key words: diesel fuel, oxidative desulphurization

INTRODUCTION

The growing consumption of mineral oil and the increase in the scale of petroleum production connected with this fact are accompanied by an increase in the portion of sulphurous petroleum in the general balance of petroleum processing. Catalytic methods of desulphurization widely used in petroleum refining industry, in particular, the processes of hydrodesulphurization have almost reached the efficiency limit. For the last years one can observe an intensive development of non-catalytic desulphurization technologies such as extraction [1], adsorption [2], the combination of oxidation and extraction [3], *etc*.

Especially noteworthy are the processes of selective oxidation of sulphur-containing compounds (SC) with the subsequent removal of high-polarity oxidation products formed. One of the promising reagents for preliminary oxidative purification of petroleum distillates from SC is presented by ozone that readily reacts with SC and polycycloaromatic hydrocarbons [4, 5], however, up till now it has not obtained any practical application. The authors of [6, 7] have demonstrated the possibility of desulphurization of both crude mineral oil, and oil fractions by means of ozonization and the subsequent removal of high-polarity products obtained.

The purpose of the present work consisted in the studies on the efficiency of oxidative desulphurization of the diesel fraction with the use of various oxidizers (ozone, the mixture of hydrogen peroxide and a formic acid, *etc.*) and on the change in the group composition of saturated, sulphur-containing and aromatic compounds in the samples under investigation.

EXPERIMENTAL

We exposed to oxidation a virgin diesel fraction (200–360 °C) sampled at the Ryazan Oil Refinery Company (RORC). The content of total sulphur (S_t) in the fraction amounted to 1.19 % with the mass fractions of sulphide-like sul-

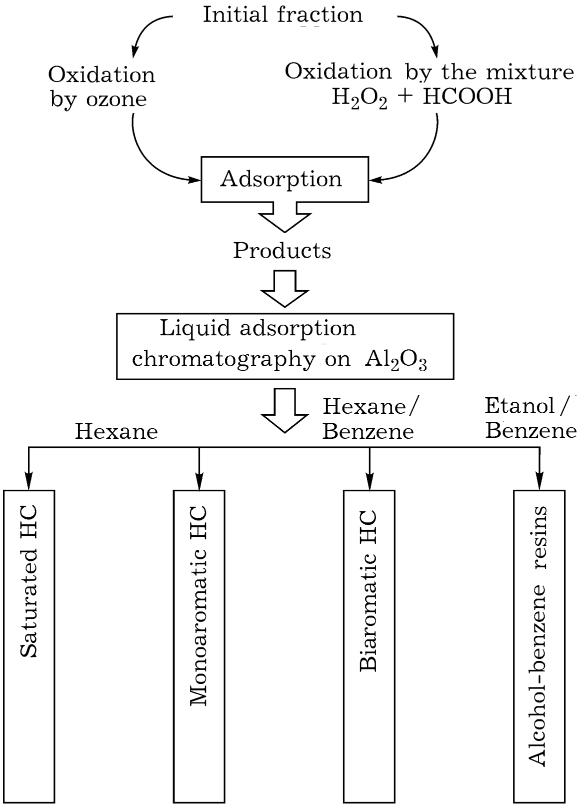

Fig. 1. Schematic outline of the experiment.

phur (S_s) equal to 0.26 %. The general pattern of the experiment is presented in Fig. 1.

The initial diesel fraction was treated with an ozone-oxygen mixture with the help of a laboratory-scale set-up equipped with a bubbling type reactor [5] (Fig. 2). Compressed oxygen (technical grade, Tomskneftekhim Ltd., Tomsk) was supplied from a cylinder *1* through a gas reducer *2* and a needle valve *3* with a flow rate amounting to 31.15 L/h to the system for gas dewatering and purification *4* which included absorbers with sulphuric acid and activated silica gel; further the mixture was passed through a rotameter *5* into an ozone generator *6*. The latter represented a battery consisted of 12 Berthelot tubes, fed in parallel by 14 kV AC current from a step-up transformer. An ozone-oxygen mixture obtained containing 3.66 g/L O_3 was supplied to a reactor *7*, wherein the mixture was bubbled through the layer of raw material. The height of the reactor amounted to 350 mm, the internal diameter was equal to 20 mm. At the bottom part of the reactor there was a Schott glass filter built-in with the pore diameter of 160 μm, to produce the stream of fine bubbles for increasing the contact interface between the gas phase and the liquid in the course of intense bubbling through the layer of the liquid. Spent gas was supplies to an analyzer of ozone. The mass of raw material loaded into the reactor amounted to 15–20 g; the time of passing the gas bubbles through the liquid layer (the contact time of the phases) was about 1 s. According to data obtained earlier by the authors of [5], the amount of absorbed ozone was varied within the range of 1.5–30 g/kg of a sample. The monitoring of the amount of ozone absorbed was performed using a Tsiklon-5.11 analyzer. The essence of the method consists in the selective UV radiation absorption by ozone at the wavelength of 254 nm. The ozonization of diesel fraction due to its low viscosity can be carried out at a room temperature.

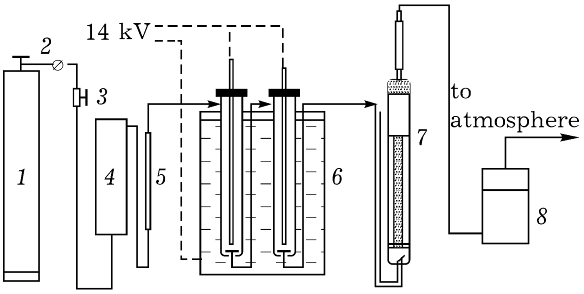

Fig. 2. Schematic diagram of ozonization set-up with a bubbling reactor: *1* – cylinder with compressed oxygen, *2* – gas pressure reducer, *3* – fine control valves, *4* – gas dewatering and purifying system, *5* – rotameter, *6* – ozone generator, *7* – reactor, *8* – Tsiklon-5.11 ozone analyzer.

The oxidation of diesel fuel by 30 % hydrogen peroxide solution (chemical purity grade, the Innovatsia Ltd., Voronezh) was carried out at the temperature of 70 °C during 1 h in the reactor supplied with an agitator, under stirring with the rotation frequency of 700 min^{-1}. The molar ratio between total sulphur and hydrogen peroxide (S_t : H_2O_2) was varied from 1 : 1 up to 1 : 20. The oxidation of diesel fuel by the mixture of hydrogen peroxide and formic acid (pure grade, Germany) was carried out by employing the technique described in [8], at the temperature of 70 °C in the reactor supplied with an agitator, under stirring with the rotation frequency of 700 min^{-1} during 1–4 h. The molar ratio values were the following: $S_t : H_2O_2 = 1 : 4$, $H_2O_2 : HCOOH = 3 : 4$.

The oxidation of diesel fuel by organic peroxides such as benzoylperoxide and di-*tert*-bulylperoxide (chemical purity grade reagents, Merck KGaA, Germany) was carried out under the same conditions as the oxidation by hydrogen peroxide. The choice of the process temperature was determined peroxide used being 1–2 °C higher than the temperature of peroxide decomposition (150 and 135 °C for benzoylperoxide and di-*tert*-butylperoxide, respectively).

After the oxidation the samples were exposed to the adsorption purification (a column modification) which was carried out using a glass column 400 mm in height and 11 mm in diameter. The adsorbent employed was presented by ASK silica gel. The temperature of adsorption was varied within the range from 20 to 80 °C. The silica gel was preliminary dried at 200 °C during 8 h. Packing the column with SiO_2 was carried out by means of a "dry" method. The ratio between the mass of a sample and the mass of a sorbent amounted to 3 : 1, the elution rate was equal to about 0.2 mL/min. The residues of a sample were removed from the silica gel with the help of hexane (analytical grade, Reaktiv JSC, Novosibirsk) which was then distilled off.

The group hydrocarbonic composition of the initial distillate, as well as of the products of its ozonization and oxidation by hydrogen peroxide-formic acid mixture with the subsequent adsorption purification was determined employing the method of liquid adsorption chromatography on activated aluminium oxide having a Brockman activity level II. With this purpose the fractions of saturated, mono- and biaromatic hydrocarbons (HC) were eluted by *n*-hexane, the fractions of triaromatic HC were eluted by a hexane-benzene mixture (analytical grade, Reactiv JSC, Novosibirsk) with a volume ratio equal to 3 : 1: resins were eluted using the mixture of ethanol (Lux grade, Mariinsk Alcohol Plant) with benzene (1 : 1 in volume). The monitoring of separation concerning different HC classes was carried out according to optical absorption spectra of eluates registered employing a Specord UV-Vis spectrometer. The mass loss due to distilling solvents out of eluates was less than 2.5 %.

The gas-liquid chromatography investigation was performed by means of a Kristall-2000M chromatograph with a 25 m × 0.22 mm quartz capillary column packed with SE-54 stationary phase, using helium as a carrier gas. With the use of a flame ionization detector (FID) a linear increase in temperature ranged from 80 to 290 °C and the column heating rate was equal to 15 °C/min for the analysis of saturated HC fractions, whereas for the fractions of aromatic HC the latter parameter amounted to 2 °C/min. For the analysis of SC we used a flame photometric detector (FPD); in this case the increase in temperature ranged from 50 to 290 °C and the column heating rate was equal to 4 °C/min.

RESULTS AND DISCUSSION

In order to increase the efficiency the adsorption process we have investigated the content of sulphur in the products of adsorption purification of ozonized diesel fraction depending on the temperature of adsorption. The best results were obtained at the adsorption temperature of 80 °C (Fig. 3). So, at the amount of ozone absorbed by a sample equal to 12 g/kg and the adsorption temperature of 80 °C the mass fraction of the total sulphur decreases down to 0.46 %. In the case of occurring the adsorption process at a room temperature this parameter amounted to 0.72 %.

The result obtained is caused by the fact that with the rise in temperature the viscosity of diesel fraction decreases. Due to this fact the diesel fraction much more readily penetrate into the sorbent pores, with involving a great number of active centres of the sorbent in the separation process. Thus, the oxidation of the diesel fraction by the ozone-oxygen mixture and the subsequent adsorption-based purification at 80 °C allow one to reduce the content of the

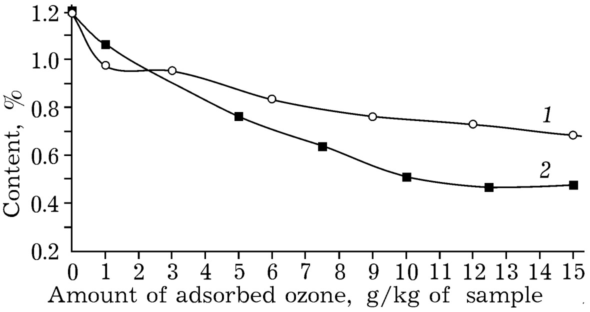

Fig. 3. Sulphur content in ozonized samples after adsorption purification at the temperature of 20 (*1*) and 80 °C (*2*).

TABLE 1

Sulphur removal level after the fraction oxidation by means of different peroxides and adsorption purification

Molar ratio $S : H_2O_2$	S_t, mass %/S_t removal level, % after oxidation with the use of:		
	H_2O_2	DTBP	BP
1 : 1	0.84/30	0.98/18	1.06/11
1 : 2	0.82/31	–	–
1 : 3	0.81/32	0.89/25	–
1 : 5	0.80/33	–	0.56/53
1 : 6	–	0.68/43	–
1 : 9	–	0.60/50	–
1 : 10	0.79/34	–	0.25/79
1 : 15	0.77/36	–	–
1 : 20	0.72/40	–	–

total sulphur therein by 62 %. In the further experiments the adsorption of oxidized samples was carried out only at 80 °C.

We have conducted a number of experiments concerning the selection of optimum conditions for the oxidation of the sample under investigation employing various peroxides. Table 1 demonstrates data concerning the desulphurization level for the diesel fraction (the oxidation by commercial 30 % aqueous solution of hydrogen peroxide) depending on the $S_t : H_2O_2$ ratio. One can see that the desulphurization level grows insignificantly with the increase in the content of hydrogen peroxide. To all appearance, this fact could be caused by an insufficient area the contact interface between aqueous and organic phases in the course of the oxidation process. With the increase in the amount of an oxidizer grows one can observe also the resinification of the fractions owing to a low selectivity of hydrogen peroxide as an oxidizing agent.

We have determined the desulphurization level due to the oxidation of the diesel fraction by organic peroxides such as benzoylperoxide and di-*tert*-butylperoxide (DTBP). Table 1 also presents data concerning the content of sulphur in the products of DTBP oxidation of a distillate fraction after the adsorption purification. Despite of a considerable excess of DTBP (up to 9 mol of the peroxide per 1 mol of sulphur in a sample) as compared to stoichiometrically required amount (2 mol of the oxidizer for a sulphur atom transition to the six-valent state such as sulphon), the content of sulphur in the products decreased only by 50 % (from 1.19 to 0.49 mass %). From the data of Table 1 one can see that benzoyl peroxide exhibits a considerable selectivity as compared to DTBP: the use of the former after the adsorption-based purification results in removing 80 rel. % of sulphur from the oxidized sample. However, in this case the consumption of the oxidizer was also high amounting up to 10 mol of H_2O_2 per 1 mol of sulphur contained in the sample.

In order to choose more selective and cheaper oxidizers we have performed the analysis of literary data. So, the authors of [8–10] described the methods for the oxidation of SC by the mixtures of commercial hydrogen peroxide and carboxylic acids (formic acid, acetic acid). The employing of the oxidizing mixture suggested in [8], has allowed us to remove more than 90 % of sulphur from the raw material composition (Table 2). In this case the consumption of oxidizer appeared much less amounting up to 4 mol of H_2O_2 per 1 mol of sulphur contained within the sample.

In order to reveal changes in the group composition of the fractions we investigated the following samples: the initial diesel fraction; the sample after oxidation by ozone (ozone consumption amounting to 12 g per 1 kg of raw material) and the subsequent adsorption purification; the product of the adsorption purification of diesel fraction oxidized by hydrogen peroxide–formic acid mixture. The results of the separation carried out according to a standard technique on activated aluminium oxide are presented in Table 3. One can see that, for the samples after oxidation the contribution of saturated hydrocarbons (alkanes, isoalkanes, naphtenes) is higher, whereas the content of aromatic compounds is lower comparing to the

TABLE 2

Sulphur removal level after the fraction oxidation by means of H_2O_2 + HCOOH mixture and adsorption purification

Oxidation time, h	S_t, mass %	S_t removal level, %
1	0.50	58
2	0.31	74
3	0.13	89
4	0.09	92

TABLE 3

Group composition of samples under investigation, mass %

Samples	HC			
	Saturated	Monoaromatic	Biaromatic	Triaromatic
Initial fraction	53.8	28.2	13.8	2.2
After oxidation by ozone	58.7	24.2	10.2	1.9
After oxidation by $H_2O_2 + HCOOH$	66.3	17.4	9.2	2.6

initial fraction. Moreover, the mixture consisting of hydrogen peroxide and formic acid exhibits much more active oxidation of aromatic compounds as compared to the ozone-oxygen mixture (40 rel. % of monoaromatic compounds and up to 35 rel. % of biaromatic compounds have been oxidized). The contribution of triaromatic compounds varies insignificantly, which, to all appearance, could be caused both by kinetic factors (the compounds with a high content in the mixture are oxidized up to a greater conversion level than the compounds with a low content), and by insufficiently selective effect of oxidizers belonging to different groups exerted with respect to aromatic compounds. In the course of diesel fraction oxidation the contribution of triaromatic compounds increases owing to the oxidation of a significant part of mono- and biaromatic compounds and the redistribution in the content of the rest groups of HC.

In order to determine the ability with respect to oxidation for various groups of compounds contained in the samples, we performed GLC analysis. Table 4 demonstrates data concerning the content of *n*-alkanes and some groups of alkylaromatic compounds in the initial fraction and in treated samples. It is known, that irrespective of the type an oxidizer chosen the oxidation reaction rate for aromatic compounds decreases according to the following order: triaromatic HC > biaromatic HC > > monoaromatic HC > naphtenes > alkanes. The reactivity of organic SC in the reactions of oxidation decreases to the following order: sulphides > thiophenes > benzothiophenes (BT) > > dibenzothiophenes (DBT). However, from the data presented one can see that the content of *n*-alkanes in the sample oxidized by ozone-oxygen mixture has decreased, in spite of the minimal relative oxidation reaction rate. To all

TABLE 4

Content of *n*-alkanes and monoarenes in the samples under investigation

Groups of compounds	Content, mass %		
	Initial fraction	After oxidation by ozone	After oxidation by $H_2O_2 + HCOOH$
n-Alkanes	33.7	31.7	46.2
Alkylbenzenes	1.7	2.0	1.3
Methylalkylbenzenes	1.8	2.2	1.6

TABLE 5

Content of some bi- and triarenes in the samples under investigation

Groups of compounds	Content, mass %		
	Initial fraction	After oxidation by ozone	After oxidation by $H_2O_2 + HCOOH$
Naphthalene	0.010	0.010	0.005
ΣMethylnaphtalenes	0.522	0.423	0.115
Σ Dimethylnaphtalenes	0.958	1.039	0.248
Σ Trimethylnaphtalenes	1.436	1.143	0.304
Phenantrene	0.060	0.100	0.057
Σ Methylphenantrenes	0.230	0.299	0.198

TABLE 6

Content of sulphur-containing compounds in the samples under investigation

Groups of compounds	Content, mass %		
	Initial fraction	After oxidation by ozone	After oxidation by H_2O_2 + HCOOH
Benzothiophene (BT)	0.0476	0.0176	0.0071
Σ Methyl-BT	0.1960	0.0743	0.0354
Σ Dimethyl-BT	0.1114	0.0195	0.0181
Dibenzothiophene (DBT)	0.0422	0.0109	0.0031
Σ Methyl-DBT	0.1405	0.0759	0.0042
Σ Dimethyl-DBT	0.0859	0.0524	0.0013

appearance, this could be connected with the fact that the molecule of ozone reacts with sulphur-containing and aromatic compounds according to the mechanism of electrophilic addition, whereas this molecule interacts with alkanes according to free radical mechanism [4]. Thus, ozone initiates the oxidation of alkanes by oxygen, which also occurs via the radical mechanism.

Table 5 displays data concerning the content of some bi- and triarenes in the samples under investigation. One can see that the oxidation level resulted from the action of ozone-oxygen mixture on naphthalene and its homologues is low, whereas the content of phenantrenes increased. As opposed to ozone-oxygen mixture, the mixture of hydrogen peroxide and formic acid exhibits a much higher selectivity with respect to the oxidation of biaromatic compounds. The content of naphtalenes has decreased by 75 rel. %. At the same time the oxidation level of phenantrenes was insignificant, which could be caused by their low content in the initial diesel fraction.

Data concerning the content of main SC groups are presented in Table 6. One can see that the mixture of hydrogen peroxide and formic results in the oxidation of SCC to a much greater extent than the ozone-oxygen mixture. The removal level for BT due to the oxidation by the ozone-oxygen mixture amounts to 69 rel. %, that for DBT is equal to 50 rel. %, and with the growth in the DBT substitution level the the removal level decreases. The content of dimethyldibenzothiophenes whose molecules are the most stable in usual processes of hydrorefining [11, 12] was reduced only by 40 rel. %. This is caused by the fact that the centre of electrophilic attack by ozone molecules represents unshared electron pairs localized at sulphur atom. With the growth of DBT substitution level, an increase in steric hindrances occurs with respect to attacking the electron pairs of sulphur atom by ozone molecules. The mixture of hydrogen peroxide and formic acid results in the oxidation of substituted BT and DBT to a greater extent than it does for non-substituted BT and DBT. To all appearance, the process of oxidation by this mixture occurs through the stage of aromatic and sulphur-aromatic compounds protonation by formic acid soluble in HC medium. Hence, the introduction of alkyl substituents should facilitate the formation of intermediate protonated products, since alkyl substituents exhibit a positive inductive effect, *i. e.* these substituents are pushing electron density through σ-bonds. As a result, the total content of DBT has decreased by 96 rel. %, the content of dimethyldibenzothiophenes has decreased by 98 rel. %. Thus, the mixture of hydrogen peroxide and formic acid serves as a selective oxidizer which reacts mainly with sulphur-containing substances reacting to a lesser extent with aromatic compounds.

CONCLUSION

1. Optimum conditions for the oxidation and the subsequent additional purification of distillate fractions from sulphur-containing compounds are established.

2. The treatment of diesel fraction by ozone-oxygen mixture results in the oxidation of all the types of compounds present in the fraction. The derivatives of BT and DBT are oxidized to a greater extent than their hydrocarbonic analogues, whereas their removal level

decreases with an increase in the substitution level of the molecules.

3. The oxidation of the fraction by the mixture of a hydrogen peroxide and formic acid results in a predominant oxidation of SC of saturated (sulphides) and aromatic (thiophenes and BT) nature as well as of aromatic hydrocarbons; the removal level for BT and DBT derivatives increases with the increase in their substitution level.

REFERENCES

1 I. V. Babich, J. A. Moulijn, *Fuel*, 6 (2003) 607.

2 S. K. Ritter, *Chem. Eng. News*, 40 (2002) 32.

3 J. C. Gentry, F. M. Lee, *NPRA 2000 Ann. Meeting*, (2000) 16.

4 S. D. Razumovskiy, G. E. Zaikov, Ozon i Yego Reaktsii s Organicheskimi Soyedineniyami, Nauka, Moscow, 1974.

5 V. F. Kamyanov, A. K. Lebedev, P. P. Sivirilov, Ozonoliz Neftyanogo Syrya, Rasko, Tomsk, 1997.

6 A. K. Lebedev, T. V. Filimonova, T. V. Antonova, Vsesoyuz. Konf. po Khimii Nefti (Thesises), Tomsk, 1988, p. 68.

7 T. V. Antonova, P. P. Sivirilov, V. F. Kamyanov, III Mezhdunar. Konf. po Khimii Nefti (Proceedings), Tomsk, 1997, p. 193.

8 Guoxian Yu, Shangxiang Lu, Hui Chen, Zhongnan Zhu, *Energy&Fuels*, 19 (2005) 447.

9 Shujiro Otsuki, Takeshi Nonaka, Noriko Takashima, *Ibid.*, 14 (2000) 1232.

10 Eika W. Qian, Franck Dumeignil, Hiroshi Amano, Atsushi Ishihara, *Prepr. Pap.-Am. Chem. Soc., Div. Pet. Chem.*, 40 (2005) 430.

11 Jae Hyung Kim, Xiaoliann Ma, *Energy&Fuels,* 19 (2005) 353.

12 Naoto Koizumi, Kentaro Hata, Akira Nishina, *Am. Chem. Soc., Div. Pet. Chem.,* 50 (2005) 382.