

Serhiy Pysh'yev, Olexander Lazorko and Michael Bratychak

OXIDATIVE PROCESSING OF LIGHT OIL FRACTIONS

*Lviv Polytechnic National University,
12 St. Bandera str., 79013 Lviv, Ukraine*

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Abstract. The analysis of oxidation processes necessary for quality improvement of oil fractions boiling to 623 K have been carried out. Different oxidative technologies for crude oil processing have been examined. Their advantages and disadvantages have been shown.

Key words: desulphurization, hydrofining, diesel fuel, jet fuel, oxidative desulphurization, sulphur, sulphoxides, sulphones.

Straight-run light oil fractions usually have properties which do not meet the demands for such commercial products as gasoline, jet, and diesel fuels. In order to improve their characteristics, first of all ecological and antioxidizing ones, their oxidation with following separation of formed products by means of filtration, rectification, adsorption, extraction, or combination of the mentioned methods may be carried out.

The essence of oxidative processing of straight-run oil fractions is oxidation of undesirable products (sulphuric compounds and those with oxidation and condensation susceptibility during exploitation) with the formation of heavier and more polar liquid products compared with the initial compounds or solid deposits. Sulphuric compounds are mainly oxidized to sulphones and sulphoxides. Thus, solid oxidation products may be separated by filtration, and liquid products – by adsorption or extraction due to the presence of polar groups (mainly S=O and O=S=O) in their structures. Moreover, boiling temperatures of sulphoxides and sulphones are higher by 40–200 K compared with corresponding hydrocarbons [1] allowing to separate them from reactive mass by ordinary distillation.

All oxidation processes of light oil fractions may be conditionally divided into 4 groups:

- aimed at fuels sweetening;
- aimed at sulphoxide and sulphones obtaining;
- aimed at decrease of sulphur total content in raw material;

- technologies for improvement of antioxidizing and other operational properties.

Oxidative sweetening of oil fractions is the most studied process and is widely used in the industry. Predominantly it is used for straight-run kerosene and gasoline fractions but not for the diesel ones due to insignificant sour sulphur content. A typical representative of sweetening processes is “Merox” process and its numerous modifications: sweetening process by “Beiker” firm, “Minalk” and “Merox without caustic” by UOP firm, “Bender” process by “Petrolight” firm, etc. The aim of all these processes is to oxidize the most undesirable products – mercaptanes – by air oxygen in the alkaline medium in the presence of a solid catalyst. As a result, mercaptanes are transformed into disulphides, which stay as a solute in the purified fuel. The sweetening takes place at 310–330 K and the pressure of 0.14–0.7 MPa [2-5].

It was shown in [6] that capital outlays on oxidative sweetening plant building are almost 12 times less than those on hydrofining plant building while the products prime cost is less by 17 %.

The processes of oxidative recovery of sulphuric compounds from straight-run oil fractions are referred to the second group. The aim of these processes is obtaining such valuable products as oil sulphoxides and sulphones.

Owing to their unique properties (*e.g.* polarity) sulphoxides and sulphones are widely used in different industries: in petroleum industry – for the production of high-effective inhibitors of solid deposits formation; for the production of corrosion inhibitors, antiscoring and antioxidizing additives; as plastifiers at polymers production; in hydrometallurgy – for enrichment and extraction of various precious and rare metals; for the production of fluorescent materials; in agriculture and animal husbandry – for animals treatment and increase of the crop capacity; as cutting fluids at metals working, *etc.* [7, 8, 9-15, 16]. The first attempts of sulphones and sulphoxides obtaining were based on the fact that sulphides and their oxidation products are dissolved in sulphuric acid with the formation of complexes [17]. In

the later papers [18] it is proposed to use raw material oxidation by hydrogen peroxide in the presence of acids, carbonyl compounds or metals for the sulphones and sulphoxides obtaining from diesel fraction of high-sulphuric Arlan oil (the total sulphur content is 2.2 mas %). In [19] the possibility of sulphones and sulphoxides obtaining from oil distillates is shown. In all cases the main attention was paid to the sulphide sulphur oxidation. Such sulphur makes approximately a half of total sulphur in the raw material. The sulphides oxidation level is up to 76 mas %.

Concerning the application of oxidation for sulphuric compounds removal, it should be noted that to date hydrofining (HF) is the only widely used industrial technology for straight-run oil fractions desulphurization. In spite of definite advantages (known theoretical bases, developed technology, catalysts industrial production) it has a series of shortcomings. This process requires expensive catalysts and hydrogen, which is expensive and scarce. The issue of the day is the decrease of hydrogen production with simultaneous demand for it. Therefore refiners create individual hydrogen plants, which were absent before. One of HF disadvantages is complication of technological flowsheet with obligatory blocks of hydrocarbon and hydrogenous gases purification from hydrogen sulphide. Another disadvantage is the necessity of hydrogen sulphide processing to obtain sulphur or

sulphuric acid. Moreover, during HF heteroatom compounds able to form protective films over metal surfaces are destroyed almost completely thereby decreasing antiwear properties of fuels. During HF natural antioxidants (disulphides and phenols) are also removed from the fuel resulting in the deterioration of fuel chemical stability; increase of its oxidation ability during storage or at high temperatures [20]. It means that fuel corrosion activity may even increase in the case of deep HF [21, 22]. The impossibility to remove sulphur, which is found in the form of condensed compounds based on thiophene derivatives, is also one of the shortcomings. The reason is spatial difficulties arising at their contact with the catalysts.

On the other hand the desulphurization degree requirements for the commercial fuels have sharply increased for the last years. The confirmation of this fact is the value of permissible sulphur content in fuels produced in the USA: 30 ppm in gasoline [23, 24] and up to 15 ppm in diesel fuel [25, 26] starting from January 2006. From 2009 the maximum sulphur content in the fuels must not exceed 10 ppm [24, 26]. The similar or even stricter requirements are set for the fuels produced in the European Union [27]. Often during hydrofining (due to the above-mentioned reasons) it is impossible to obtain fuel with such low sulphur content.

Table

**Effect of fractional composition
on the sulphur removal degree**

No.	Fractional composition of raw material, K	Process conditions (presence of water or catalyst)	Sulphur removal degree, %
1	Wide diesel fraction (approx. 453–623)	Cr ₂ O ₃	23.88
2	> 553	Cr ₂ O ₃	41.84
3	Wide diesel fraction (approx. 453–623)	Water : raw material – 1:10	19.40
4	553–623	Water : raw material – 1:10	27.59
5	Wide diesel fraction (approx. 453–623)	Copper pyrozol polychelate	29.85
6	553–623	Copper pyrozol polychelate	32.18
7	Wide diesel fraction (approx. 453–623)	-	22.39
8	553–623	-	26.44
9	Start boiling point–553	-	71.88

Therefore, the production of fuels with low sulphur content and good lubricating and antioxidizing properties is a very urgent question. Oxidation processes are one of the alternative ways of productions. Many works [28-34, 35-38, 39-44] are dedicated to the oxidation of sulphuric compounds present in distillate fuels by oxygen, hydrogen peroxide, or air oxygen to sulphoxides and sulphones with their following extraction. Thus the total sulphur decreases with sufficient completeness and selectivity.

At Leningrad Technological Institute (Russian Federation) the desulphurization process of straight-run oil fractions has been studied in rotating autoclave in the presence of 3% NaOH. The conditions of the process are: temperature 393–453 K, pressure 1–2 MPa, process time 30 min, ratio between raw material and alkali aqueous solution 1:1, air is the oxidant. The alkaline medium is oxidation inhibitor of hydrocarbon part of the fraction. The sulphur removal degree is 25–36 % for the fraction with boiling limits 513–543 K, 69 % – for the fraction 473–513 K and 100 % – for the fractions 353–413 K and 413–473 K. In order to accelerate the process it was suggested to carry out the process in the presence of a catalyst (chloric copper, 0.005–0.08 % calculated from the fraction mass) in oxidative column of bubble type [41, 44]. Such modification was applied for the desulphurization of diesel fraction 473–573 K. The best results of desulphurization were 59–62 %.

Similar results have been obtained at the Department of Chemistry and Technology of Petroleum and Gas of Lviv Polytechnic National University. The oxidation of the components with various fractional composition was carried out (*vide* Table). Straight-run wide diesel fraction with sulphur content of 0.67 mas % and its individual components were used as a raw material.

The oxidation was carried out in a reactor of bubble type in the presence of water, and without it. Water was used as an oxidation inhibitor [16]. In order to examine the possibility to increase the process selectivity, typical homogeneous catalysts (*vide* Table) were used in the amounts typical of their application in the industry (0.03 mas % calculated for raw material).

The experiments were carried out at 453 K and 3.0 MPa during 30 min. Adsorption was used for products separation.

The comparison of the experiments 1 and 2, 3 and 4, 5 and 6, and 7 and 8 (Table 1) shows that application of raw material with narrower fractional composition allows to increase slightly the oxidation rate and to extract more selectively the oxidation products. The sulphur removal degree increases for the fractions

> 553 K and 553–623 K compared with wide diesel fraction.

The higher sulphur removal degree (No. 9 in Table) is achieved at the desulphurization of lighter raw material (fraction start boiling point–553 K) compared with heavier fractions (No. 7-8 in Table).

Due to the above mentioned facts concerning impossibility of deep sulphur removal during HF the problem of oxidative afterpurification of hydrofined fuels is of great interest [45-49]. The possibility of such fuels production is shown in [50]. Authors propose to use oxidative desulphurization for afterpurification of hydrofined fuels with the aim of fuels production with sulphur content of $(3-8) \cdot 10^{-6}$ %. The experimental plant for running commercial tests has been built.

The investigations with hydrogenate of wide diesel fuel with sulphur content of 0.055 mas % were carried out at the Department of Chemistry and Technology of Petroleum and Gas of Lviv Polytechnic National University. It was shown that it is possible to obtain commercial diesel fuel with sulphur content of 0.010 mas % at 453 K and 2.5 MPa. The obtained fuel meets the requirements for the commercial diesel fuels I [51]. The sulphur removal degree is 81.8 %.

The fourth group of oxidative processes is aimed at the improvement of thermo-oxidative stability of jet fuels (JF) since under the operation conditions they are inclined to oxidative or thermal condensation with the formation of solid deposits disabling the fuel system of airplanes. Existing technologies are aimed at the oxidation of compounds which are present in JF and capable of condensing. On the other hand, in [16] the results of non-catalytic oxidative desulphurization of straight-run kerosene fractions are presented. They show the possibility to obtain commercial jet fuels from the raw material with boiling limits 413–553 (573) K and initial sulphur content of 0.15–0.46 mas %. The obtained JF have better lubricating properties compared with the products obtained during hydrofining.

Since the lubricating and antioxidizing properties of the commercial diesel fuels (DF) have only recently become a problem of vital importance, detailed information regarding their improvement in the produced products is absent in the literature.

Thus, oxidative purification and refining of light oil fractions are very promising methods despite a series of disadvantages they have: long time of the (3 h), presence of additional stages (sedimentation, washing and drying), usage of alkali and catalyst. Separation of oxidation products from purified fractions is carried out usually by means of adsorptive fractionation, which makes the process more bulky. Moreover, the majority

of fuel desulphurization investigations by oxidation method are aimed at the examination of afterpurification of hydrofined fuels. Only a few of them examine the possibility to obtain commercial diesel fuels directly from straight-run raw material. In any case, the data about the operational properties (lubricating, antioxidizing *etc.*) of the produced fuels are absent in spite of the fact that this way is rather promising (*e.g.* the production of oxidatively purified diesel fractions with good lubricating properties, which may be used as additives for hydrofined fuels).

Though existing methods of oxidative purification and refining of light oil fractions are not widely used or are only being developed, they are perspective and worth paying attention to. After solving of the problem concerning oxidation of sulphuric compounds of straight-run fractions without catalyst or using relatively cheap commercial catalysts and simple separation of oxidation products such processes will be competitive to hydrofining. Moreover, another valuable product – concentrate of sulphones and sulfoxides – can also be obtained from these processes.

References

- [1] Nikolskiy B. (Ed.): Spravochnik khimika: Goskhimizdat, Leningrad 1963, 1.
- [2] Asselin G. and Stormont D.: Oil and Gas J., 1965, **63**, 90.
- [3] Bezvorotnyi P., Alikin A., Mazgarov A. *et al.*: Neftepererabotka i Neftekhimiya, 1999, **7**, 14.
- [4] Petrolieri D'Italia, 1973, **7**, 51.
- [5] Sorkin Y.: Osobennosti pererabotki sernistykh neftei i okhrana okrugashchei sredy. Khimiya, Moskva 1975.
- [6] Sharipov A.: Khim. Techn. Topliv i Masel, 1998, **4**, 9.
- [7] Bolshakov G.: Seroorganicheskie soedineniya neftei. Nauka, Novosibirsk 1986.
- [8] Suniyaev Z. (Ed.): Khimiya neftei. Khimiya, Leningrad 1984.
- [9] Nikitin Yu., Murinov Yu. and Rozen A.: Uspekhi Khimii, 1976, **XLV**, 2233.
- [10] Akhmetov L., Kolbin A., Ismagilov F. *et al.*: Khim. Techn. Topliv i Masel, 1999, **3**, 8.
- [11] Sharipov A.: Khim. Techn. Topliv i Masel, 2001, **1**, 43.
- [12] Garipov T. and Chervyakov D.: IV Nauchnaya sessiya po khimii i tekhnologii organicheskikh soedineniy sery i sernistykh neftey. Zinatne, Riga 1976, 70.
- [13] Radceva G., Ryakhovskaya N. and Sharipov A.: *ibid*, 103.
- [14] Sharipov A.: Neftekhimiya, 1991, **31**, 275.
- [15] Nikolaev A., Torgov V., Andrievskiy V. and Galcova E.: Khimiya processov ekstrakcii. Nauka, Moskva 1970.
- [16] Paniv P.: PhD thesis, Lviv 2002.
- [17] Sharipov A.: Khim. Techn. Topliv i Masel, 1991, **4**, 2.
- [18] Sharipov A., Nigmatulin V., Nigmatulin I. and Zakirov R.: Khim. Techn. Topliv i Masel, 2006, **6**, 45.
- [19] Sharipov A. and Nigmatulin V.: Khim. Techn. Topliv i Masel, 2006, **1**, 38.
- [20] Magaril R.: Teoreticheskie osnovy processov pererabotki neftei. Khimiya, Moskva 1996.
- [21] Smidovych E.: Tehnologiya pererabotki neftei i gaza. Chast 2. Khimiya, Moskva 1980.
- [22] Vishnyakova T., Golubeva I. Popova T. *et al.*: Khim. Techn. Topliv i Masel, 1990, **7**, 28.
- [23] US Environmental Protection Agency, Air and Radiation, EPA420-R-99-023, December 1999.
- [24] <http://www.epa.gov/fedrgstr/EPA-AIR/2001/April/Day-13/a8927.htm>.
- [25] US Environmental Protection Agency, Air and Radiation, EPA420-R-00-026, December 2000.
- [26] US Environmental Protection Agency, February 2001.
- [27] Ishihara A.: Appl. Catalysis A: Genera, 2005, **279**, 279.
- [28] Karaulova E.: Khimiya sulfidov neftei. Nauka, Moskva 1970.
- [29] Avdeeva L., Mashkina A., Sharipov A. *et al.*: IV Nauchnaya sessiya po khimii i tekhnologii organicheskikh soedineniy sery i sernistykh neftey. Zinatne, Riga 1976, 245.
- [30] Mashkina A., Sharipov A., Lyapina N. *et al.*: Neftekhimiya, 1984, **XXIV**, 106.
- [31] Sharipov A., Masagutov R., Suleimanova Z. and Faizrakhmanov I.: Neftekhimiya, 1989, **XXIX**, 551.
- [32] Dudina R., Avdeeva L. and Vlasova L.: Neftekhimiya, 1979, **XIX**, 462.
- [33] Varnakova G., Mashkina A., Kirik N. *et al.*: Kinetika i Kataliz, 1984, **XXV**, 837.
- [34] Mashkina A., Varnakova G., Zagryackaya L. *et al.*: Kinetika i Kataliz, 1981, **XXII**, 607.
- [35] Suleymanova Z., Kolychev V., Pais M. *et al.*: AC SSSR № 4335292/23-04, Publ. 15.03.1990.
- [36] Luk'yanica V. and Galperin G.: Neftekhimiya, 1985, **XXV**, 103.
- [37] Lunin V., Francuzov V. and Likhterova N.: Neftekhimiya, 2002, **42**, 195.
- [38] Lunin V., Likhterova N., Torkhovskiy V. *et al.*: Khim. Techn. Topliv i Masel, 1999, **4**, 38.
- [39] Proskuryakov V., Rozental' D., Vasilieva G. and Semenov G.: VI Nauchnaya sessiya po khimii seroorganicheskikh soedineniy neftei i nefteproduktov. Ufa 1961, 26.
- [40] Sbornik nauchnykh trudov: Raboty v oblasti khimii i tekhnologii topliva. Khimiya, Moskva-Leningrad 1964, 168.
- [41] Sbornik nauchnykh trudov: Raboty v oblasti khimii i tekhnologii topliva. Khimiya, Moskva-Leningrad 1964, 173.
- [42] Sbornik nauchnykh trudov: Khimiya seroorganicheskikh soedineniy sodergashchihsyah v neftyah i nefteproduktah. Khimiya, Moskva-Leningrad 1964, **7**, 192.
- [43] Proskuryakov V., Rozental D. and Vasilieva G.: AC SSSR, № 161845, Publ. 1.04.1964.

- [44] Sbornik nauchnyh trudov: Trudy Vsesoyuznogo instituta pererabotki i ispolzovaniya topliva. 1961, **10**, 64.
- [45] Diehl F., Chapus N., Kasztelan S. and Morel F.: Hydrocarbon Eng., 1999, **4**, 67.
- [46] Danhong W.: Appl. Catalysis A, 2003, **253**, 91.
- [47] Larive J.: Hydrocarbon Eng., 2001, **6**, 15.
- [48] Morris P., Baade W. and Jordan R.: *ibid*, 23.
- [49] Criterion Catalysts and Technologies L.P.: *ibid*, 25.
- [50] Levy R., Rappas A., Decanio S. and Nero V.: World Refining, 2001, **12**, 24.
- [51] DSTU 3868-99. Palyvo dieselne. Technichni umovy.

ПРОЦЕСИ ОКСИДАЦІЙНОГО ПЕРЕРОБЛЕННЯ СВІТЛИХ НАФТОВИХ ФРАКЦІЙ

Анотація. Проведено аналіз процесів окиснення, спрямованих на покращання якості прямогонних нафтових фракцій, які википають до 623 К. Охарактеризовано напрямки використання оксидативних технологій перероблення нафтової сировини. Показано їх переваги та недоліки.

Ключові слова: десульфуризація, гідроочищення, дизельне пальне, реактивне пальне, оксидативне знесірчування, сірка, сульфоксиди, сульфони.