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Oxidative Desulfurization of Hydrocarbon Raw Materials

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Abstract—The recent literature data on various methods of oxidative desulfurization of hydrocarbon raw materials, mainly of motor fuels, in homogeneous and heterogeneous conditions has been reviewed.

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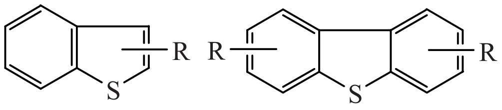
More and more rigid requirements for sulfur contents of motor fuels stimulate search for new ways of purification of hydrocarbon raw materials from sulfur compounds and modernization of existing desulfurization technologies. In most developed countries (Europe, USA, Japan), the maximum accepted sulfur content for motor fuels is presently set at 50 ppm [1–5], and the German regulation enforced in 2001 prohibits use of fuels with sulfur contents exceeding 10 ppm.

Removal of sulfur from diesel fuel is most commonly performed by hydrodesulfurization at T 350–450°C and p_{H_2} 3 MPa in the presence of alumina-supported Co–Mo or Ni–Mo catalysts. Such processing allows the sulfur content of fuel to be decreased to 300–500 ppm. For further purification one should resort to alternative, hydrogen-free technologies. Technologies for deep desulfurization of hydrocarbon fuels are fairly well documented (for example, see reviews published up to 2005 [6–9]). In the present paper we made an attempt to summarize new data on oxidative desulfurization of motor fuels, reported over the past 5–6 years. The abundant literature on hydrodesulfurization which is a principally different, reductive process, is beyond the scope of our review.

Oxidative Systems for Conversion of Sulfur Compounds

The main classes of petro-sulfur compounds are thiols, dialkyl and cycloalkyl sulfides, alkyl aryl sulfides, as well as heteroaromatic compounds, specifically thiophene derivatives. The sulfur compounds that should be removed from diesel fuel fractions to reduce the sulfur contents of the latter from 300–500 ppm to the required level of 10–50 ppm comprise primarily benzothiophene, dibenzothiophene, and their alkyl derivatives [10, 11].



R = H, alkyl.

Sulfur compounds in oil fractions are presently most commonly oxidized with hydrogen peroxide [12] in the presence of various catalysts. This oxidant as a 30% aqueous solution was used for oxidizing the diesel fraction of Arlan oil containing 2.2 wt % of sulfur to obtain sulfoxide concentrates [13]. Peroxo complexes with vanadium [14] and niobium [15] salts we used to oxidize alkyl aryl sulfides to corresponding sulfoxides and sulfones. The reactions occurred in high yields in a two-phase system with oxidant present in the aqueous phase and substrate, in the organic phase. An alternative procedure suggested by Sharipov and Nigmatullin [16] involves oxidation with hydrogen peroxide in foam emulsions in the presence of metals (Mo, V, W) and subsequent catalytic decomposition of sulfones into sulfur dioxide and hydrocarbon. De Fillipis and Scarsella [17] performed detailed research into the mechanism of oxidation of model petro-sulfur compounds (butanethiol, thiophenol, diphenyl sulfide, benzothiophene, dibenzothiphene) with a mixture of hydrogen peroxide and formic acid in various solvents to show that the oxidation kinetics depends on the aromaticity of the organic matrix. The oxidation rate is well described by a first-order equation and increases with increasing C/H ratio in the solvent molecule. The authors suggest that with thiols and sulfides a more intricate oxidation pathway takes place than with benzo- and dibenzothiophenes.

Dibenzothiophenes and its mono- and dialkyl derivatives were oxidized in various oxidative systems; therewith, the reactivity of dialkylbenzothiphenes was found to be much affected by the position of the alkyl groups. The most facile desulfurizarization of dialkylbenzothiophes occurred on the $CoMo/Al_2O_3$ catalyst [18, 19]. In the oxidation of benzothiophene, dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene under the action of *tert*-butyl hydroperoxide on Mo/Al_2O_3, the most active with respect to dibenzothiophene was a catalyst containing 16% of molybdenum, and further increase of the metal content of the catalyst adversely affected its catalytic activity [20]. The following reactivity order of sulfur compounds on the 16% Mo/Al_2O_3 catalyst was established:

dibenzothiophene > 4-methyldibenzothiophene
> 4,6-dimethyldibenzothiophene > benzothiophene.

An interesting example of the oxidation of benzothiophene and dibenzothiophene to sulfones in mild conditions is provided by the reaction with hydrogen peroxide in the presence of crown ethers and in the absence of any metal compounds [21]. Enzymatic oxidation of dibenzothiophene catalyzed by laccase in the presence of 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) was compared with oxidation with hydrogen peroxide in the presence of phosphotungstic acid [22]. The oxidation rate constant of dibenzothiophene in the presence of the enzyme at 40°C in the hexane–ethanol system was higher by a factor of 70 than in the presence of phosphotungstic acid, implying certain preference for the enzymatic oxidation. On the other hand, treatment of diesel fuel containing 342 ppm of sulfur at 60°C gave an almost sulfur-free fuel within 3 h [22]. Of other biological desulfurization methods for benzothiophene-containing fuels we can mention here a method involving use of thermophilic bacteria *Mycobacterium sp. X7B* after preliminary hydride-sulfurization [23]. The combination of these two method allowed the sulfur content of the fuel to be decreased by 86%.

The widespread oxidants for petro-sulfur compounds are various alkyl hydroperoxides. Thus, the oxidation of sulfides of oil fractions with *tert*-amyl, *tert*-butyl, and *tert*-cumyl hydroperoxides in the presence of lower carboxylic acids showed that these starting materials can be used to obtain sulfoxide concentrates in yields of up to 94% [12]. Zhou et al. [24] performed catalytic oxidative desulfurization of dibenzothiophene in decalin using the oil-soluble oxidant cyclohexanone peroxide with a MoO_3 catalyst supported on a weakly acidic macroporous cation-exchange resin. A 100% conversion of dibenzothiophene into dibenzothiophene sulfone could be attained at 100°C within 40 min. Other oil-soluble alkyl peroxides were also tried to establish the following activity order:

cyclohexanone peroxide > *tert*-amyl hydroperoxide
> *tert*-butyl hydroperoxide.

The authors suggested a mechanism of oxidative desulfurization, involving initial coordination of alkyl hydroperoxide with MoO_3 on the surface of the cation-exchange resin, which increases the electrophilicity of the peroxide oxygen [24]. Quite recently Liu et al [25] suggested potassium ferrate as an oxidant for deep desulfurization of diesel fuel. Under optimal conditions at the K_2FeO_4/S ratio of 7.0, the sulfur content of the fuel could be decreased by 97% (from 457 to 15.1 ppm).

Oxidative Desulfurization on Heterogeneous Catalysts

Heterogeneous systems comprising various solid supports (salts, oxides, activated carbon, zeolites) and peroxide oxidants (hydrogen peroxide or alkyl hydroperoxides) have received wide acceptance for removing sulfur compounds from motor fuels. Thus Caero et al. [26] have studied oxidation with hydrogen peroxide on a vanadium catalyst of a series of model compounds: 2-methylthiophene, 2,5-dimethylthiophene, benzothiophene, dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene. The example of a model diesel fuel prepared from hexadecane and the listed compounds was used to establish the following activity order:

4-methyldibenzothiophene > 2-methylthiophene
> 2,5-dimethylthiophene > 4,6-dimethyldibenzothiophene.

Excess oxidant was found to enhance water formation which, in its turn, decelerates oxidative desulfurization. The authors reasonably concluded that the quantity of hydrogen peroxide added to the reaction mixture should be limited.

tert-Butyl hydroperoxide was used as a selective oxidant for a variety of sulfur compounds (methyl phenyl sulfide, diphenyl sulfide, 4-methyldibenzothiophene, 2,5-dimethylthiophene) on CoAPO-5 heterogeneous catalysts (Co/Al 0.15) and 15% MoO_3/Al_2O_3 [27]. The oxidation rate increased with increasing electron density at the sulfur atom and was much higher on the cobalt catalyst than on the molybdenum catalyst. At high conversions of sulfur compounds, sulfones were single oxidation products, whereas at low conversions, small amounts of sulfoxides were also formed. According to UV and visible spectroscopy data, the species involved in the redox reaction also control the overall process rate [27]. Of other solid supports used for thiophene oxidation with hydrogen peroxide, we can mention titanium silicate (TS-1) [28]. The thiophene oxidation pattern at 60°C was found to be affected by the crystal structure of TS-1 and treatment of the support with HCl. Manganese and cobalt oxides on Al_2O_3 also catalyze air oxidation of sulfur compounds in diesel fuel at 130–200°C and atom-spheric pressure [29]. Upon subsequent extraction of oxidation products with polar solvents, the sulfur content decreased to 40–60 ppm. Comparison with hydrodesulfurization results showed that sulfur compounds that are the most active in this process are also highly active in oxidative desulfurization.

A high degree of purification (98%) was attained in mild conditions by treatment with hydrogen peroxide in the presence of polymolybdates on an Al_2O_3 support [30]. Control of the preparation of the catalyst by IR, Raman, and ^{31}P and ^{27}Al NMR spectroscopy and X-ray diffraction analysis revealed decomposition of the catalyst during synthesis to form hepta- and octamolybdates, as well as phosphate ions on the surface [30]. An effective catalyst for oxidative desulfurization of diesel fuel is 0.06% Ag/TS-1 prepared by impregnation. Under the action aqueous hydrogen peroxide in the presence of this catalyst the sulfur content of the fuel decreased from 136.5 to 18.8 mg l^{-1} within 4 h [31].

Of titanium-containing catalysts active in oxidative desulfurization diesel fuel with hydrogen peroxide, we would like to mention Ti/HMS which proved to be highly active in oxidation of dimethylbenzothiophene [32]. The latter was removed by 90% from its model mixture with *n*-octane, and the sulfur content of diesel fuel could be decreased from 226 to 23 ppm at 333 K and the H_2O_2/S molar ratio of 4:1.

Molybdenum-containing catalytic systems are among the most active heterogeneous systems for oxidative desulfurization of diesel fuel. A number of such catalytic systems were recently suggested by Mexican researchers [33] who explored oxidative desulfurization under the action of hydrogen peroxide in the presence of Mo/γ-Al_2O_3. The activity of the catalyst is primarily dependent on the presence of hepta- and octamolybdates on its surface and on the amount of phosphates added. The use of this catalyst at 333 K allows the sulfur content of the fuel to be decreased from 320 to 10 ppm. One of the key stages of the mechanism of oxidative desulfurization, suggested by the authors, is formation of hydroperoxymolybdate fragments of the catalyst surface and their subsequent reaction with dibenzothiophene derivatives to oxidize the latter to sulfones [33].

Activated carbon is a commonly used support for heterogeneous oxidative desulfurization [34, 35]. Its application allows to oxidize remove hydrogen sulfide in gaseous fuel by oxidation with atmospheric air at 150°C [34] and also to perform oxidative desulfurization of diesel fuel under the action of hydrogen peroxide [35]. The higher the absorptive capacity of activated carbon, the higher its activity in benzothiophene oxidation; formic acid additives drive the oxidation reaction. The use of such system allows the sulfur content of diesel fuel to be decreased from 800 to 142 ppm. Additional adsorptive treatment of diesel fuel with activated carbon decreases the sulfur content to 16 ppm.

Yu et al. [36], too, made use of activated coal for oxidative desulfurization of diesel fuel with hydrogen peroxide to remove 98% of sulfur with losses of no more than 3.5%. Systems containing metal ions and aldehydes were found to be effective in oxidation of dibenzothiophenes and oxidative desulfurization of diesel fuel with air oxygen [37, 38]. Cobalt(II), nickel(II), and manganese(II) acetates in the presence of *n*-octanal and *n*-hexanal provide a 99% conversion of dibenzothiophene into sulfone within 15 min at 40°C. By combining oxidation with adsorption on Al_2O_3 or SiO_2 and extraction with a polar solvent Murata et al. [37] could remove more than 97% of sulfur from fuel. The Co/Al_2O_3 and Mn/Al_2O_3 catalysts prepared from Co and Mn acetates showed a fairly high activity in oxidation of dibenzothiophene (up to 62%) with an oxygen/aldehyde system [38]; at the same time, the Ni/Al_2O_3 catalyst prepared from nickel acetate proved to be inactive in this reaction.

Zapata et al. [39] tested a series of solid catalysts for oxidative desulfurization of diesel fuel with hydrogen peroxide and established the following activity order:

$$Pt > Cr_2O_3 > Mn_xO_y > Co - Mo/Al_2O_3.$$

Manganese oxides (Mn_3O_4, Mn_2O_3, and MnO_2) were found to be roughly equally active, irrespective of the concentration of hydrogen peroxide. The authors suggested that oxidative desulfurization competes with catalytic decomposition of H_2O_2, but over a short time (up to 10 min) a 60–70% thiophene conversion could still be attained [39]. Lakshmi Kantam et al. [40] reported on a high catalytic activity of the VO(acac)$_2$ complex on an TiO_2 support in oxidation of sulfides to sulfoxides with *tert*-butyl hydroperoxide. The same authors obtained the same sulfide conversion (99%) but a larger sulfone fraction (up to 44%) in the oxidation products by separately using TiO_2 and VO(acac)$_2$.

The heterogeneous system comprising SBA-15 molecular sieves and phosphomolybdic acid $H_3PW_{12}O_{40}$ was used for oxidativ desulfurization with *tert*-butyl hydroperoxideом of a model fuel made of isooctane and benzothiophene [41]. This system, acting both as a catalyst and as an adsorbent, is capable of removing up to 90% of dibenzothiophene in one stage. As shown by IR spectroscopy, desulfurization in accompanied by formation of peroxide intermediates on the catalyst surface. Good results in benzothiophene oxidation were obtained with a nanocrystalline meso-porous titanium silicate catalyst TS-1 [42]. The catalyst was obtained by nanocasting of a nanoporous SMK-3 carbon. Compared with a usual mesoporous titanium silicate TS-1, the nanocrystalline catalyst proved to be more active in oxidation of thiophene and dimethyl-benzothiophenes with hydrogen peroxide.

The supported vanadium catalysts V_2O_5/Al_2O_3 and V_2O_5/TiO_2 were found to be feasible for oxidative desulfurization of synthetic diesel fuel under the action of H_2O_2 at atmospheric pressure and 60°C [43]. It was shown that nitrogenous compounds present in the fuel prevent adsorption of dibenzothiophene on the catalyst surface; therewith, the catalyst activity depends on the type of the nitrogenous compound and decreases in the following order: quinoline > indole > carbazol.

Adsorption Methods of Oxidative Desulfurization

The efficiency of oxidative desulfurization of hydrocarbon fuel is much enhanced if the oxidation process is followed by adsorption of oxidation products on a solid adsorbent. Thus the heterogeneous system on the basis of modified aluminum silicate was used as an adsorbent in desulfurization and denitrogenation of a model fuel of *n*-tetradecane and xylenes and containing dibenzothiophene, aniline, indole, and carbazol [44]. Adsorption of N- and S-containing compounds on the adsorbent surface is accompanied by formation of charge-transfer complexes and suppressed by aromatic hydrocarbons present in the fuel. The highest degrees of denitrogenation and desulfurization (62.5%) were observed when oxidation was combined with adsorption of oxidation products. Saripov and Nigmatullin [45] made use of silica gel to adsorb the oxidation products of a straight-run diesel fraction and catalytic and thermal cracking gas oil with hydrogen peroxide in the presence of a mixture of sulfuric and acetic acids; as a result, the sulfur content of the fuel could be decreased from 482 to 50 ppm.

Adsorption desulfurization of model diesel fuels containing 500 mg g^{-1} of organic sulfur as thiophene, tetrahydrothiophene, and 4,6-dimethylbenzothiophene was performed in a static system and in a flow reactor on zeolite treated with ammonium hexafluorogallate and containing gallium ions [46]. As shown in the cited work, arenes and olefins retard adsorption of sulfur compounds, and thiophene is poorer adsorbed than tetrahydrothiophene and 4,6-dimethyldibenzothiophene.

Oxidative desulfurization of light gasoil (sulfur content 39 ppm) in the presence of the heterogeneous catalyst 16% MoO_3/Al_2O_3 was performed by the action of *tert*-butyl hydroperoxide [47]. More and more active oxidation of sulfur compounds was observed as the O/S ratio was increased to 15, and got slightly less active as the ratio was further increased. The oxidation of each individual compound: dibenzothiophene, 4,6-dimethyl-dibenzothiophene, and C_3-dibenzothiophene, was a first-order reaction with the activation energy of about 32 kJ mol^{-1}. Further absorption treatment of the fuel desulfurized by oxidation decreased its sulfur content to 5 ppm and lower. Denitrogenation by the same procedure allowed the nitrogen content of the fuel to be decreased from 13.5 to 0.8 ppm [47].

Combination of peroxide oxidation of sulfur compounds in motor fuel in the presence of heterogeneous carriers, followed by adsorption of oxidation products was described in a series of patents [48, 49]. The heterogeneous catalysts were solid acid catalysts and/or activated charcoal containing a transition metal oxide. The acid catalysts were chosen of the following group of compounds: sulfated zirconia, sulfated alumina, sulfated tin oxide, sulfated iron oxide, tungstated zirconia, and tungstated tin oxide [49]. Velu et al [50] made use of adsorption desulfurization on a Ni/SiO_2–Al_2O_3 adsorbent to remove sulfur from reactive fuels with initial sulfur contents of 736 and 380 ppm [50]. The adsorptive capacity of the adsorbent was improved 2.5 times if the fuel was preliminary freed of traces of 2,3,7-trimethylbenzothiophene. An optimal adsorptive capacity of the adsorbent (10 mg S g^{-1}, particle size 0.15–0.25 mm) could be attained without using additional pressure to force the solvent through adsorbent bed.

Effective oxidative desulfurization involving catalytic oxidation of sulfur compounds with molecular oxygen in the presence of a heterogeneous catalyst, followed by adsorption on activated charcoal in mild conditions (25°C) was also reported by Ma et al. [51]. More active among the sulfur compounds were found to be benzothiophenes with bulky substituents. An advantage of the proposed procedure is the lack of necessity to perform oxidation in a water–motor fuel biphasic system.

Liu et al. [52] made use of the aluminum silicate adsorbent MCM-41 with varied SiO_2/Al_2O_3 ratio (100, 50, and 30) for deep desulfurization of diesel fuel containing 1786 ppm (at 373 K). The adsorption capacity of sulfur compounds decreases with increasing SiO_2/Al_2O_3 molar ratio in the adsorbent, and sulfur is removed by 95% on the adsorbent with $SiO_2/Al_2O_3 = 50$ at the initial stage and additionally by 75% at the total elution volume of 17 ml. Increased temperature is a negative factor, whereas Cu^+ ions favor adsorption by forming π complexes with sulfur compounds [52]. Peroxide oxidation of model sulfur compounds: thiophene, 2-methylthiophene, benzothiophene, dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene and oxidative desulfurization of diesel fuel were performed under the action of *tert*-butyl hydroperoxide in the presence of the heterogeneous catalyst MoO_3/Al_2O_3 in a static reactor [53]. This catalyst is highly active but gradually loses activity due to leaching of the metal and adsorption of sulfones. The same procedure was used for desulfurization of raw oil [54]. It was based on the application of a mixture of alkyl hydroperoxide, acid, and powdered iron oxide. The reaction involves formation of peroxo acid and hydroxyl radicals. The latter are formed due to the presence of iron oxohydroxide which, according to [54], has a special affinity to the hydrocarbon medium.

Liquid-Phase Oxidative Desulfurization

The most common oxidant used in liquid-phase oxidative desulfurization is hydrogen peroxide in combination with transition metal compounds. Mondal et al. [55] made use of a two-phase system with a phase-transfer agent (Fe–TAML). The reaction was performed in a weakly alkaline medium using *tert*-butanol as solvent acting to solubilize dibenzothiophenes and their oxidation products. The method allows about of 75% of sulfur to be removed from the starting fuel (after additional treatment with silica gel). The process involves oxidation of alkylbenzo- and alkyldibenzothiophenes with the $Fe/TAML/H_2O_2$ system which facilitates adsorption of sulfur compounds on silica gel. Al-Shahrani et al. [56] performed desulfurization of diesel fuel with the oxidizing system comprising Na_2WO_4, 30% H_2O_2, and acetic acid under two-phase conditions: At 70°C after less than 1 h the total sulfur content of the model fuel containing dibenzothiophene and 4,6-dimethyldibenzothiophene has decreased from 1100 to 40 ppm. Otsuki et al. [57] performed oxidative desulfurization of light gasoil containing 1.35% of sulfur, vacuum gasoil containing 2.17% of sulfur, and model sulfur compounds (thiophene, benzothiophene, and dibenzothiophene derivatives) with a mixture of hydrogen peroxide and formic acid [57]; as a result, the sulfur contents decreased to 0.01 wt %. Extraction of sulfur compounds with dimethylformamide is more efficient for oxidation products than for the parent thiophene derivatives. The same oxidative system (hydrogen peroxide in the presence of 96% formic acid in a stoichiometric amount with respect to sulfur compounds, was used for purifying distillates of low- and medium-viscosity fractions of high-sulfur West Siberian petroleum [56]. After additional purification of the oxidate with *N*-pyrrolidone the sulfur content of oil fractions decreased 3 times.

Molybdenum peroxo complexes containing in the coordination sphere by two sulfoxide molecules as ligands were found to actively catalyze the oxidation of diesel sulfides with 30% H_2O_2 [59, 60]. The maximum conversion of sulfides into sulfoxides of 78% could be reached with molybdenum naphthenate as a source of metal. This method is disadvantageous in that the catalyst is irreversibly lost due to its dissolution in the organic phase. Systems comprising mixtures of 30% H_2O_2 with various organic solvents and acids showed the same efficiency in converting sulfides of oil fractions into sulfoxides, those with formic acid being the most active [59].

Rao et al. [61] made use of an isobutyraldehyde/oxygen mixture without a metal catalyst to oxidize dibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene. The efficiency of this system in combination with extraction with a polar solvent was exemplified by oxidative desulfurization of diesel fuel containing 448 ppm of sulfur. This procedure allowed the sulfur content in a two-phase system to be decreased to 77 ppm; the oxidized fuel was then passed through a silica gel column to decrease its sulfur content to 31 ppm.

Ali et al. [62] performed successful oxidative desulfurization of diesel fuel by treatment with a system comprising hydrogen peroxide and an acid catalyst (formic or acetic acid), followed by extraction of oxidation products with acetonitrile. The oxidation at 50°C and atmospheric pressure allowed 92% of sulfur to be removed. Simple extraction of fuel with acetonitrile without preliminary oxidation removed no more than 45% of sulfur, and, therewith, aromatic hydrocarbons are also partially extracted. The rate of oxidation of dibenzothiophene to sulfone increases with temperature. At 20°C up to 70% of dibenzothiophene remains unoxidized in 90 min and at 80°C, as little as 6%. However, such an elevated temperature is not recommended, since many useful components of fuel are, too, oxidized. Formic acid stronger affects oxidation than hydrochloric or acetic acids. By combining oxidation (50°C, atmospheric pressure) and extraction the authors could decrease the sulfur content of diesel fuel by an order of magnitude: from 1044 to 100 ppm, degree of sulfur removal 92%. This method of deep desulfurization is suggested as complementary to hydropurification for the maximum removal of sulfur. Shiraishi and Hirai [63] used the same approach for desulfurization of vacuum gasoil with a mixture of hydrogen peroxide with acetic acid followed by extraction with aqueous acetonitrile [63]. At a 50–100-fold excess of hydrogen peroxide, the sulfur content of gasoil was 57% of the initial value within 6 h and reached a minimum within 30 h. The maximum desulfurization degree (89%) was reached through a combination of oxidation with extraction with 84% aqueous acetonitrile. Comparing the efficiency of hydropurification and oxidative desulfurization the authors gave preference to the latter process, specifically milder conditions and higher reactivity of vacuum gasoil to oxidation compared with lighter fractions.

Diesel fuel can be efficiently purified from sulfur compounds in mild conditions in a water-in-oil emulsion composed of the diesel fraction, 30% H_2O_2, and electrophilic catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ [64, 65]. By treatment in this system followed by extraction the sulfur contents of the diesel fuel and direct gasoil could be decreased from, respectively, 500 and 312 to 1 ppm. In this case, the amphiphilic component functions not only as catalyst but also as emulsifier [65].

Another two-phase nonaqueous system containing acetonitrile and a mixture octane and decane was used to oxidize benzothiophene to benzothiophene sulfone [66]. Equilibrium studies on this system revealed its potential use for quantitative oxidation of sulfur compounds and oxidative desulfurization of various motor fuels. Oxidation followed by extraction also works well at the first stage of purification of diesel fuel by the action of 30% H_2O_2 in the presence of the heterogeneous catalyst WO_x/ZrO_2 containing 15% of tungsten [67]. The first stage was performed in a static reactor at 333 K and atmospheric pressure, after which oxidation products were extracted with a polar solvent; as a result, the sulfur content of the diesel fuel could be decreased from 320 to 90 ppm.

An interesting system for profound purification of fuel from sulfur was suggested by McKinley and Angelici [68]. The procedure involves fivefold extraction of model fuel containing 400 ppm of sulfur with a mixture of 70% of DMF and 30% of H_2O in the presence of $Ru(NH_3)_5(H_2O)^{2+}$, during which the latter reacts with thiophene derivatives (Tf) to form the complex $Ru(NH_3)_5(Tf)^{2+}$; as a result, the sulfur content decreases to 25 ppm.

A two-phase system comprising motor fuel and a mixture of formic acid, H_2O_2, and a phase-transfer catalyst (quaternary ammonium salt) was reported by Zhao et al. [69]. The authors suggested that if the concentration of the quaternary ammonium salt is higher than 0.0019 M it can transfer the polar fragment of the oxidant $[HCOO^-]$ to the nonpolar organic phase; the complex formed in the course of transfer decreases the polarity of the oxidant and the apparent activation energy of the process. Based on the reaction kinetics, the reaction was suggested to have a pseudo-first order.

Other Methods of Oxidative Desulfurization

Desulfurization with Ionic Liquids

Over the past years desulfurization of various motor fuels has been suggested to perform by extraction with ionic liquids (ILs) [9]. Ionic liquids containing Cu(I) and Ag(I) ions were found to the especially efficient due to their tendency for forming π complexes with thiophene derivatives [70]. Chongpin et al. applied ILs obtained by reaction of 1-butyl-3-methylimidazolium chloride with anhydrous powdered CuCl, containing $CuCl_2^-$, $Cu_2Cl_3^-$, and $Cu_3Cl_4^-$ anions resistant to moisture and air, for desulfurization of a model fuel [71]. These systems revealed a high desulfurizing activity toward gasoline. For instance, the ionic liquid $BMImCu_2Cl_3$

extracted 23% of sulfur compounds, whereas $BMImBF_4$ extracted no more than 11%. Potent complex-forming agents dissolved in gasoline hinder extraction of sulfur compounds with IL. As a rule, ILs in themselves, in the absence of oxidants, fail to provide a high degree of sulfur removal. For example, the tungsten and molybdenum peroxo complexes $[WO(O_2)_2$ Phen $H_2O]$ and $[MoO(O_2)_2$ Phen] (Phen is 1,10-phananthroline) immobilized in ILs (3-butyl-1-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 3-methyl-1-*n*-octylimidazolium hexafluorophosphate and tetrafluoroborate) do nothing but extract dibenzothiophene but inactive in its oxidation [72]. Addition of 30% H_2O_2 in an IL creates conditions for catalytic oxidation and extraction, and the degree of sulfur removal increases to 99%. In the absence of ILs, phenanthroline complexes can remove no more than 50% of sulfur. This finding provides evidence in favor of combining catalytic oxidation and extraction. Studying the ability of 1,3-dimethylimidazolium dimethyl phosphate [MMIM][DMP] and 1-butyl-3-methylimidazolium dubutyl phosphate [BMIM][DBP] to extract sulfur from diesel fuel over a wide range of sulfur concentrations showed that the solubility of dibenzothiophene and benzothiophene in aqueous solutions of ILs at 25°C varies in the following order:

[BMIM][DBP] > [EMIM][DEP] > [MMIM][DMP].

Therewith, dibenzothiophene is soluble better than benzothiophene [73]. Of the ILs studied, the most suitable for desulfurization of diesel fuel was found to be [EMIM][DEP] which is fairly highly reactive toward sulfur, poorly soluble in fuel, and affects only slightly other properties of fuel. Of interest is the use in desulfurization of gasolines of ILs synthesized from organic acids (formic, acetic, and benzoic) and nitrogenous bases (aniline, piperidine, and diethylamine) [74]. After threefold extraction of catalytic cracking gasoline with the mentioned ILs, the sulfur content of the latter decreased from 240 to 30 ppm, and the content of aromatic hydrocarbons, from 26 to 14%. Ionic liquids can be regenerated by treatment of the extract with an excess of low-boiling paraffins and repeatedly used for desulfurization. A high efficiency of ILs in desulfurization of diesel fuel was demonstrated by the example of ILs containing 1-butyl-3-methylimidazolium as cation and tetrafuoroborate, hexafluorophosphate, octyl sulfate, ethyl sulfate, and dimethyl phosphate [75]. The suggested technological scheme involving the steps of extraction and regeneration of ILs, allowed the sulfur content of diesel fuel from 500 to 10 ppm.

Alkylation

Arias et al. [76] accomplished successful desulfurization of gasoline by alkylation of low-molecular thiophenes (3-methylthiophene) with alkenes (2-methylbut-2-enol) in the presence of acid catalysts (silica-supported 12-phosphotungstic and 12-silicotungstic acids) followed by distillation of fuel fraction [76]. This process is accompanied by cracking and catalyst poisoning with nitrogen-containing admixtures in the fuel, as well as catalyst carbonization.

Electrochemical Desulfurization

Wang et al. [77] reported successful deep desulfurization of diesel fuel by means of electrochemical catalytic oxidation followed by extraction of oxidation products.

Another approach to desulfurization, specifically electrochemical catalytic oxidation on a complex anode in a flow-through reactor, was described in [78]. The anode was activated with activated carbon-supported chromium oxide CeO_2/C, the electrolyte was aqueous cerium nitrate, and the cathode was a copper plate. The optimal conditions for desulfurization are as follows: cell voltage 3.2 V, $Ce(NO_3)_4$ concentration 0.08 M, CeO_2 load 5 wt %, volume flow rate 300 ml/min. Under these conditions, the sulfur content of the fuel could be decreased from 310 to 50 ppm.

Plasma Desulfurization

An efficient technique of oxidative desulfurization is exposure to organic compounds in the liquid phase to plasma, especially to plasma together with oxygen [79, 80]. The advantage of the liquid-phase technique over gas-phase is that the cooling liquid can fast quench primary products and suppress side reactions [81]. The ratio of oxygen flow to plasma power is a factor that controls the desulfurization process at –85°C; at appropriate conditions the desulfurization degree reaches 99% with respect to thiols and 79% with respect to thiophenes [82]. In the constructed kinetic model of plasma oxidative desulfurization the plasma reaction in the liquid phase is essentially the gaseous reaction occurring under special conditions. The authors of [82] suggested a mechanism of plasma oxidative desulfurization with the key stage involving electron transfer on the oxygen molecule and formation of thiyl and alkyl radicals by electron impact on the thiol, sulfide, or thiophene molecule [82].

Ozonation

Among other methods of oxidative desulfurization of hydrocarbon raw materials we can mention desulfurization of heavy petroleum fractions by ozonolysis and radiolysis [83]. This method not only allows one to destroy condensed sulfur compounds and polyarene structures, but also to obtain on their basis potent emulsifiers [84, 85]. Preozonation of diesel fuels can favor their subsequent hydropurification. Comparison of the results of hydropurification of ozonated and unozonated direct diesel fraction gave evidence for the efficiency of preliminary ozonolysis. Thus, the total sulfur content of the fuel after hydropurification of the ozonated diesel fraction is three times lower (0.032 wt %) than for the unozonated fraction (0.099 wt %). The same result was obtained with polycyclic aromatic hydrocarbons whose content in the fuel after ozonolysis and hydropurification was 1.5 wt % against 2.2 wt % for the direct fraction [83]. Preozonation of the gasoline and diesel fractions with subsequent treatment on a ZSM-5 zeolite catalyst containing 70 wt % of zeolite (SiO_2/Al_2O_3 = 60) and 30 wt % of aluminum oxide at 320–460°C gave fuels with octane numbers higher than 90 and arene contents 56–49% and 61–52%, respectively [86].

Ultrasonication

Ultrasonication of diesel fraction in the presence of aqueous hydrogen peroxide and a quaternary ammonium salt as a phase-transfer catalyst allows the sulfur content of the fuel to be decreased to a level below 0.25% [87, 88]. The formation of by-product 2- and 3-benzothiophene sulfones can be avoided by using a fluorine-containing phase-transfer catalyst [87]. After ultrasonication of diesel fuel in the presence of aqueous hydrogen peroxide, three layers form: oxidized diesel fuel (upper layer), residue (lower layer), and aqueous layer (medium layer). The residue comprises less than 1% of the starting fuel and contains about 2% of sulfur [88]. Oxidativeм desulfurization removes no more than 66% of sulfur within 2.5 h [89, 90], whereas by combining ultrasonication and oxidative desulfurization Mei et al. could remove more than 99% within a few minutes [88], and the yield of the purified fuel was 87%.

Desulfurization in Supercritical Water

Desulfurization of diesel fuel can also be performed using supercritical water [91–94] which, at temperatures above 250°C, behaves like aprotic organic solvents [95]: Its density, dielectric constant, and ability to H-bond formation are much reduced. Desulfurization of sulfones in supercritical water at 380°C for 1 h in the presence of KF and CsF involves an almost quantitative conversion of diphenyl sulfone and dibenzothiophene sulfone [96] to 2-hydroxybiphenyl and phenol, respectively.

The presented evidence shows that oxidative desulfurization of various kinds of motor fuels can serve as a reasonable complement to the large-scale hydropurification process and also as an independent method of deep desulfurization. Taking into account that efficient liquid-phase oxidative desulfurization necessitates large quantities of hydrogen peroxide and organic solvent for extraction of oxidation products, we can suggest this method will be used on a scale comparable with that for hydropurification.

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