

ADVANCES IN DESULFURIZATION RESEARCH OF LIQUID FUEL

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The new requirements for sulfur content in liquid fuels demand the use of novel deep desulfurization processes. 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene and their alkyl-substituted derivatives are the key substances that need to be separated from diesel fuel and fuel oil. These compounds require higher hydrogen consumption in the hydrodesulfurization process and the use of additional infrastructure in the treatment facility. The common hydrogenation catalysts are not very effective for the hydrogenation of these compounds, and new innovation for catalysts is required. The desulfurization of fuel oil obtained from oil shale is also becoming important and has different technological needs than other fuels. This paper critically discusses the non-hydrodesulfurization processes for liquid fuels, such as extraction, oxidation, and adsorption. These processes, their development, and recent advances in this research field are briefly evaluated as possible deep desulfurization methods.

Introduction

In Europe the sulfur level in max mass% for liquid fuels is presently limited at 0.015, 0.035, and 0.2 for petrol (gasoline), diesel fuel, and light fuel oil, respectively [1]. New sulfur limits of 0.003–0.005 mass% (30–50 ppm) for petrol and diesel fuel will be introduced in the European community and USA in coming years [2, 3]. The current technology of hydrodesulfurization is quite adequate for the present standards [3], however the hydrotreating process is limited to the production of ultra-low sulfur fuels, and the consumptions are too high to meet future requirements.

It must be emphasized that desulfurization processes are also essential for the production of fuel oil from oil shale and for oil obtained by the utilization of used tires. The authors of this paper are working in the last field. Although the desulfurization of non-transportation fuels in stationary applications can be realized in emissions by binding up sulfur oxide with

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calcium oxide [4], problems with the utilization of the obtained toxic compounds remain. Therefore the desulfurization processes of fuel oils are of current interest. Requirements for sulfur content will approach extremely low levels, preferably even zero content, in the near future [3], forcing intensive research into alternative technologies.

One confounding factor in this research is that the reactivity to hydrodesulfurization of organosulfur compounds in liquid fossil fuels varies widely. In diesel fuel and fuel oil fractions 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene and other alkyl-substituted derivatives of dibenzo-thiophene are relatively inert to hydrotreating [5].

The conventional reaction model of hydrodesulfurization of diesel fuel and fuel oil does not work effectively in the ultra-deep desulfurization range down to sulfur content 100 ppm or less. The catalyst volumes must be three times more in the case of 50 ppm, and four times more if the aim is to reach the final sulfur content of 30 ppm [6]. A thorough survey concerning the reactivity of sulfur compounds is given by Cremlyn [7]. Hydrotreating processes are not discussed in this paper as many monographs [7–10] and papers [11–14] on the subject are available.

This paper discusses the non hydrodesulfurization processes, such as, extraction, oxidation, adsorption, the combination of these processes, and the combination of these processes with hydrodesulfurization to reduce the consumption of hydrogen. The development of the mentioned processes is given, along with a discussion of recent studies in this field.

Extraction

The well-known UOP Merox extraction process [15] for removing mercaptanes is used for liquefied gases and for all liquid fuel raw fractions. Mercaptanes are extracted with caustic solution. The solution containing Merox catalyst and dissolved mercaptanes are oxidized with air to disulfides. The separated disulfide oil can be hydrotreated or sold as a special product.

Mercaptanes are the most slightly removable sulfur compounds of liquid raw fuels, and the caustic extraction process is widely applied in the production of liquid fuels.

Many extraction processes for removing sulfur-containing compounds have been patented. Some of them are discussed below. Extraction with polyethylene methylether decreases sulfur content by 30% in petrol, diesel fuel, gas oil, and other raw oil fractions [16]. Extraction process of gas oil with aqueous acetone, ethanol, mesityl oxide, and formic acid is also patented. The reduction of sulfur content was estimated to be in the range from 86 to 96% [17]. Unpublished experiments conducted at our institute, found that these solvents resulted in much lower extraction percentages under the same conditions.

Based on our experiments it may be concluded that it is impossible to obtain low sulfur content in desulfurization process only with extraction process. However, an extraction process combined with hydrotreating or oxidation can be very effective. Patented extractive agents used in combination with hydrotreating include: methanol, acetonitrile, monomethylformamide, dimethylformamide, *N*-methyl-pyrrolidone, furfural, dimethylsulfoxide [18], and polyethylene glycols [19].

Extraction of sulfur compounds from gas oil using polyethyleneglykol dimethylether reduces sulfur content by 71%. Deep desulfurization was obtained using the following hydrotreating [20]. The extraction of raw petrol using the same extractive agent and only a mild hydrotreatment followed by complete removal of mercaptanes and thiophenes resulted in 94% removal [19]. Extraction with heterocyclic nitrogen compounds (pyrrolidones, etc.) and using the following hydrotreating guarantees sulfur content to be reduced below 0.01mass% [21].

Analogical results were obtained while using dimethylformamide or furfural as extractive agents combined with hydrotreating [18]. The desulfurization yield for light oil and straight-run light gas oil was enhanced by first extracting the sulfur-containing compounds using acetonitrile followed by photochemical reaction (UV radiation) combined with air bubbling through the reaction medium. Sulfur content was reduced from 0.2 to 0.05% [22]. In contrast the above study, most extractive processes are carried out after an oxidation step, as discussed in the next chapter.

Oxidation

Using the oxidation process it is possible to convert thiophene, benzothiophene, dibenzothiophene and their methyl and higher alkyl derivatives into sulfones and sulfoxides. These compounds can be removed from the mixture by extraction with relative polar solvents, adsorption, cooling or pyrolysis into sulfur dioxide. Desulfurization *via* oxidation has been studied already since the beginning of the 1960s. Some concrete examples from this period are presented below.

Oxidation with peroxides in the presence of a Ni-V catalyst followed by removal of the oxidized sulfur compounds by thermal decomposition at 300–400 °C in the presence of ferric oxide liberates sulfur dioxide. The next step in the desulfurization process by oxidation was hydrogenation in the presence of Co/Mo catalyst. From petroleum fraction boiling above 250 °C, 40% sulfur was removed by oxidation and 45% by hydrogenation [23, 24]. Arabian crude oil containing 2.6 mass% of sulfur was dissolved in petroleum-ether and treated with butyl hydroperoxide in the presence of molybdenum catalyst, the mixture was then heated at 90 °C for a period of 60 hours. Sulfur content after separation by cooling was found to be 1.6 mass% [25]. However, the removal of oxidized sulfur compounds was not complete.

In another example, *tert*-butyl hydroperoxide was used for oxidation of crude oil in the presence of vanadium acetylacetonate at 90 °C. Conversion rate of up to 74% was obtained for sulfur compounds [26]. The same results were obtained by oxidation with peroxides at 400–415 °C and 60–65 atm [27]. The sulfur conversion rate by oxidation of sulfur compounds from petroleum vacuum residue using peroxides reached 50% [28]. This result is not bad for such a heavy oil. Obviously, the removal of oxidized sulfur compounds was not complete. Presented examples may be quite instructive. It shows that alternative methods to the widely used hydrogenation process for reducing sulfur content in raw petroleum and its heavy fractions have been sought after for thirty years. The legislation of new sulfur limits is now forcing the issue and promoting new research into this essential technology. Fuel oil obtained from oil shale or wasted tires is of particular concern. The current standard allows a maximum of 0.8 mass% sulfur content in the fuel oil of oil shale. In the near future this norm will be likely lowered and consequently, the desulfurization of shale oil will be required.

It was demonstrated that it is possible to oxidize thiophene derivatives completely, using peroxides [29]. This is of primary importance for the desulfurization of diesel fuel and higher oil fractions, as thiophene derivatives are the primary sources of sulfur in these fuels. Of academic interest, molybdenum peroxo complexes can also act as oxidation agents [30]. During the 1990s, a number of industrially significant processes for desulfurization of petroleum fractions by oxidation with peroxides and solvent extraction were studied. These resulted in removal rates of 65–80% [31], 89% [32], and 90% [33].

Peroxides are expensive agents compared to the air. However, oxidation of sulfur compounds of raw fuels using air, oxygen, or ozone provisionally gave low conversion of up to 45% [34]. Some relatively cheap oxidants, such as nitrogen oxides and nitric acid, were studied, but the tests gave inadequate results [35]. Ten years later in a modified oxidation process with nitrogen oxides, sulfur was removed from diesel oil in the range of 66–97% and from residual oil 70–86%, respectively [36].

An interesting process was worked out by Guth *et al.* [37]. Desulfurization of petroleum oils was carried out with nitrogen oxides and oxygen to convert organic sulfur into sulfur trioxide which was absorbed with concentrated sulfuric acid. The removal of sulfur was, however, relatively low. Probably one of the first attempts to desulfurize shale oil with nitric acid was patented by Schulz *et al.* [38]. Tam and Kittrell *et al.* [39–42] published many works about oxidizing gas oil and other petroleum fractions with nitrogen oxides or nitric acid. In all cases the oxidized products were removed by solvent extraction.

In recent years there have been many publications about deep desulfurization processes of liquid fuels by oxidation. Deep desulfurization was reached by oxidation with hydrogen peroxide in the presence of phospho-tungstic acid catalyst and a phase-transferic agent [43]. Shiraishi

et al. [44] obtained deep desulfurization by photosensitized oxidation using a triplet photosensitizer in an oil/water two-phase liquid-liquid extraction system. However, two follow up studies, utilizing oxidation and extraction, failed to remove enough sulfur to reach the deep desulfurization level. For gas oil, they reached 0.22 mass% [45], and for diesel fuel 0.01 mass% [46].

The most desirable result was obtained by peroxyacid oxidation ($\text{HCOOH}/\text{H}_2\text{O}_2$). Removal of sulfones and sulfoxides, created during oxidation, was carried out by extraction followed by adsorption with silica gel to reach sulfur content levels of 7.0 ppm and 0.0000%, respectively [47]. Another effective process has been suggested by Mei *et al.* [48, 49]. Phosphotungstic acid, tetraoctyl ammonium bromide and ultrasound were used at 75 °C to complete the oxidation. The oxidized product was then extracted with acetonitrile. Under these conditions dibenzothiophene and its derivatives were removed from diesel fuel at a rate of more than 99%.

In recent years many desulfurization processes with peroxides have been patented: removal of sulfur from 250 ppm to 5 ppm in diesel fuel [50], sulfur removal in diesel fuel from 0.557% to 0.0008% [51], and from gas oil to 82% [52]. In 2004 a patent application concerning desulfurization with oxidation was presented. Oxidation of crude oil was carried out by hydrogen peroxide in the presence of a catalyst, surface-active agent and radiation with sonic energy at 125 °C and *ca* 3 atm. The resulting sulfur content was 0.7%, reduced from 2.5% [53].

Li *et al.* [54] suggested an interesting oxidation catalyst which is also phase transfer agent. Oxidation was carried out using hydrogen peroxide for 30 minutes at 60 °C and 8 minutes at 90 °C. The turnover number was estimated to be higher than 300. After the process the catalyst was separated by centrifugation, and oxidized sulfur compounds were removed with extraction by N-methyl-2-pyrrolidone. Ultra-deep desulfurization with sulfur content below 0.1 ppm in diesel fuel was achieved. The feed-stock was prehydrotreated diesel fuel, containing sulfur 0.053 mass%. In a patent application [55] it was shown that sulfone obtained from dibenzothiophene, created in oxidation process, was converted into biphenyl and hydrogen sulfide by hydrogenation. Dibenzothiophene sulfone was hydrogenated under milder conditions than dibenzothiophene. A product containing 55 ppm sulfur was obtained from gas oil in a two step process.

In recent years several patent applications concerning oxidation with ozone and oxygen have been presented. Sherman [56] presents oxidation with sub-micron size bubbles of ozone for desulfurization of diesel fuel, but the conversion rates of sulfur are not given. In another application, heterogeneous oxidation of transport fuel with oxygen in the presence of a solid catalyst at temperature of 160 °C and pressure of 14 atm, reduced sulfur content from 233 ppm to 12 ppm (95% removal) [57].

The treatment of raw shale oil with hydrogen peroxide in formic acid in the presence of limonate ore (containing iron and nickel) at 70 °C presented in [58] resulted in nitrogen removal of up to 99.5%, sulfur up to 13%, dienes

up to 22%, and alkenes up to 22% [58]. However, this process is not effective for reducing sulfur content, as the catalyst is not very effective at oxidizing sulfur compounds. Furthermore, it may be supposed that these results cannot be carried mechanically over to Estonian shale oil.

Adsorption

Like extraction processes, adsorption alone cannot technologically reach the deep desulfurization levels for liquid fuels.

Since its development began in 1998, much attention has been paid to the Phillips S Zorb process [59]. In the cited paper it was written: "Reducing hydrogen consumption by avoiding hydrotreating can save a refinery significant operating costs...". The Zorb process is carried out in the presence of hydrogen and modified zinc oxide on a carrier. Sulfur from the sulfur compounds is carried over to hydrogen sulfide, which was by chemisorption bound with zinc oxide as zinc sulfide.

There are many patents and patent applications in the field of desulfurization by chemisorption, production of novel sorbents, and regeneration of sorbents. One example is a process for producing a sorbent composition, comprised of zinc oxide, silica and alumina, as a carrier, with a metal or metal oxide, (preferably nickel) as a promotor [60–62]. Similar patents utilizing zinc titanate [63] and zinc ferrite [64] were presented.

The detailed process for these desulfurization methods is described as follows. A hydrocarbon containing fluid stream was contacted with hydrogen (mol ratio 0.2:1 to 1:1), solid sorbent particulates (about 20 to 150 microns), which consist from zinc oxide and a promotor, preferably reduced nickel, on a carrier. Separated adsorbent, where sulfur was bound in the form of zinc sulfide, was regenerated with an oxygen-containing stream, and contacted with a hydrogen-containing stream to reduce the unreduced nickel [65, 66].

The regeneration and activation processes of sorbent are described in many patents [67–69]. In 2004 a complementary patent application concerning the above mentioned processes was presented [70]. Another process, in which oxidation is combined with chemisorption on zinc oxide in the presence of hydrogen was also presented [71]. The oxidation process was carried out with peroxy acetic acid in which 4,6-dimethyldibenzothiophene was completely converted to sulfoxide and sulfone. The separated organic phase was treated with hydrogen stream on zinc oxide. After this process, sulfur content reaches 2.45 ppm. The novelty of the process is that sulfoxides and sulfones are more easily converted to hydrogen sulfide than thiophene derivatives.

Many other oxides in addition to zinc oxide are also presented as chemisorbent agents. For example: manganese [72], copper [73], tin [74], and even cadmium [75], niobium [76], gallium [77], silver [78], tungsten and

molybdenum oxides [79], have all been presented as chemisorbent agents. Also of note is the use of noble metals as promoters of sorbents [80].

Shell Oil Co has presented a process for deep desulfurization of petroleum fractions, for example gas oil at 350 °C and 20 bar. A zinc oxide, nickel on alumina catalyst was used. The activity permanence of catalyst was illustrated with the sulfur removing rate as follows: from 750 ppm to 5 ppm after 9 hours and to 10 ppm after using the catalyst during 100 hours. After 260 hours the conversion of ZnO to ZnS was 94% [81]. This patent application is very similar to the Phillips S Zorb process mentioned above.

An adsorptive hydrodesulfurization catalyst was developed and evaluated for the use of kerosene in for fuel cells [82]. A catalyst containing 13% Ni and ZnO was certified as an adsorptive hydrodesulfurization agent. Keeping an average of less than 0.03 ppm of sulfur for one year and 1,110 thousand km is now considered possible for fuel cell powered vehicles. This process requires hydropretreated fuel. A nickel adsorbent with magnesia promotor for deep desulfurization of fuel with low sulfur content, preferably for fuel cells, was also presented [83] and again preceding hydrotreating was used.

Daimler-Chrysler AG has presented a method for deep desulfurization of engine fuel by adsorption on board a motor vehicle. The adsorption material is an oxide (Al_2O_3 , MgO, SiO_2 or TiO_2) with metal additives [84, 85].

Ma and Song *et al.* [86, 87] presented a method for deep desulfurization of hydrocarbon fuels at ambient or elevated temperatures and pressures by adsorption only without the need for additional hydrogen. The adsorbents presented are a transition metal chloride, an activated nickel adsorbent, a metal ion exchanged zeolite, a metal ion impregnated zeolite, nickel carried on silica-alumina, sulfided Co/Mo/alumina, and regenerated sulfided metal.

Regeneration of adsorbent was carried out by elution with solvents. Concentrated sulfur compounds from the adsorbent were hydrogenated. The above-mentioned method is very interesting, but in the presented examples the adsorbent became saturated very quickly and is therefore difficult to put into practice. A method for preparation of Cu(I)-Y-zeolite and desulfurization of diesel fuel with that has been published [88–90]. Desulfurization with this adsorbent occurs through formation of a π -complex between Cu^+ ions and the benzo-condensed thiophenic rings. This complex is much stronger than a complex with aromatics without sulfur allowing for a 99% desulfurization (from 297.2 to 0.032 ppm). The capacity of these sorbents was not very high.

Ionic liquids

Ionic liquids as selective extraction agents of sulfur compounds are discussed separately, because of their novelty and theoretical interest. The use of ionic liquids for selective extraction of sulfur compounds from diesel fuel was described for the first time by Bösman *et al.* [91]. Provisionally the

best results were obtained with AlCl_3 -1-butyl-3-methylimidazolium chloride (BMIMCl/ AlCl_3) however, the desulfurization rate was not high (85%).

The same authors have also obtained better results with this agent [92]. Deep desulfurization using a chlorine-free ionic liquid (anion is octylsulfate and cation N-octyl-N-methylimidazolium) is also presented [93]. This agent is not as sensitive to water as aluminium complexes. A review on the use of ionic liquids is presented by Sheldon [94]. In Germany, a survey was published by Wasserscheid and Keim [95], and a detail review about room-temperature ionic liquids was presented by Welton in 1999 [96].

Presently, ionic liquids are only of academic interest for desulfurization, much like as also biomethods for removing of sulfur [97].

Conclusions

Presently the most attractive process for deep desulfurization of petrol and diesel fuel is the Phillips S Zorb process, however, oxidation processes for desulfurization offer good possibilities for higher fractions such as fuel oil.

The driving force for the implementation of sulfur removal technology are the new requirements for sulfur content in fuel oil and fuel oil obtained from oil shale and from wasted tires.

This review of desulfurization processes is necessary to aid in the planning of future experiments for the purpose of forwarding development and innovation in the field of deep desulfurization.

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