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Alternative Processes for Removing Organic Sulfur Compounds from Petroleum Fractions

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This work discusses the processes for removing sulfur from fuels, and problems related thereto, including conventional and improved processes of hydrodesulfurization, and alternative technologies and processes for obtaining fuel with extremely low sulfur content, which are in the process of research and development. It is anticipated that alternative processes already developed or those being researched will be applied as an addition to the currently most commonly used process of hydrodesulfurization, which is based on selective heterogeneous catalysts. Reviewed are new achievements in the development of the hydrodesulfurization process regarding new catalysts and reactors, the research and development possibilities of the adsorption and extraction processes, as well as the biodesulfurization process.

Key words:

Sulfur, petroleum fractions, alternative process, desulfurization

Introduction

One of the major tasks of the petroleum industry is the production of gasoline and diesel fuels with ultra-low sulfur content. Current legislation limits the maximum content of sulfur in gasoline and diesel fuels to 10 mg kg⁻¹. Reducing sulfur content in fuels is important in order to reduce their impact on the environment and protect public health. The effect of sulfur from fuels on the environment is mainly associated with its conversion into sulfur oxides that form during combustion in the engine. Beside the facts that it pollutes the environment and affects air quality, sulfur is also harmful to modern vehicles more sensitive to the quality and purity of fuel. A higher concentration of sulfur in fuels significantly decreases the efficiency and lifetime of emission gas treatment systems in cars.^{1–4}

Review section

Advanced hydrodesulfurization processes

Hydrodesulfurization (HDS), a mild form of hydrocracking, is a refining process used for removing organic sulfur compounds from petroleum fractions. Organic sulfur compounds like thiols, sulfides, and thiophenes can be readily removed from petroleum fractions using conventional HDS catalysts, sulfidized CoMo/Al₂O₃ i NiMo/Al₂O₃ compounds, and conventional reactors. However, the efficiency towards the removal of so-called refractory sulfur compounds, such as dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), is greatly reduced. The efficiency of the HDS process can be increased by developing new catalysts and new reactors.

New types of CoMo and NiMo catalysts with increased hydrogenation activity and selectivity have been developed by applying new techniques and technologies. New reactor designs have also been developed, such as reactors with multiple levels or reactors with different catalyst structures. It is expected that the best results will be achieved by

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combining the improved activity catalysts with the new design reactors.^{5–10}

Furthermore, HDS catalysts with excellent desulfurization efficiency have been developed by combining new types of catalytically active species, such as noble metals, and new carrier materials such as those based on improved amorphous silica-alumina (ASA). However, the use of noble metals in HDS processing is limited due to their susceptibility to sulfur poisoning, which is why they are used only after most of the organic sulfur compounds and hydrogen sulfide are removed from the feeds. In order to increase the catalysts resistance to sulfur poisoning, new types of bi-functional HDS catalysts have been developed. The HDS process that uses catalysts based on noble metals is conducted in two or more steps, which include multi-level catalyst systems in order to achieve deep desulfurization and hydrogenation.^{5–7,9–13}

One of the ways to improve the HDS process is to change the direction of reaction streams, i.e. conduct the hydrodesulfurization countercurrently, which can lead to some satisfactory concentration profiles (Fig. 1). The feed is introduced at the top of the reactor and the hydrogen at the bottom where its presence is preferred. H₂S is removed from the reactor top avoiding possible recombination reactions with olefins in the exit mixture.

An example of an advanced HDS reactor is the reactor where the hydrodesulfurization reactions are taking place in an ebullated catalyst bed. This process is used for treating heavier petroleum fractions that cause very fast deactivation of conventional HDS catalysts because of excessive coke formation. During this kind of processing, very good heat transfer efficiency can be achieved so the overheating of the catalyst carrier is minimized and the formation of coke is decreased.

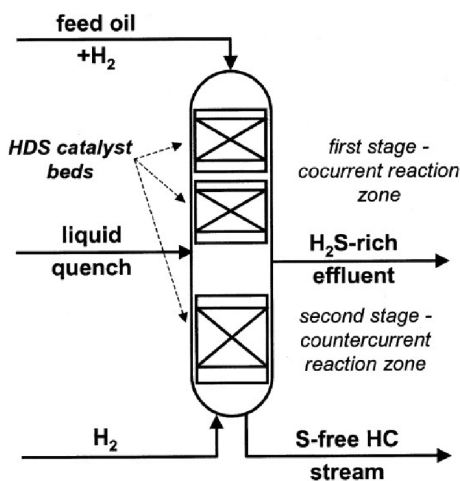


Fig. 1 – Schematic diagram of the countercurrent HDS process⁷

In the ebullated bed process, the catalyst particles, the feed, and the hydrogen are in fluidized state, which enables very good mixing. The clogging and erosion of the catalyst particles is minimized and the reactor operates in almost isothermal conditions with constant, rather small, pressure drop. Also, the ebullated bed reactor enables control of the catalyst activity by allowing constant addition and removal of catalyst particles.^{6,7}

Adsorptive desulfurization

Adsorption can be used for desulfurization of petroleum fractions based on the ability of solid adsorbent material to selectively adsorb organic sulfur compounds. There are two types of adsorptive desulfurization: adsorptive desulfurization during which physical and/or chemical adsorption of organic sulfur compounds takes place on the surface of the adsorbent, and reactive adsorption desulfurization during which organic sulfur compounds react with chemical species on the surface of the adsorbent and the sulfur is chemically bound, usually in the form of sulfide, while the newly-formed hydrocarbon compound is released into the stream. The efficiency of adsorptive desulfurization is for the most part influenced by the adsorbent properties: capacity, selectivity, stability and ability to regenerate.^{7–9,14} Materials used as adsorbents for desulfurization include different forms of activated carbon, zeolite, metallic oxides and porous metals.¹⁵

Adsorptive desulfurization on activated carbons

Activated carbon and carbon fibers are well-known multipurpose adsorbents used for treating different gases and liquids. Their surface structure and other surface properties can be adjusted in order to improve adsorption efficiency.^{16,17}

Specific application of activated carbon as adsorbent depends on the molecules that are being targeted for adsorption. Adsorption on activated carbon can be physical, which depends on the size and volume of the pores, or chemical, which depends on the chemical properties of the surface, i.e. chemisorption surface properties.¹⁸ Adsorption on activated carbon can be carried out in several types of reactors such as batch vessel reactor, continuously stirred reactor, and in fixed or fluidized bed column reactors. The advantage of the fluidized bed column reactors is its ability to achieve high mixing efficiency. However, after some time, increased wearing and erosion of the adsorbent particles occurs.¹⁹ These drawbacks of the fluidized bed adsorption column as well as high prices of powder activated carbon, mean that the adsorptive desulfurization could be competitively carried out in

fixed bed columns with granulated activated carbon. The saturated activated carbon must be regenerated in order for it to be used again. The most commonly used method of regeneration is thermal treatment, but chemical and biological treatments as well as ultrasound could be used.^{20,21}

Mužić et al.^{15,22–26} have conducted several studies of adsorptive desulfurization of diesel fuel using commercially available activated carbons as adsorbents. The fixed bed adsorption experiments by Mužić et al.,^{25,26} where activated carbon SOLCARB C3 (Chemviron Carbon, Belgium) was used to treat a diesel fuel, resulted with output sulfur concentrations of less than 0,7 mgkg⁻¹. The calculations by Mužić et al.²⁶ have shown that fixed bed adsorptive desulfurization of a previously hydro-treated diesel fuel could be carried out on industrial scale. For the feed capacity of around 10⁵ kg h⁻¹, a two fixed bed column system with each bed depth of 17,32 m and activated carbon SOLCARB C3 load of 93,5 t should be used to achieve ultralow sulfur concentration and enable continuous 24 hour a day operation (Fig. 2).

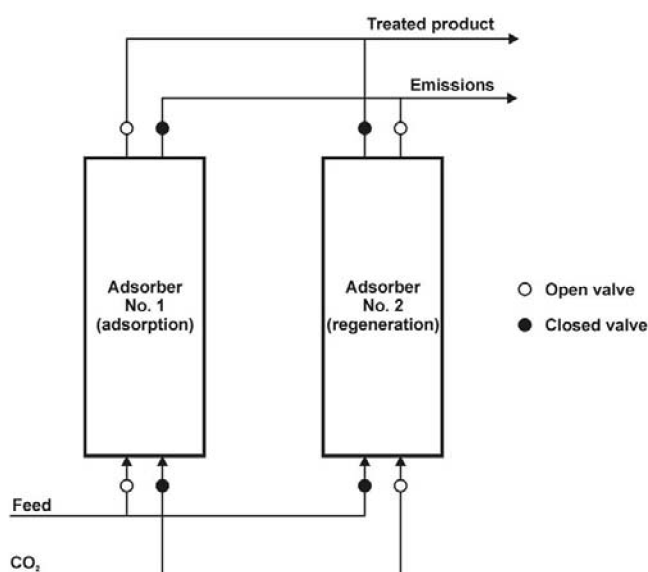


Fig. 2 – Schematic diagram of a continuous adsorptive desulfurization system²⁶

Adsorptive desulfurization on zeolites

Zeolites can be efficiently used as adsorbents for selective adsorption of polar molecules and heterogeneous organic molecules, which contain sulfur and other non-hydrocarbon species. These adsorbents are hydrophilic and can contain relatively large voids inside its structures. Synthetic zeolites have precisely defined crystalline, so-called aluminosilicate, structures with exact pore sizes and pore distribution. This allows them to selectively adsorb

molecules in correlation to their size, composition, polarity and other physical properties.¹⁵

Mužić et al.²⁷ have studied the removal of DBT from model gasoline and the results have shown that the best adsorptive desulfurization was achieved by Y-zeolite, which removed most of the DBT in the shortest time. It was determined that for the Y-zeolite there was less heterogeneity in the system, higher probability that chemisorption was the prevailing mechanism, and the mono-molecular layer was being formed.

Reactive adsorption desulfurization

– The S-Zorb process

Reactive adsorption desulfurization is a process where the metal-based adsorbent bonds the sulfur on the surface and forms disulfide. In the USA, the S-Zorb process was developed for removing sulfur from gasoline and diesel fuels by reactive adsorption (Fig. 3).^{6,7,9,14}

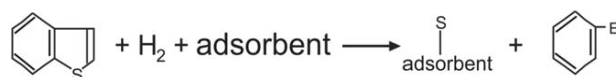


Fig. 3 – S-Zorb reactive adsorption schematic diagram⁶

The S-Zorb process is based on fluidized bed technology and is conducted at relatively severe conditions; temperatures between 340 and 400 °C and pressures between 2 and 20 bars. The sulfur atom in the organic sulfur compound is first adsorbed on the surface, after which it reacts with the adsorbent and the newly-formed hydrocarbon is released into the main stream.

It is presumed that the adsorbent is based on a reduced metal that reacts with the sulfur forming metallic sulfides.

The used adsorbent is continuously removed from the reactor and transported into the regeneration chamber. The sulfur is removed from the surface of the adsorbent by burning and the formed SO₂ is sent to the sulfur plant. The adsorbent is then reduced with hydrogen and recycled back to the reactor. The process schematic is shown in Fig. 4.^{5,7,9,14}

Extractive desulfurization

Extraction can be used for desulfurization because of higher solubility of organic sulfur compounds in appropriate solvent than other hydrocarbons present in a petroleum fraction. The organic sulfur compounds are removed from the feed into the solvent, after which the mixture of sulfur rich solvent and feed is separated. The organic sulfur

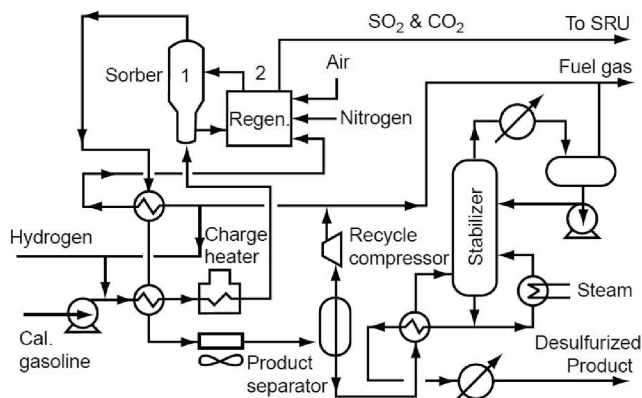


Fig. 4 – S-Zorb process schematic diagram⁹

compounds are removed from the solvent by distillation and the solvent is recycled. The extractive desulfurization process schematic is shown in Fig. 5.^{9,14}

The biggest advantage of extractive desulfurization is the possibility of conducting it at relatively low temperatures and pressures while the hydrocarbon compounds in the feed remain mainly intact. The industrial equipment needed for carrying out this process is conventional, with no special requirements, so it can easily be integrated into refineries. In order for the process to be efficient, several conditions must be met: organic sulfur compounds must be fully soluble in the solvent, the solvent must have a different boiling point in relation to the removed organic sulfur compounds, and the solvent must be nontoxic and relatively cheap so the process can be economically viable. Satisfactory levels of desulfurization between 50 and 90% were achieved with sulfolane, acetone, ethanol, polyethylene glycol, and some nitrogen containing solvents.^{9,14}

The efficiency of extractive desulfurization is mainly restricted by the solubility of the organic sulfur compounds in the applied solvent, which is why it is very important to properly choose the solvent taking into account the nature of the present organic sulfur compounds.^{6,9,14}

Extractive desulfurization with sulfolane

Sulfolane is a commercial name for 2,3,4,5-tetrahydrothiophene-1,1-dioxide, a clear and colorless fluid commonly used as solvent in the industry. Sulfolane is an organic sulfur solvent with good solubility in water, and can be selectively used for extraction of polar sulfur compounds and aromatics from hydrocarbon mixtures. Sulfolane exhibits somewhat higher affinity towards thiophenic sulfur in comparison to BTX compounds and olefins.

Adžamić et al.^{28,29} have studied the batch extraction of organic sulfur compounds from FCC gasoline with sulfolane. Achieved were removal efficiencies of up to 89% of total sulfur content. It was determined that sulfolane is highly selective of mercaptanes and lighter thiophenes. Also determined was its lower selectivity for heavier thiophenes; the sulfur content in the raffinate comprises mostly lighter thiophene compounds.

An industrial size process called Sulf-X was developed for extractive desulfurization of FCC gasoline with sulfolane, and was commercially used at the Sisak Refinery (INA d.d., Croatia). The extraction was carried out in columns, i.e. extractors with perforated plates.

Extractive desulfurization with ionic liquids

Ionic liquids are solutions almost exclusively made up of ions with melting point usually below 100 °C, i.e. they are mostly fluids at room temperature.

Ionic liquids have very high electric conductivity, very low vapor pressure; they are inflammable and have high thermal stability, a wide range of liquidity, and the ability to separate several components.

The miscibility of ionic liquids with water and organic solvents varies with the length of substituted chain on the cation, and with the choice of anion. Thus, ionic liquids can be formulated to behave as acids, bases or ligands. Despite their very low vapor pressure, some ionic liquids can be distilled under vacuum at temperatures of around 300 °C.^{30,31}

Ionic liquids have exhibited rather low affinity towards paraffins and olefins, somewhat higher affinity to aromatics, while their affinity towards thiophenes and methylthiophenes is very high. The structure and size of cations and anions of ionic liquids influence the ability to remove particular components. The affinity of ionic liquids towards aromatics increases with the density of the π electron. However, ionic liquids are capable of removing organic sulfur compounds without removing

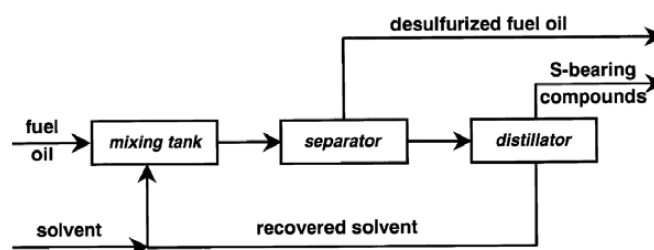


Fig. 5 – Schematic diagram of the extractive desulfurization process⁷

aromatics at the same time, which is desirable because when the feed is gasoline this does not cause the reduction in octane number.^{14,32}

Eßer et al.³³ give a good recent overview of desulfurization with different types of ionic liquids, particularly the most promising water-stable and less costly 1-n-butyl-3-methyl-imidazolium-octylsulphate. Given the poor extraction of alkylthiols and sulfides, the formation of liquid-clathrates and π - π interaction is assumed the main driving force for extraction. Furthermore, nitrogen compounds are found to be more efficiently extracted than sulfur compounds. The main problems are the extraction efficiency of a limited number of organic sulfur compounds for particular ionic liquid, cross-solubility of hydrocarbons, and the regeneration of expensive ionic liquid compounds.

Extractive distillation desulfurization

GTC Technology Inc. has developed an extractive distillation desulfurization process GT-DeSulfTM for removing organic sulfur compounds from FCC gasoline without octane number loss and without increasing hydrogen consumption. The GT-DeSulfTM process utilizes a proprietary aromatics selective solvent, which is effective in extracting thiophenic sulfur species and aromatics, and to a limited extent, mercaptans and sulfides as well. Since olefins are not extracted, this is indeed a 'selective' desulfurization system. The application is, however, limited to a light and a middle FCC cut, with specified boiling point range of up to 180 °C. This is probably due to a substantial amount of aromatics present in the heavier FCC fraction, which would render an effective sulfur species separation difficult.

A desulfurized/dearomatized olefin rich gasoline stream and an aromatic stream containing the sulfur compounds are formed after treatment in a GT-DesulfTM reactor. The first stream is directly used as a gasoline blend stock. The aromatics fraction with the sulfur compounds is sent to a HDS reactor. The GT-DesulfTM process is economically favorable due to an integrated approach to the refinery processing (segregated sulfur removal and aromatics recovery), and lower hydrogen consumption since less FCC naphtha is treated in the HDS reactor.^{5,7,14}

Oxidative desulfurization

Oxidative desulfurization is a process during which organic sulfur compounds are oxidized and subsequently removed from the feed by a separation method. The methods used for separating oxidized sulfur compounds from treated fuel feeds in-

clude extraction, adsorption, distillation, and thermal decomposition.

During oxidative desulfurization, the refractory sulfur compounds, such as DBT, are oxidized to form sulfones. Sulfones have higher polarity compared to the initial sulfur compounds, which is why they are more easily removed from petroleum fractions. In practice, the oxidative desulfurization process has encountered some technological and economic problems. When the process includes extraction, an additional problem of product loss occurs. In addition, the oxidative desulfurization process is a source of new, so-called, sulfonic waste which requires special treatment.^{7,9,14,34,35}

The research of oxidative desulfurization is being conducted using different oxidizers including nitrogen oxides and acids such as NO/NO₂ and HNO₃, t-butyl-hypochlorite, highly toxic RuO₄, persulfate based oxidizers, and H₂O₂-H₂SO₄ systems. The introduction of regulations stipulating ultralow sulfur content in fuels caused the hydrogen peroxides to become the most used oxidizing agents; peroxides such as H₂O₂ and tert-butylhydroperoxide (TBHP) with catalyst support. Other oxidizing agents include in-situ formed per-acids, organic acids, phosphate acid and heteropolyphosphate acids, Fe-tetra amido macrocyclic ligand (Fe-TAML), Fenton and Fenton-like compounds, as well as solid catalysts such as those based on titanium-silica, W-V-TiO₂, solid bases such as MgLa metal oxides or hydrotalcites, Fe oxides and oxidizing catalysts based on monoliths. These compounds can effectively oxidize organic sulfur compounds into sulfones with less residue formation.^{7,14,34-38}

The advantages of oxidative desulfurization in comparison to conventional HDS, include the requirement of rather moderate reaction conditions, no need for expensive hydrogen, and higher reactivity of aromatic sulfur compounds in oxidation reactions since the electrophilic reaction with sulfur atom is enhanced by higher electron density of aromatic rings. Alkyl groups attached to the aromatic ring increase the electron density on the sulfur atom even more. The reactivity is also dependent on the type of catalyst.

Unipure Inc. has developed an oxidative desulfurization process, based on H₂O₂ oxidation assisted by formic acid, called ASR-2 (Fig. 6). The sulfone species formed during this process are separated by extraction or adsorption. During processing, an aqueous phase is applied along with a dissolved oxidation catalyst. Organic sulfur compounds are converted to sulfones at nearly atmospheric pressure and mild temperature (up to 120 °C) within short residence times (about 5 min). The

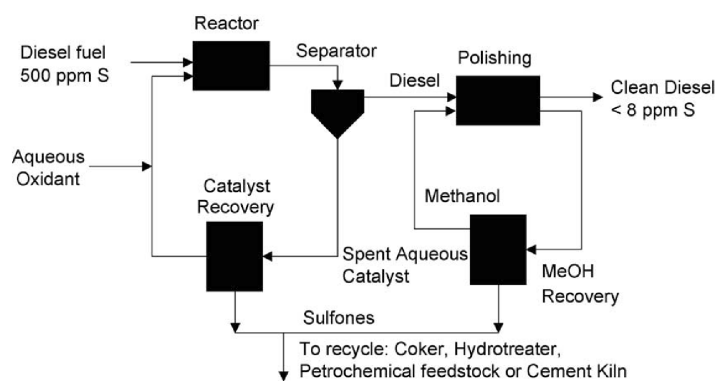


Fig. 6 – Schematic diagram of the ASR-2 process¹⁴

main limiting step of this process is oxidation of the organic sulfur compounds.

The kinetics of the oxidation reaction can be improved by employing photons or ultrasound.^{7,14} SulphCo Inc. has developed an oxidative desulfurization process which utilizes ultrasound power during H_2O_2 sulfur oxidation in the presence of tungsten phosphoric acid. Ultrasound decreases the reaction time by one order of magnitude. The SulphCo process operates at 70–80 °C under atmospheric pressure. The residence time for the ultrasound reactor is reported to be only 1 min. Achieved were desulfurization efficiencies for crude oil and diesel of up to 80 and 98% sulfur removal.^{7,14,39}

Lyondell Chemical Co. and UOP LLC in cooperation with EniChem S.p.A have developed a t-butyl-hydroperoxide (TBHP) based commercial oxidative desulfurization processes that, depending on the version, utilizes extraction or adsorption for sulfone separation. The greatest advantage of this kind of single liquid system is simple reactor engineering, enabling the application of a fixed bed column (Fig. 7). The major drawback is the high price of TBHP, and the waste treatment of t-butyl alcohol as an accompanying product, as well as sulfone waste treatment. t-Butyl alcohols could find use as potential octane boosting compounds for gasoline.^{14,37,40}

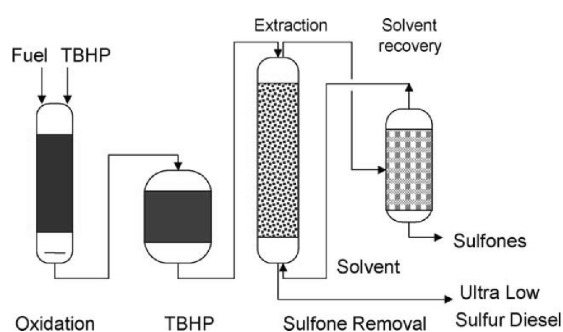


Fig. 7 – Schematic diagram of the Lyondell Chemical oxidative desulfurization process¹⁴

Photochemical extractive desulfurization

The photochemical extractive desulfurization process combines photochemical reactions with extraction of the organic sulfur compounds with an aqueous-soluble solvent.

The organic sulfur compounds are suspended in an aqueous-soluble solvent and irradiated by UV or visible light in a specially designed photoreactor. This results in the oxidation of the sulfur compounds. The polar compounds formed are rejected by the non-polar hydrocarbon phase and are concentrated in the solvent. Photochemical reaction is assisted by a photosensitizer species such as 9,10-dicyanoanthracene (DCA). Acetonitrile, which provides relatively high solubility of initial and oxidized sulfur compounds, was found to be the most suitable solvent.

After photooxidation, the solvent and the hydrocarbon phases are separated, as in extractive desulfurization. In addition, the aromatics from the solvent as well as the photosensitizer from the solvent and desulfurized hydrocarbon stream must be recovered to increase product yield and economic efficiency. Aromatics are usually recovered by liquid–liquid extraction using light paraffinic solvents subsequently blended into the desulfurized fuel stream. DCA is removed by adsorption, using a silica gel as an adsorbent. It can be returned to the process after desorption with aqueous solution of acetonitrile. All of these processes are rather common refinery processes (though not all of the chemicals are common) that can be easily integrated into the refinery and do not require special equipment or conditions. This photooxidation process exhibited high selectivity to the removal of organic sulfur compounds from light oils, catalytic-cracked gasoline and vacuum gas oils. For fuels with higher aromatics content, efficiency is slightly lower but it was claimed that above 99% of the sulfur was removed from a vacuum gas oil.⁷

Biodesulfurization

Biodesulfurization is a process that removes organic sulfur compounds from fossil fuels using enzyme-catalyzed reactions. Biocatalytic sulfur removal from fuels has applicability for producing low sulfur gasoline and diesel fuels. Certain microbial biocatalysts have been identified that can biotransform sulfur compounds found in fuels, including ones that selectively remove sulfur from DBT heterocyclic compounds (Fig. 8).

Energy Biosystems Inc. has developed a biodesulfurization process involving the removal of organic sulfur compounds from distillate or naphtha streams using bacteria. The distillate stream is first mixed with an aqueous media containing the bacte-

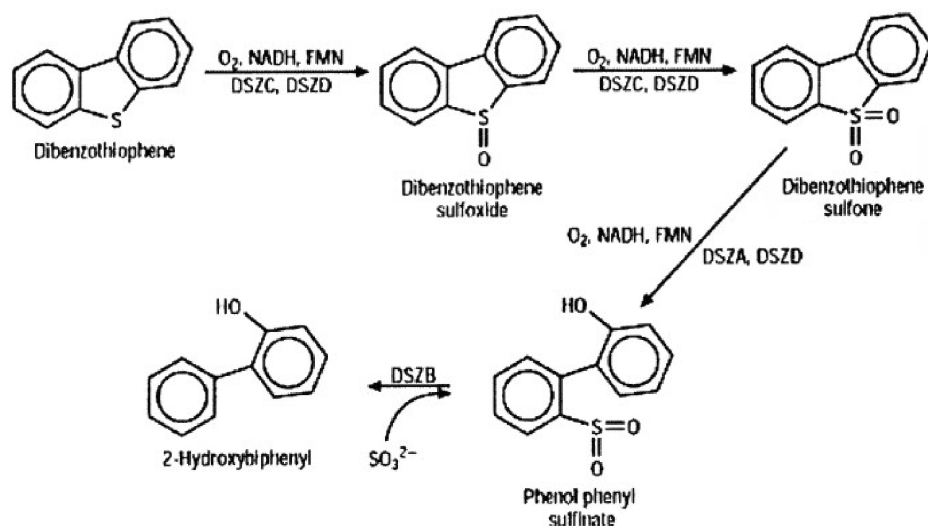


Fig. 8 – Pathway of biological desulfurization of DBT various bacterial species⁹

ria, caustic soda, and nutrients for the bacteria. Enzymes in the bacteria first oxidize the sulfur atoms and then cleave some of the sulfur–carbon bonds. The sulfur exits the process in the form of hydroxyphenyl benzene sulfonate, which can be used commercially as a feedstock to produce surfactants. Designs based on pilot plant studies combine biodesulfurization with conventional hydro-treating to produce low sulfur diesel fuel.^{9,41}

Gallagher et al.⁴² reported a sulfur-specific pathway in microbial desulfurization of DBT using *Rhodococcus* strain IGTS8. Two routes of desulfurization have been identified. Stationary phase cells produce 2-hydroxybiphenyl as the desulfurized product and use the 2-hydroxybiphenyl-2-sulfinate, rather than the sulfonate, as the key intermediate.⁹

Kobayashi et al.⁴³ studied the reaction mechanism of biodesulfurization using whole cells of *Rhodococcus erythropolis* KA2-5-1, which have the ability to convert DBT into 2-hydroxybiphenyl. The relative desulfurization activities of various alkyl DBTs were reduced in proportion to the total carbon numbers of alkyl substituent groups. Alkyl DBTs that had six carbons of alkyl substituent groups were not desulfurized. The type or position of alkyl substituent groups had little effect on desulfurization activity.

The desulfurization activity of each alkyl DBT, when mixed together, was reduced. This was caused by apparent competitive inhibition of substrates.⁹

Omori et al.⁴⁴ isolated strain SY1, identified as a *Corynebacterium* sp., on the basis of the ability to utilize DBT as a sole source of sulfur. Strain SY1 could utilize a wide range of organic and inorganic sulfur compounds, such as DBT sulfone, dimethyl

sulfide, dimethyl sulfoxide, dimethyl sulfone, CS₂, FeS₂, and even elemental sulfur. Strain SY1 metabolized DBT to DBT-5-oxide, DBT-sulfone, and 2-hydroxybiphenyl, which was subsequently nitrated to produce at least two different hydroxynitrobi-phenyls during cultivation. Resting cells of SY1 desulfurized toluenesulfonic acid and released sulfite anion.⁹

Biodesulfurization, which operates under ambient temperature and pressure, is expected to be a complement and a promising alternative to conventional HDS. How-

ever, biodesulfurization of fuels is still not a commercial technology because some problems have to be solved. Stability and lifetime of biocatalyst are two crucial factors. In order to solve these problems, cell immobilization, which has been widely studied and applied in recent years, is considered a potential method, and is becoming the focus of biodesulfurization research. Compared with suspension cell, biodesulfurization with immobilized cells has some advantages: ease of biocatalyst separation from the treated fuels, low risk of contamination, high stability, and long lifetime of the biocatalyst.⁴¹

Recent discoveries related to biodesulfurization mechanisms may lead to commercial applications of biodesulfurization through engineering recombinant strains for over-expression of biodesulfurization genes, removal of end-product repression, and/or by combining relevant industrial and environmental traits with improvements in bioprocess design.

With bioprocess improvements that enhance biocatalyst stability, achieve faster kinetics, improve mass transfer limitations, temperature and solvent tolerance, as well as broaden substrate specificity to attack a greater range of heterocyclic compounds, biocatalysis may be a cost-effective approach to achieve the production of low sulfur gasoline.⁹

Conclusion

Alternative desulfurization processes, including advanced HDS processes, separation, adsorption and extraction, oxidation, and biodesulfurization processes are being developed because the conventional HDS process is experiencing difficul-

ties in producing fuels in accordance with latest regulations, i.e. environmentally friendly fuels. From the technological standpoint, it was prudent to first try to improve the current HDS catalysts and reactors, but it soon became clear that if significant advancement were to be made, new types of HDS catalysts and reactor designs had to be developed. At the same time, the research and development of adsorptive, extractive and oxidative desulfurization and biodesulfurization processes intensified. Up to this point, several commercial processes have been developed and successfully installed in refineries, including the reactive adsorption S-Zorb process and extractive desulfurization Sulf-X process. However, for the most part, these alternative desulfurization processes are still being researched and developed in laboratories and pilot plants, but some very encouraging results indicate real economic viability and widespread commercial application is not far away. It should be noted that more research is needed and all processes should be able to find their place on the market.

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