Desulfurization from Gas Oil: sulfur removal of gas oil to 10 ppm

Author: Vincenzo Piemonte - Associate Professor - University "Campus Bio-Medico" of Rome.

1. Introduction

The source of energy most used in the world is crude oil. Major portions of the crude oils are used as transportation fuels such as diesel, gasoline and jet fuel. However, the crude oil contains sulfur, typically in the form of organic sulfur compounds. The sulfur content and the API gravity are the properties that have more influence on the value of the crude oil. The sulfur content is expressed as a percentage of sulfur by weight and varies from less than 0.1% to greater than 5% depending on the type and source of crude oils[1].

The removal of organo-sulfur compounds (ORS) from diesel fuel is the key to reduce air pollution, reducing the emission of toxic gases (such as sulfur oxides) and other polluted materials. The adsorption desulfurization process is one of the easily and fast method to remove sulfur from diesel oils[2].

The adsorptive desulphurization of gasoline over nickel based adsorbent, provide high capacity and selectivity for the adsorptive desulfurization of gasoline. The adsorption involves C-S bond cleavage as evidenced, forming ethyl benzene from benzothiophene in the absence of hydrogen gas.

The hydrodesulfurized straight run gas oil having less than 50 ppm sulfur is treated with activated carbon fiber to attain the ultra-low sulfur gas oil having less than 10 ppm sulfur, for example.

The next paragraphs describe the desulphurization of gasoline with some of the used methods.

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[1]Desulfurization of Gasoline and Diesel Fuels, Using Non-Hydrogen Consuming Techniques, Abdullah Al-Malki, King Fahad University of Petroleum and Minerals, October 2004

[2]Adsorption Process of Sulfur Removal from Diesel Using Sorbent Materials, Isam A. H. Al Zubaidy, Fatma Bin Tarsh, Noora Naif Darwish, Balsam Sweidan Sana Abdul Majeed, Aysha Al Sharafi, and Lamis Abu Chacra, Journal of Clean Energy Technologies, Vol1, No. 1, January 2013

2. Current Desulfurization Technologies

Diesel fuel is a multi-purpose petroleum fuel used in all transportation machines. It is also one of the largest sources of air pollution, having serious health impacts. Besides soot or fine particles, diesel fueled engines also emit nitrogen oxides that can form ground level ozone.

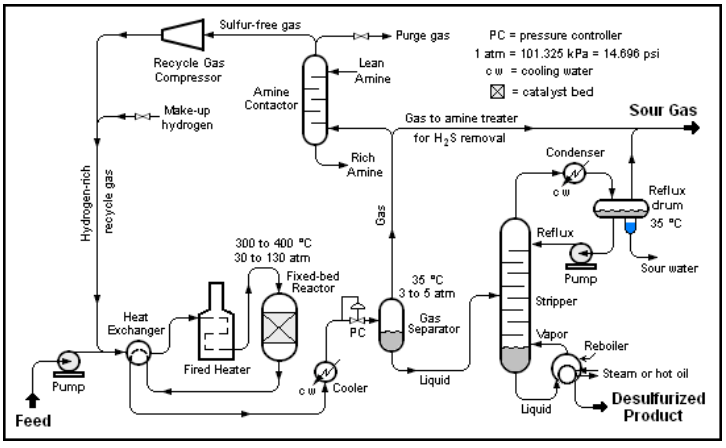
The following are the desulfurization processes currently in use, underlining in red which allow to reach a sulfate content of ~10 ppm.

Hydrodesulfurization (HDS)

Removing sulfur (S) from natural gas and from refined petroleum products (such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils) is widely done by HSD (catalytic chemical process). Removing the sulfur reduces the sulfur dioxide (SO_2) emissions that result from using those fuels in automotive, residential, industrial furnaces, etc.

Usually, the HDS process converts a number of organo-sulfur compounds to H_2S and sulfur-free organic compounds. This can be done through catalytic treatment with hydrogen at elevated pressures, between 150 and 3000 psi, and elevated temperatures, between 290 and 455 °C, using metal catalysts such as $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$[3].

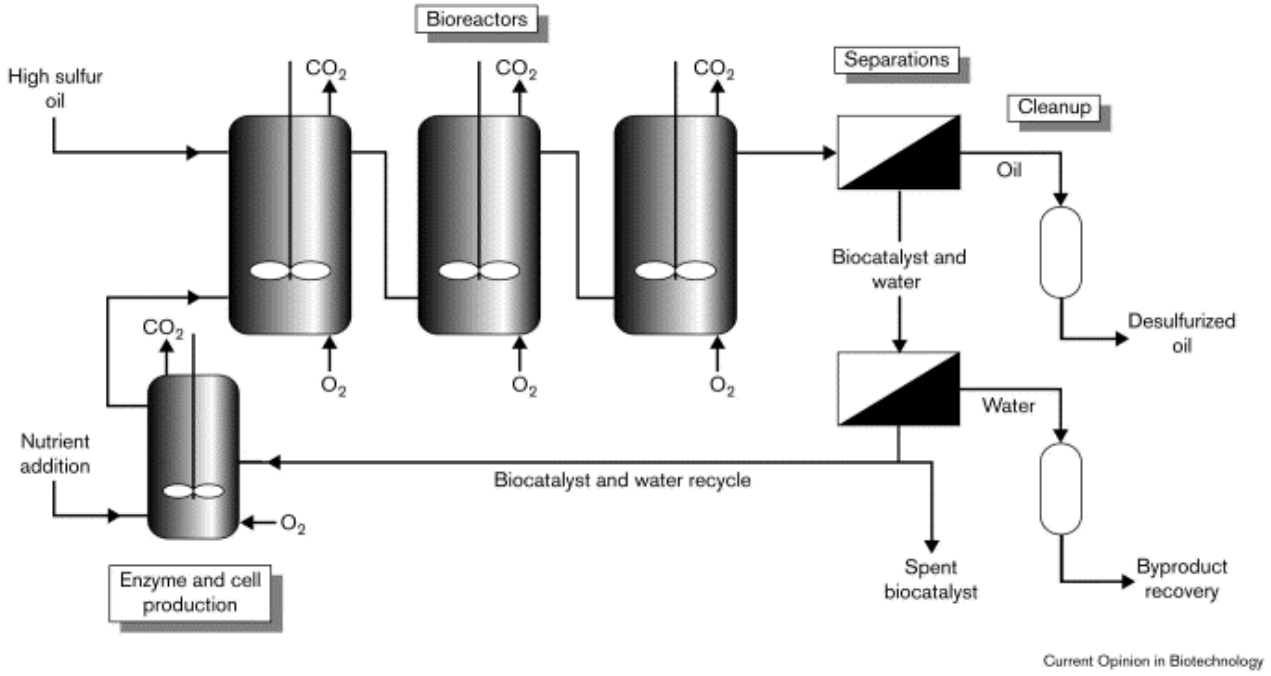
Refineries may produce the ultra-low sulfur diesel (ULSD), controlling hydrotreating conditions and appropriate catalysts. For diesel, a two-stage deep desulfurization process is sufficient to meet the 10ppm sulfur target. The first stage reduces the sulfur level to below 250 ppm and second stage produces diesel product with10 ppm sulfur about.



[3]Biodesulfuritazion of Petroleum Distillates-Current Status, Opportunities and Future Challenges, Olawumi O. Sadare, Franklin Obazu and Michael Olawale Daramola, Environments 2017, 4, 85.

Biodesulfuritazion (BDS)

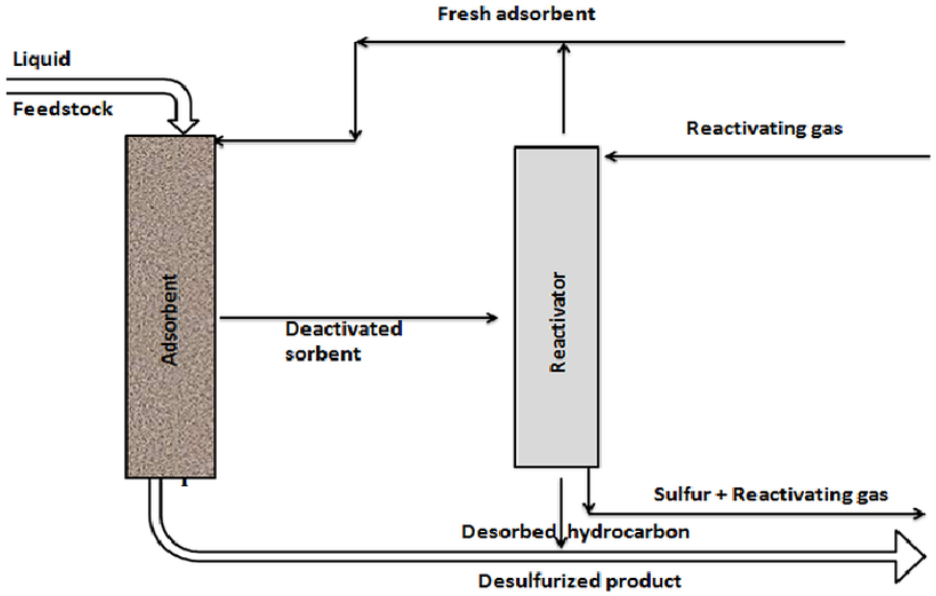
Biodesulfurization (BDS) is based on the application of microorganisms that selectively remove sulfur atoms from organosulfur compounds. It is a technology that complements the traditional hydrodesulfurization of fuels. Enzymes in the bacteria selectively oxidize the sulfur, cutting carbon-sulfur bonds. BDS will operate at ambient temperatures and atmospheric pressure, requiring less energy than conventional HDS methods to achieve sulfur levels of current regulatory standards. BDS generates a fraction of the CO_2 when in association with HDS, not requiring hydrogen. Additionally, BDS removes some key sulfur-containing compounds, that aren't easy removed by HDS process. BDS can be used instead of, or complementary with, HDS[4].



Adsorptive Desulfurization (ADS)

In adsorptive desulfurization process, over sulfated Chondroitin Sulfate (OSCs) are adsorbed into a specified solid adsorbent so as to produce none- or low-sulfur fuel. Adsorptive desulfurization is classified into direct adsorption desulfurization and reactive adsorption desulfurization, depending on the interaction between OSCs and the adsorbent.

[4]Petroleum Microbial Biotechnology: Challenges and Prospects, Wael A. Ismail, Jonathan D. Van Hamme, John J. Kilbane, Ji-Dong Gu, Frontiers, Septembers 2017

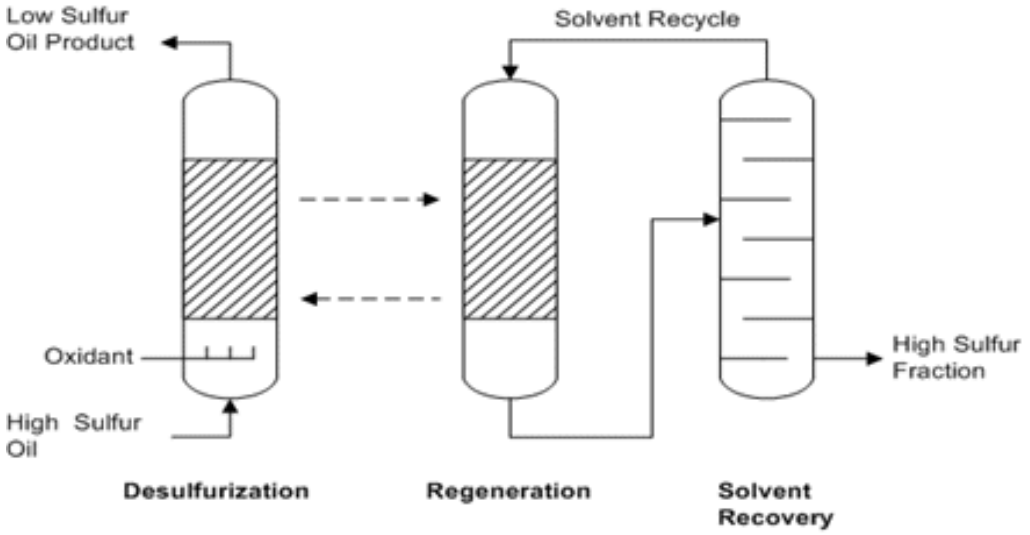


Oxidative Desulfurization (ODS)

The oxidative desulphurization oxidizes the sulfur compounds to their corresponding sulfoxides (1-oxides) and sulfones (1, 1-dioxides), unlike the HDS method where sulfur compounds are reduced to form SO_2. ODS for the reduction of sulphur is carried out at low temperature (~50 C) and pressure[5]. It is carried out using mild operation conditions of pressure and temperature, and there is no need for expensive hydrogen. However, the technique uses huge amounts of oxidizing agent and need a separation procedure to recover the catalysts. In addition, the reaction isn't very selectivity and activity, and therefore an extended reaction time is required.

The most desirable result was obtained by peroxyacid oxidation ($HCOOH/H_2O_2$). 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.

[5]https://www.researchgate.net/profile/Amir_Farshi/publication/279197357_Sulfur_reduction_of_heavy_fuel_oil_by_oxidative_desulfurization_ODS_method/links/558ea00c08ae1e1f9bacac29/Sulfur-reduction-of-heavy-fuel-oil-by-oxidative-desulfurization-ODS-method.pdf



DS2Tech Desulfurization Process

Desulfurization of fuel Using Imidazolium-based ILs

N-butylimidazole-derived dialkylphosphate ionic liquids removes aromatic sulfur compounds (S-compounds) from fuel oils, preferring aromatic S-compound versus toluene.

Two types of ionic liquids, 1-alkyl-3-methylimidazolium [AMIM] tetrafluoroborate and hexafluorophosphate and trimethylamine hydrochloride, are potentially applicable for sulfur removal from transportation fuels.

The extractive and oxidative deep desulfurization of model fuel oils using a low-viscosity ionic liquid, (1ethyl3-methylimidazolium dicyanamide $[C_2mim][N(CN)_2]$), are investigated by Yu and coworkers[6]. $[C_2mim][N(CN)_2]$ is capable of effectively extracting thiophene (TS) and dibenzothiophene (DBT) from oils. The sulfur content in the raffinate phases is only $\sim$10 ppm after a few extraction steps.

Desulfurization of fuel using quaternary ammonium -based ionic liquids

An amphiphilic catalyst, composing of lacunary anion$[PW_{11}O_{39}]_7$ and quaternary ammonium cation $[C_{18}H_{37}(CH_3)_3]N_+$, assembled in hydrophobic ionic liquid emulsions, can oxidize the sulfur compounds present in oil into their corresponding sulfones (in ambient reaction conditions),with the aim of deep desulfurization of the gasoline.

[6]Yu, G., Li, X., Liu, X., Asumana, C., & Chen, X. (2011). Deep Desulfurization of FuelOils Using Low-Viscosity-Ethyl-3-methylimidazolium Dicyanamide Ionic Liquid. IndEng Chem Res, 50(4), 2236-2244.

This ionic liquid emulsion system could be recycled five times with a not considerable decreased in catalytic activity. Furthermore, the mechanism of catalytic oxidation desulfurization was elaborated, and the total sulfur level of real gasoline can be decreased from 1236 to 65 ppm after catalytic oxidation using an ionic liquid emulsion system.

3. Conclusion

In view of new stringent environmental regulations, utilization of sulfur-containing fuel oils has limitations regarding emission of sulfur dioxide. Technology for reduction of sulfur in diesel fuel below 15 ppm is currently available. Chemical oxidation in conjunction with ionic liquid extraction can increase the removal of sulfur sharply. Ionic liquids can extract aromatic sulfur-containing compounds at ambient conditions without H_2 consumption. In addition, ionic liquids can't mix with fuel, and the used ionic liquids can be regenerated and recycled by solvent washing or distillation. The ionic liquids can be recycled six times, without considerable loss of activity, reducing the sulfur content in real commercial diesel fuel from 64 to 7.9 ppm with a sulfur removal of 87.7%.

Another 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.[7].

[7]Advances in desulfurization research of liquid fuel, H. Rang, J. Kann, V. OJA, Oil Shale, 2006, Vol. 23, No. 2, pp. 164–176