



A Review on Bio- And Adsorptive Desulfurization of Diesel Fuel

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Authors' contributions

This work was carried out in collaboration between all authors. Author MMO did the literature searches, designed the study, wrote the protocol and the first draft of the manuscript. Author DSA also contributed and managed the literature searches. Authors DSA and SCUN supervised the study. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2016/26909

Editor(s):

(1) Masafumi Tateda, Department of Environmental Engineering, Graduate School of Engineering, Toyama Prefectural University, Japan.

Reviewers:

(1) Linfeng Yang, University of Alberta, Edmonton, Canada.

(2) Shengqiang Wang, Nankai University, China.

(3) Timur Bilalov, "Kazan National Research Technological University", Kazan, Russia.

Complete Peer review History: <http://sciencedomain.org/review-history/15252>

Mini-review Article

Received 10th May 2016
Accepted 23rd June 2016
Published 1st July 2016

ABSTRACT

Aims: To review some previous work on biodesulfurization and adsorptive desulfurization of diesel fuel.

Study Design: The emissions from fossil fuels have been established to be a major contributor to global warming and acid rain which deteriorates the environment and infrastructures. In refineries, hydrodesulfurization (HDS) method is currently used to remove thiols, sulfides and thiophenes compounds present in lower-boiling petroleum fractions, but the removal of benzothiophenes (BT) and dibenzothiophenes (DBT) contained significantly in middle-distillate petroleum fractions (MDPF) e.g. diesel via HDS is difficult due to the presence of substitutions which are believed to sterically hinder access of the sulfur atom to the catalyst surface. Over the years there have been several regulatory standards and researches on limiting the sulfur content of petroleum products. The development of complimentary desulfurization techniques that will remove these recalcitrant compounds from the MDPF is therefore essential. Biodesulfurization (BDS), a process in which

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sulfur is removed from a substance by an enzymatic process yielding sulfate or sulfide as a product; and Adsorptive Desulphurization (ADS), a process which removes sulfur from a substance through the use of adsorbents are amongst the complementary methods being explored for the removal of sulfur present as DBT in MDPF.

Methodology: The review highlights the study by some listed authors on biodesulfurization and adsorptive desulfurization of diesel fuel respectively.

Results: The potentiality of ADS using different types of adsorbents are continuous area of research as little or no report of their commercialization has been reported. Also, for the BDS, most research focus has been on aerobic desulfurization with currently little evidence for the potentiality of a commercially significant anaerobic desulfurization.

Conclusion: The current trends toward stricter regulations on the content of sulfur in fuels provide enough incentive for the continued search for improved complementary desulfurization technique.

Keywords: Biodesulfurization; adsorptive desulfurization; dibenzothiophenes; diesel fuel.

1. INTRODUCTION

The combustion products from fossil fuels are harmful to the environment. Carbon dioxide emissions have been established to be a major contributor to global warming. Sulfur and nitrogen oxides emissions are pollutants which have been shown to be responsible for acid rain, which deteriorates the environment and infrastructures [1]. Governments throughout the world have recognized the problems associated with these emissions and are taking steps to reduce them through legislations. Environmental agencies are also imposing more stringent regulatory standards on the sulfur content of petroleum products.

Sulfur is present in crude oil as hydrogen sulfide (H_2S), as organosulfur compounds or as elemental sulfur, S, with concentration typically between 0.05 and 5.0% (by weight), although values as high as 13.95% have been reported. In general, the distribution of sulfur in crude oil is such that the proportion of sulfur increases along with the boiling point of the distillate fraction. As a result, the higher the boiling range of the fuel, the higher the sulfur content will tend to be. For example, a middle-distillate-range fraction like diesel fuel will typically have higher sulfur content than the lower-boiling-range fraction like gasoline. Also, the proportion, stability and complexity of sulfur compounds are greater in heavier crude oil fractions [2].

In refineries organic sulfur are removed from crude oil-derived fuels by HDS. HDS is a catalytic process that converts organic sulfur to hydrogen sulfide gas by reacting crude oil fractions with hydrogen at pressures between 1.03 MPa and 20.7 MPa and temperatures between 290°C and 455°C, depending upon the

feed and level of desulfurization required [3]. Organic sulfur compounds mainly thiols, sulfides, and thiophenes in the lower-boiling fractions of petroleum, e.g., the gasoline range, are readily removed by HDS. However, middle-distillate fractions, e.g., the diesel range, contain significant amounts of BT and DBT, which are recalcitrant and comparatively more difficult to remove by HDS. Among the most refractory of these compounds are DBT with substitutions adjacent to the sulfur component. Due to their resistance to HDS, these compounds represent a significant barrier to reaching very low sulfur levels in middle-distillate-range fuels [4]. There is therefore the need for complementary method for the removal of these refractory compounds. BDS and ADS are amongst the complementary methods being explored.

2. REVIEW

During the past decade, many countries have imposed a reduction of sulfur level to 10 ppm fuels, to reduce harmful emissions from the combustion of fuel. In the European Union, the standard "Euro V", which specifies a maximum of 10 ppm sulfur in diesel fuel for most road vehicles, has been applied since 2009. In Russia, the formal technical requirements for fuels were introduced by Government Decree No. 118, "Technical Regulation on requirements for automotive and aviation gasoline, diesel and marine fuel, jet fuel and heating oil." Three automotive standards cover fuel quality: Type I (Euro 3), Type II (Euro 4) and Type III (Euro 5) with a sulfur content of 350 ppm, 50 ppm and 10 ppm, respectively. The quality of diesel fuels in the US has been specified by ASTM D975, which covered seven qualities diesel fuel oils for different types of diesel engines; since 2010, ultra-low sulfur diesel (ULSD) with a sulfur

content of 15 ppm, is the new standard for all on-road diesel fuel while non-road diesel engine fuel also move to ULSD in 2014. This makes review of desulfurization of fuel interesting and useful for researches in the field.

This study is limited to the review of some work that has been done on BDS and ADS. BDS is a process in which sulfur is removed from a substance by an enzymatic process yielding sulfate or sulfide as a product [5]. During a BDS process, alkylated dibenzothiophenes (Cx-DBTs) are converted to non-sulfur compounds, for example, 2-hydroxybiphenyl (2-HBP) and sulfate. Whereas, ADS is a process that depends on the ability of an adsorbent to selectively adsorb organo-sulfur compounds. It is based on selective adsorption of such compounds onto tailored surfaces which are employed as adsorbents. It is an efficient process yielding clean fuel free from sulfur under modest process conditions by utilizing adsorbent materials known to be multifunctional in terms of structural, textural and surface properties to match the requirement for the adsorption of sulfur containing compounds including refractory compounds.

Removal of the recalcitrant DBT present in diesel fuel is desirable as it allows stringent regulation standards on the sulfur content to be met, considering the adverse effects of emissions of its pollutants on the environment and health of human beings.

2.1 Review on Biodesulfurization

Two main pathways have been reported for DBT bio-utilization: ring-destructive (degradation) and sulfur-specific (desulfurization) pathways. To date, two ring-destructive pathways for metabolism of DBT have been recognized. One of the ring-destructive pathways that results in mineralization of DBT is that described by [6] in which *Brevibacterium sp.* DO, capable of using DBT for growth as the sole source of carbon, sulfur and energy was isolated. During DBT mineralization three metabolites were identified: DBT sulfoxide (DBTO), DBT sulfone (DBTO₂) and benzoate. This pathway resulted in the complete mineralization of DBT, with the release of the sulfur atom as sulphite stoichiometrically, which was then oxidized to sulfate. Ring-destructive pathways are not commercially useful for the petroleum industry because the use of the carbon skeleton of sulfur compounds by the bacteria reduces the fuel's calorific value.

Grossman [7]; Izumi et al. [1] and Wang and Krawiec [8] isolated bacteria that desulfurize DBT and a variety of other organic sulfur compounds typically found in petroleum oils via a sulfur-selective oxidative pathway which does not remove carbon. This pathway involves the sequential oxidation of the sulfur component followed by cleavage of the carbon-sulfur bonds. Though there is no common model compound that can be used for all the various petroleum fractions, [9] used DBT as a model thiophene, and benzylsulfide as a model aliphatic sulfide, in the study of BDS. Kim et al. [10] and Lizama et al. [11] reported that sulfate-reducing bacteria have been utilized to desulfurize model compounds and fossil fuels; and several investigators have reported that a sulfur-specific pathway could be carried out by aerobic and anaerobic bacteria. Monticello [2] and Ohshiro and Izumi [12] isolated several aerobic bacterial strains able to selectively oxidize the sulfur atom of DBT without degrading the carbon skeleton. All of these isolated strains produce 2-hydroxybiphenyl (HBP) as an end product of the process, with the exception of *Brevibacterium sp.* strain DO, which also degrades the carbon skeleton [13]. Lee et al. [14] reported that *Rhodococcus rhodochrous* IGTS8, isolated by [15] has perhaps been the most extensively studied. Diverse metabolic capabilities of microorganisms have been exploited by man in diverse ways, and microbial transformation is considered a major route for complete degradation of petroleum components [16].

2.2 Review on Adsorptive Desulfurization

Nada, et al. [17] studied the desulfurization of a simulated diesel fuel by different adsorbents in three different adsorption beds containing commercial activated carbon (AC); Cu-Y zeolite; and layered bed of 15wt% AC, followed by Cu-Y zeolite operated at ambient temperature and pressure. The adsorbents tested for total sulfur adsorption capacity followed the order AC/Cu-Y zeolite > Cu-Y zeolite > AC. Waqas et al. [18] studied selective adsorption desulfurization of diesel oil by impregnating different metals which included Fe, Cr, Ni, Co, Mn, Pb, Zn and Ag on montmorillonite clay (MMT) by wet impregnation method. In the procedure, stoichiometric amounts of 0.2 M solution of different metals precursors i.e. Fe(NO₃)₃, Cr(NO₃)₂, Ni(NO₃)₂, Co(NO₃)₂, MnCl₂, Pb(NO₃)₂, ZnCl₂ and Ag(NO₃)₂ were mixed with 3 g of modified clay. The results showed that high desulfurization was brought about by Zn-MMT. Also, the surface area, pore

size and pore volume of the MMT was found to increase many fold with Zn impregnation. Thitiwan et al. [19] investigated the removal of DBT from n-octane using an adsorption process with sewage sludge-derived activated carbons (S-ACs) at ambient conditions. The effect of varying the type of activating agent (ZnCl₂, HNO₃ and KOH), activating agent: char weight ratio (0.5 - 6 w/w), carbonization temperature (400 - 800°C) and time (0.5 - 2 h) on the physicochemical properties and the adsorption capacity of the S-ACs were investigated. All the studied parameters were found to play an important role on the physicochemical properties as well as the surface chemistry of the S-ACs. The DBT adsorption capacity increased with the increase of oxygen-containing functional group, especially the carbonyl group. The S-AC prepared by KOH-activation exhibited the highest adsorption capacity with up to 14.12 mg/g or around 70.6% DBT removal, which were greater than that of a commercial activated carbon (C-AC). The adsorption of DBT via S-AC followed the Langmuir isotherm. Khodadadi et al. [20] showed that copper oxide (CuO) nano particles could be used as adsorbent for the desulfurization of liquid fuels. The result showed that temperature has an effect on removal of total sulfur and that the sorption rate of sulfur removal

was independent of whether the sample was agitated or not. The kinetic study for this adsorption process showed that the reaction path was second order. Xiaoliang et al. [21] studied two model diesel fuels (MD-1 and MD-2) with different concentrations of DBT over Adsorbent-6, which was prepared from CoMo oxides supported on γ -alumina (CoMo/ γ -Al₂O₃; CoO: 3wt%; MoO₃: 14wt%; Surface area: 183 m²/g; Pore volume: 0.4755 ml/g; Average pore size: 102 Å). MD-1 contains the same molar concentration of DBT, 4-methyldibenzothiophene (4-MDBT), dimethyldibenzothiophene (4,6-DMDBT), and 1 methylnaphalene (1-MNA) while MD-2 contains only one sulfur compound, DBT; and the total sulfur concentration in MD-1 and MD-2 was 486 ppm and 200 ppm respectively. The ADS of MD-1 over Adsorbent-6 at 50°C was studied, and it was found that the adsorption selectivity increases in the order of DBT > 4-MDBT > 4,6-DMDBT. Also the ADS of MD-2 over Adsorbent-6 at 50°C and 150°C were conducted, and it was found that the performance was poorer at 150°C than at 50°C indicating that lower temperature is better for the adsorptive desulfurization over that type of adsorbents. The summary of the review on adsorptive desulfurization is shown in Table 1.

Table 1. Summary of the review on adsorptive desulfurization

| Author | Type of fuel | Adsorbent type | Sulfur adsorption capacity |
|------------------------|----------------------------------|--|---|
| Nada, et al. [17] | Simulated diesel fuel | (AC) (100%) Cu-Y zeolite (100%) AC(15wt%)+CuYzeolite (75%) | AC/Cu-Y zeolite > Cu-Y zeolite > AC |
| Waqas, et al. [18] | Diesel | MMT + Fe(NO ₃) ₃ MMT + Cr(NO ₃) ₂ MMT + Ni(NO ₃) ₂ MMT + Co(NO ₃) ₂ MMT + MnCl ₂ MMT + Pb(NO ₃) ₂ MMT + ZnCl ₂ MMT + Ag(NO ₃) ₂ | High desulfurization was brought about by Zn-MMT |
| Thitiwan, et al. [19] | n-octane | S-ACs + ZnCl ₂ S-ACs + HNO ₃ S-ACs + KOH | S-ACs + KOH exhibited highest adsorption capacity |
| Khodadadi, et al. [20] | Liquid fuels | CuO nano particles | The sorption rate of sulfur removal was independent of sample agitation |
| Xiaoliang, et al. [21] | Model diesel fuels MD-1 and MD-2 | Adsorbent-6 | Lower temperature is better for the ADS over this type of adsorbent |

3. CONCLUSION

There is no gainsaying the fact that any work on desulfurization of diesel is desirable as it allows stringent regulation standards on the sulfur content to be met, considering the adverse effects of emissions of its pollutants on the environment and health of human beings. The potentiality of ADS of real and model diesel using different adsorbents types like nano particles; different types of clays impregnated with different chemical precursors; and sewage sludge are continuous area of research with the advantage of some of the adsorbents being regenerable but little or no report of their commercialization has been reported. For BDS, the ring-destructive pathway is not commercially useful for the petroleum industry because the use of the carbon skeleton of sulfur compounds by the bacteria reduces the fuel's calorific value. Also, there is currently little evidence for the potentiality of a commercially significant anaerobic desulfurization as most BDS research focus has been on aerobic desulfurization. The current trends toward stricter regulations on the content of sulfur in fuels provide enough incentive for the continued search for improved complementary desulfurization technique.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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