

Novel approach to produce ultra low sulfur diesel fuel by non-hydrodesulfurization process coupled with bio-desulfurization technique to meet environmental standards

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Abstract

Coupling of non-hydrodesulfurization process with bio-desulfurization process can bring benefits to produce ultra-low sulfur diesel fuels. Under operating condition of 65°C and atmospheric pressure, the sulfur content present in diesel fuel decreased from 766 $\mu\text{g g}^{-1}$ to 7.14 $\mu\text{g g}^{-1}$ by non-hydrodesulfurization process using persulfate as oxidizing agent. The non-hydrodesulfurization diesel fuel was used for bio-desulfurization technique using the *Rhodococcus sp* and *Methylomonas methanica* separately. An experiment was conducted in two phase medium [non aqueous to aqueous ratio, 15:85 to 100:0 (i.e., 0-100% diesel)]. Microbial strains were observed to follow classic monod type growth kinetics under the present range of substrate maximum growth rate ($\mu_{\text{max}} = 0.096 \text{ hr}^{-1}$ and 0.098 hr^{-1}) and half saturation constant ($K_s = 71$ and 77 mg dm^{-3}) for *Rhodococcus sp* and *Methylomonas methanica*, respectively. This bio-desulfurization process was conducted in a trickle bed reactor under continuous mode that was coupled with non-hydrodesulfurization unit. The sulfur content present after bio-desulfurization technique using *Rhodococcus sp* and *Methylomonas methanica* was 4.22 $\mu\text{g g}^{-1}$ and 4.06 $\mu\text{g g}^{-1}$, respectively. This was equivalent to 99.93% sulfur removal and was 1.78 times better than Bharat IV norms.

Key words

Bio-desulfurization, Non-hydrodesulfurization, Strains, Sulfur

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Introduction

The sulfur content in diesel fuel is continuously being reduced by regulations imposed various countries. The European Union norms suggests to reduce the sulfur content to less than 10 $\mu\text{g g}^{-1}$ in 2010 (Aida and Funakoshi, 1998). The current industrial method for removal of sulfur from diesel fuel is hydrodesulfurization (HDS) that operates under high temperature and high pressure (Song, 2003). HDS is not effective in removing heterocyclic sulfur compounds such as dibenzothiophenes (DBT) and its derivatives. Non-HDS has given an alternative technology for deep desulfurization (Andraeas *et al.*, 2004). During non-HDS process, the sulfur containing compounds are oxidized using persulfate reagent

followed by adsorption, extraction and precipitation to remove sulfur and convert these compounds to their corresponding sulfoxides and sulfones (Attar and Corcoran, 1978). Numerous studies developed by research experts indicate that the maximum sulfur removal should around 8.04 $\mu\text{g g}^{-1}$. Some microbial biocatalysts have been identified that can transform sulfur compounds which otherwise is very difficult to be removed by conventional non-hydrodesulfurization (Babich and Mouljin, 2003). In this regard, most attention is being given to Kodama 4S pathway of *Rhodococcus sp* and *Methylomonas methanica* which can remove sulfur from substituted and unsubstituted thiophene hindered sulfur containing compounds (Brancold and Kocal, 2002). A few established works have been reported on bio-

desulfurization of model organosulfur compounds (Babich and Mouljin, 2003). The optimal pH required for the growth of bacterium is 7.5 to 8 (Dahalan *et al.*, 2014). Coupling of non-HDS process with bio-desulfurization tends to reduce the sulfur content from $766 \mu\text{g g}^{-1}$ to $4.06 \mu\text{g g}^{-1}$. Any unused compounds that remain during the process can be removed by water washing and extraction. Depending on the solvents used, the oxidized and other compounds are separated from diesel fuel by gravity separation and centrifugation (Bharami *et al.*, 2001). The diesel fuel is washed with water to remove any traces of dissolved extraction solvent and polished using other methods such as adsorption process. Solvent is separated from the mixture by a simple distillation to recycle and re-use. The development and application of oxidation-adsorption-extraction-precipitation-bio desulfurization is considered among the most desired options because they can lower the thiophene hindered type sulfur compounds. Thus, in view of the above the present investigation was conducted to study the coupling of non-hydrodesulfurization process with bio-desulfurization process and examine its relative efficiency in the production of ultra-low sulphur diesel fuels. This could minimize the production and emission of harmful of sulphur compounds which are formed during combustion of fuels with high sulphur content.

Materials and Methods

Experimental set up

Bacterial culture and its conditions

Rhodococcus sp: These are Gram-negative, aerobic obligate bacteria. The cells are spheroid shape and the average size of the cells range between 0.5 and 3.5 μm . They are arranged mainly individually or in small clusters or chains. They grow under strict aerobic conditions in common substrates, on which they form irregularly large colonies producing water-soluble exopigment (pyocyanine and fluoresceine), which diffuse into the atmosphere and dyes it into yellow or blue-green. The temperature range of their growth is 0–42 °C with optimum temperature being 35°C.

Methylomonas methanica: The methane-utilizing isolate was Gram-negative and motile shaped rod 0.7 μm wide and about 1.3-1.8 μm long. In a static liquid culture, the methane utilizing isolate gave rise to a pink surface pellicle. The methods for enrichment, inoculated media were incubated in a 1:1 or a 1:19 methane-air atmosphere at 25°C, 28°C or 37°C, though they were incubated in a 1:4 methane-air atmosphere at 30°C in the present study for three to six weeks for enrichment (Kumi *et al.*, 1999).

Reactants used in Non-HDS unit: Hydrotreated diesel fuel feedstock from Tatipaka refinery, acetic acid, n-hexane, n-hexene, methanol, silica-alumina, aluminium oxide,

molecular sieves, furfural, N-N-dimethyl formamide, hydrogen peroxide, persulfate reagent was used as reactants in the Non-HDS unit.

Bio-desulfurization : Beef extract and peptone for bacteriology (E. Merck, Mumbai); NaCl GR (SPIC, Tuticorin); methanol, acetone, purified NaOH pellets, isopropyl alcohol, glacial acetic acid and HCl were used. *Rhodococcus sp* was purchased from NCIM, Pune (no.2891) and *Methylomonas methanica* was imported from Merck (Australia).

Analytical method : Biomass concentration in the reaction broth was determined by dry weight method, in which the broth was centrifuged @ 30,000 rpm for 20 min at -21°C and is dried at 60°C overnight.

Experimental method : At 50-90°C (Breyse *et al.*, 2003), a mixture of hydrotreated diesel fuel, 40 g of toluene, 59.5 g of hexane and persulfate reagent was stirred continuously with diesel fuel for about 30 min form a precipitate which was mixed with hydrogen peroxide and catalyst (1% Si-Al/Al₂O₃) (Chan *et al.*, 2000). The precipitate obtained was taken for GC-MS analysis to find the extent of oxidation (Macaud *et al.*, 2000). Entrained water droplets are removed. Oxidizer was used to convert S in S-containing compounds to sulfones. Molecular sieves adsorbent was (Cstorena *et al.*, 2002) used to provide information on the overall rate of adsorption of sulfur on packed bed (Jorjani *et al.*, 2004) followed by acid treatment. The aqueous acid phase was discarded (Furuya *et al.*, 2003). The mixture was washed and allowed to settle down. The precipitated diesel fuel was further treated in a trickle bed reactor (diameter = 0.081 m, height = 0.55 m and constant bed porosity = 0.7). The experiment was performed with *Rhodococcus sp* and *Methylomonas methanica* separately which followed classic Monod type growth kinetics. Pith balls were used as immobilization (Mukhopadhyaya *et al.*, 2006). Bacterial medium was circulated through the packed bed until the bio-film thickness on the sphere became 0.00001m. The reactor was continuously pumped with air at 560 dm³ hr⁻¹ in upward direction. The diesel fuel obtained from outlet stream was analyzed using different techniques.

Results and Discussion

In order to explore the promotion of persulfate reagent to Non-HDS with bio-desulfurization of diesel fuels, total sulfur removal at different reaction time was determined under four different conditions as listed in Table 1. It compared the percentage of sulfur removal, rate constant and correlative coefficient respectively for different reaction systems for non-HDS unit. It can be observed that the all the parameters had an ascent from hydrogen peroxide-acetic acid, persulfate reagent to use of non-HDS coupled with Bio-desulfurization, respectively.

The formation of sulphoxides and sulphones was evident from the spectra as shown in Fig. 1. These results were further supported by our earlier reactions using model compounds (Fabrizio, 1998). It may be concluded that hindered sulfur compounds can undergo bio-desulfurization process leading to corresponding sulphoxides and sulphones (Karaca and Yildiz, 2005). The non-HDS process with bio-desulfurization of diesel fuels fitted first order kinetics because the correlative coefficients (R) of reaction rate constants were good (Hugill and Taylor, 2001). The efficiency of non-HDS process with bio-desulfurization technique is was 1.47 times better than oxidative desulfurization using ultra sound. During the process, the hindered sulfur compounds can undergo bio-desulfurization process leading to the formation of sulphones (Isay *et al.*, 2010). Further, in the presence of excess bacterial strains the reaction will form final sulphones products. Another point worth mentioning here is the reactivity of different sulfur compounds in diesel samples. Looking at the sulfur speciation of these samples in term of their peak heights, the following observations can be drawn: the reactivity of sulfur compounds depends on the position of alkyl groups on the DBT. The peaks of C₄DBT, C₃DBT, C₄BT, and C₃BT disappeared, while the peaks of C₁BT, C₂BT, DBT, C₁DBT, C₂DBT compounds did not react completely. This could be explained by the reactivity of sulfur DBT as a result of electron density of the alkyl group contributions.

Diesel sample after Non-HDS process was analyzed using gas chromatography-mass spectrometry (Fig.1). The GC-MS data confirmed that some aromatic hydrocarbons were removed along with sulphones during extraction. The Non-HDS process with bio-desulfurization technique resulted in some thiophene hindered type sulfur removal in addition to other aromatic hydrocarbon species. This was probably due to small polarity differences between the sulfur containing compounds and other aromatic hydrocarbons removal during bio-desulfurization. This process resulted in removal of sulfur compounds and formation of sulphoxides and sulphones that were relatively polar as compared to original sulfur species (Table 2). This gives preference to sulfur compounds that gets easily separated with minimum impact on removing other aromatic hydrocarbons. The results of these experiments revealed some useful information about bio-desulfurization process. *Methylomonas methanica* showed higher activity for removal of sulfur than *Rhodococcus sp.*

It was observed that if one of the aromatic rings gets saturated, it is easier to break C-S and C-S-H bond. However, in the absence of hydrogen, S removal mostly depends on the concentration of substrate (McFarland *et al.*, 2001). Under high acidity, the reaction proceeds through dealkylation route followed by desulfurization.

Table 1 : Comparison and contrast with Non-HDS reaction systems

Reaction systems	Total sulfur removal %	k min ⁻¹	Correlative coefficient (R)
H ₂ O ₂ -CH ₃ COOH	29.6	0.02368	0.9598
Persulfate reagent during oxidation	74.1	0.42376	0.9776
Persulfate reagent with adsorption and extraction after Non-HDS process	99.06	0.2148	0.9901
Non-HDS process with Bio-desulfurization using <i>Rhodococcus sp.</i>	99.76	0.2624	0.9956
Non-HDS process with Bio-desulfurization using <i>Methylomonas methanica</i>	99.90	0.2790	0.9982

Table 2: Sulfur compounds in diesel fuel after the process

Sulfur compounds	Original diesel fuel (µg g ⁻¹)	Desulfurized diesel fuel after Non-HDS process coupled with Bio-desulfurization using <i>Rhodococcus sp.</i> (µg g ⁻¹)	Desulfurized diesel fuel after Non-HDS process coupled with Bio-desulfurization using <i>Methylomonas methanica</i> (µg g ⁻¹)
BT	31.04	No detected	No detected
4-MDBT	59.14	No detected	No detected
C ₁ DBT	16.43	No detected	No detected
4,6-DMDBT	50.54	0.40	0.40
1,4-DMDBT	97.44	No detected	No detected
C ₂ DBT	130.52	1.22	0.99
TMDBT	143.43	1.29	1.30
C ₃ DBT	126.87	0.65	0.5506
C ₄ DBT	110.59	0.66	0.76
Total	766	4.22	4.06

(BT – Benzothiophene, DBT-Dibenzothiophene, DM – Dimethyl, TM-Trimethyl)

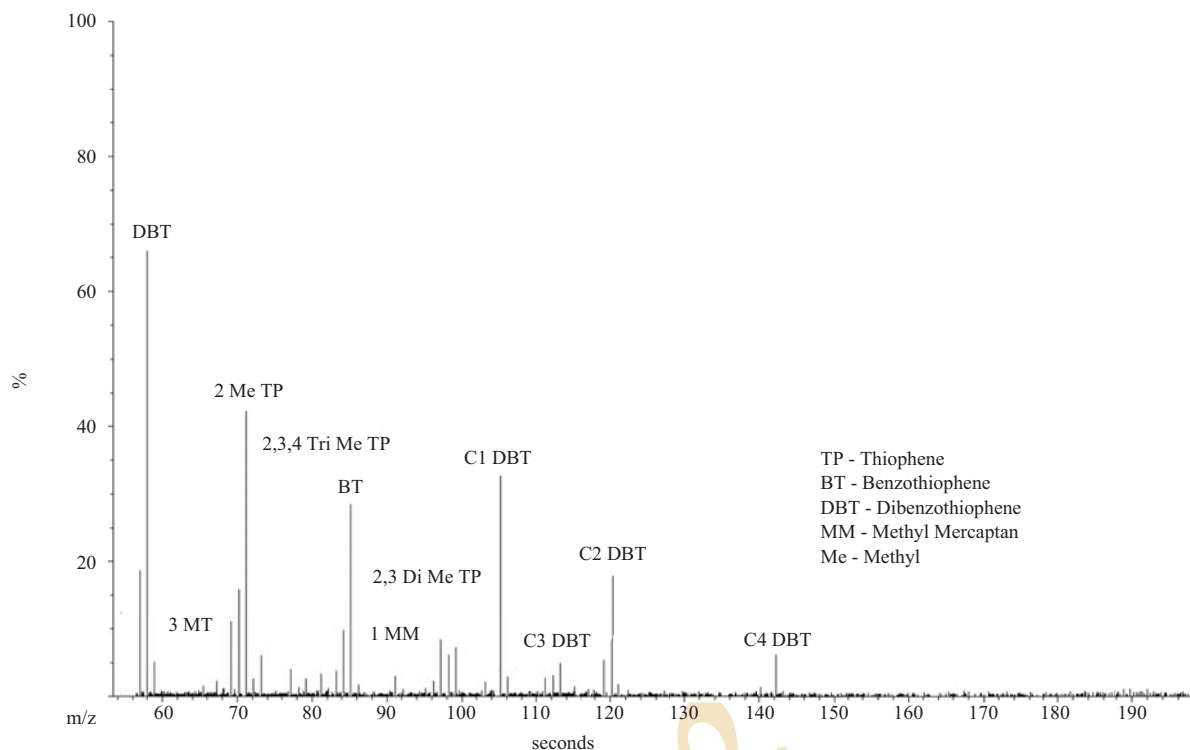


Fig. 1 : GC-MS spectra of sulfur speciation in diesel fuel

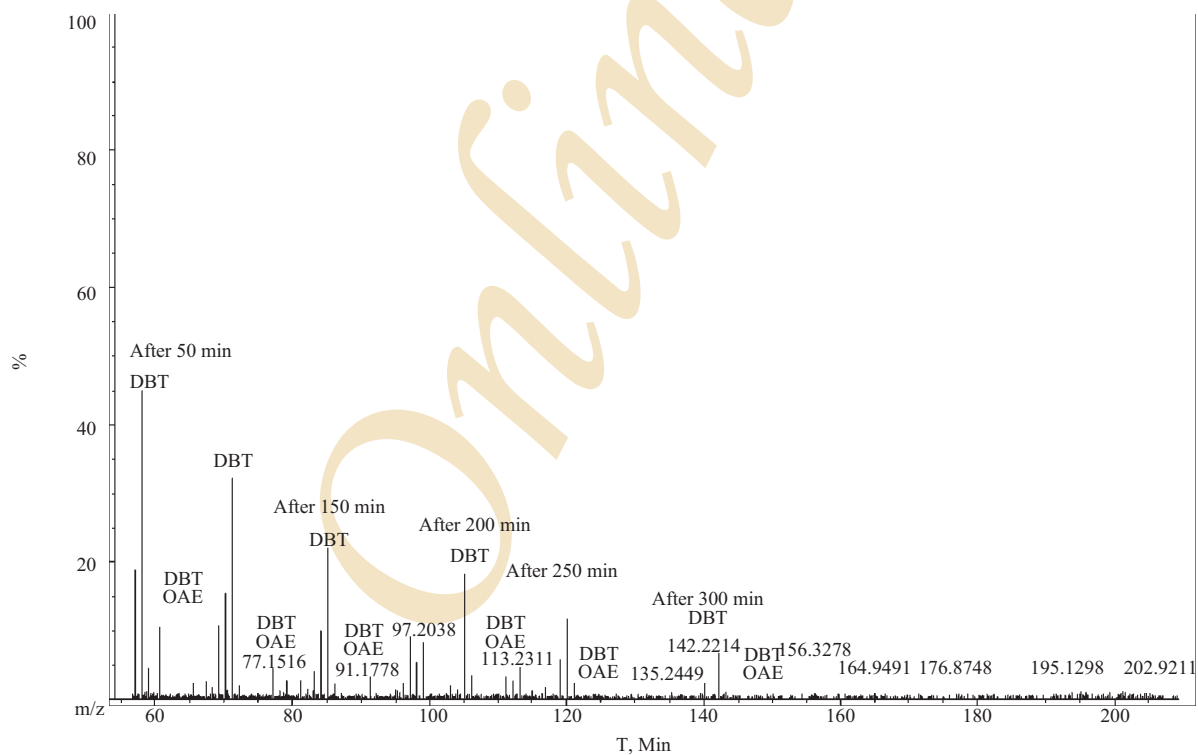


Fig. 2 : GC-MS spectra of DBT during Non-HDS process

Fig. 2 is another unique revelation that highlights newer facts and figures. The mass spectra were used to identify the peaks. No library compounds were available for comparison purpose; however, the result from the model compound DBT was used to identify some of these compounds. The mass of DBT resulted in the following named compound dibenzo [b,d] thiophene 4,6-dioxide with total mass of 264 as represented in the following formula $C_{14}H_{10}SO_2$. From the previous work and the results of this study, it is clear that most of the untreated diesel was thiophene hindered types. It is noted that during the process, the maximum percentage of sulfur compounds were removed from diesel fuel. It was concluded that the only groups that would contribute to the total mass of the resulting sulphones were those with attached alkyl groups, which already existed in the original sulfur compounds. Therefore, scanning of certain mass that would represents methyl molecular mass would give various isomers of the sulphones product.

Fig.3 gives a clear picture of FT-IR spectroscopy indicating removal of thiophene hindered type sulfur compounds after non-HDS process with bio-desulfurization technique. For these experiments, adsorbance spectra were collected in the range $4000-1000\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} with 64 scans/spectrum. The left and right panels showed high and low wave numbers regions of the spectra. The main spectral features were located at 1457.52, 1619.97, 3954.91. The peak 3425.85 appeared as negative feature and corresponded to the surface hydroxyl group. For all the spectra, due to background subtraction a decrease in the intensity of negative peak with increasing temperature indicated growth of the peak. As a result, sulfur removal increased, the concentrations of hydroxyl functionalities decreased even though the intensities of peaks the removal of sulfur increased.

This Non-HDS process using persulfate reagent followed by Bio-desulfurization was found to be the most

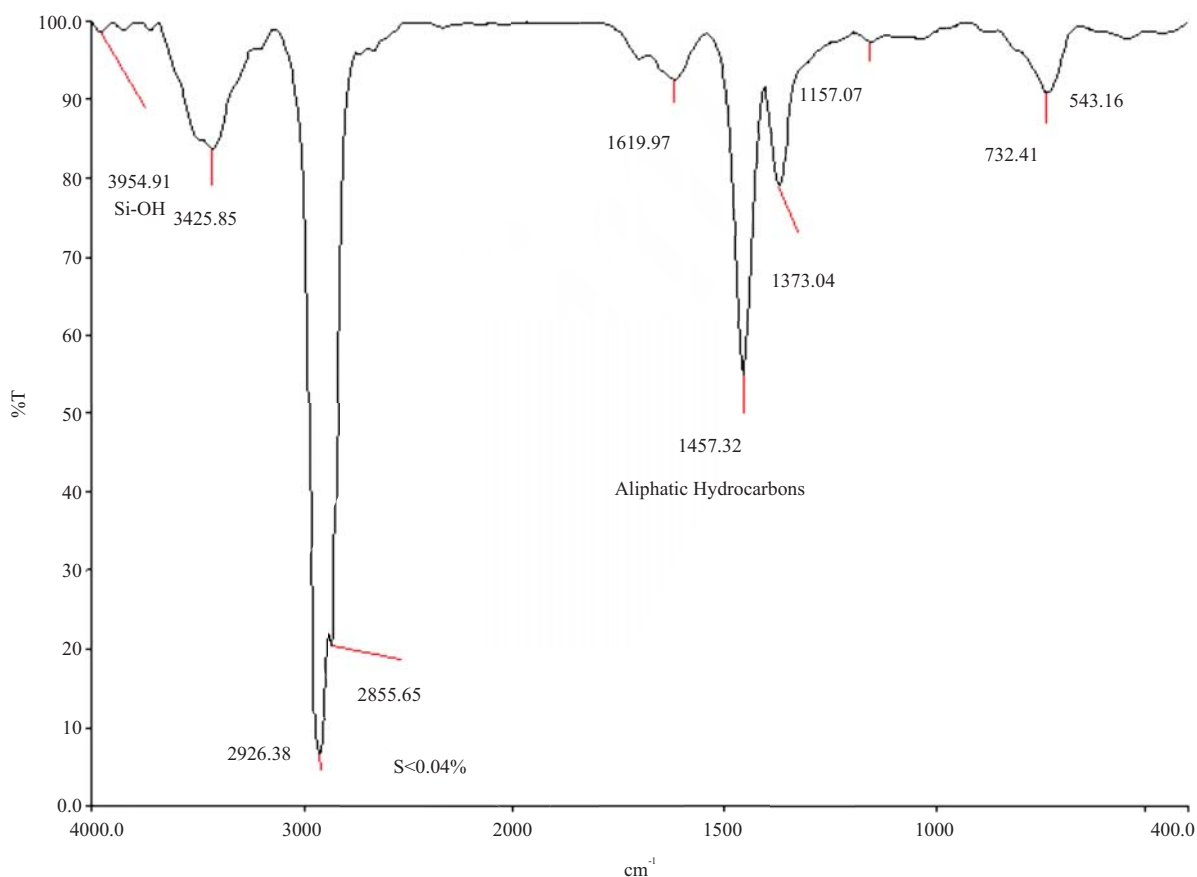


Fig. 3 : Part of FT-IR Spectroscopy showing sulfur content in diesel fuel after the process

promising approach for reduction of sulfur from $766 \mu\text{g g}^{-1}$ to $4.22 \mu\text{g g}^{-1}$ using *Rhodococcus sp* and $4.06 \mu\text{g g}^{-1}$ using *Methylomonas methanica*. This was equivalent to 99.93% sulfur removal and was 1.78 times better than Bharat IV norms. The sulphones identified can become good references for future studies.

A detailed analysis of all the tables and figures revealed that this innovative coupling of non-HDS process with Bio-desulfurization has huge potential to pave a different pathway for researchers to work and produce ultra-low sulfur diesel fuel at cheap rates in laboratory. A detailed research work in future might also help to scale-up the processes to industrial level for production of environment friendly ultra-low sulphur diesel fuel in large quantities for domestic and commercial use.

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