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Biodesulphurization process for removal of sulphur from fuel oil

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Abstract :-Diesel and heavy fuel oil, especially low sulphur heavy stock (LSHS) contain organic sulphur compounds which are major source of air pollution. Hydrodesulphurization process is used to remove sulphur compounds from fuel oil. However, alkylated thiophenes (sulphur containing compounds) are difficult to remove from fuel oil by present hydrodesulphurization process. Therefore, extensive development work has been carried out in the field of Biodesulphurization process for removal of alkylated thiophenes (sulphur containing compounds found in diesel) from diesel and heavy fuel oil by using desulphurization enzymes produced by selected bacterial strain. This paper reviews few of the work on biodesulphurization process for removal of sulphur from fuel oil.

Keywords: - Biodesulphurization, Hydrodesulphurization, desulphurization enzymes

Introduction

All the fossil fuels contain organic sulphur compounds. Sulphur di-oxide is released into the atmosphere from the combustion of fossil fuels remains one of the most prominent intractable issues of environmental concern. It is a major contributor to the generation of acid rains which accelerates corrosion of buildings and monuments, kills forest, poisons lake. Inhalation of sulphur-di-oixide also have adverse health effects as inhibition of breathing, respiratory illness and aggravation of existing cardiovascular disease.
Hydrodesulphurization (HDS) is used in refineries to remove sulphur from fuel oil. Hydrodesulphurization is a high pressure (150-250 psi) and high temperature (200-450°C) process that uses hydrogen gas for reducing the sulphur in fuel oil to hydrogen sulphide which is then separated from the fuel oil. However, hydrodesulphurization units are highly expensive to build and operate. In addition certain sulphur compounds such as polyaromaticsulphurhetrocycles (PASH), and dibenzothiophenes are difficult to remove from fuel oil by present hydrodesulphurization process.These limitations of hydrodesulphurization process prompted researchers to venture into the Biotechnology to find an alternate process of desulphurization.
Biodesulphurization process had been started in the early 1950s, and there was no significant progress made till 1980s. In early 1980s, U.S Department of Energy & other organisations sponsored work around the country to find a permanent solution for the sulfur problem. But, the bacteria, which they applied for commercial desulphurization technologies were not preferred, because they attacked the hydrocarbon portion of polyaromaticsulphurhetrocycles (PASHs) and only coincidentally solubilized the sulphur molecules, to water thus removing them from oil. Many of the polyaromatic molecules like naphthalene, phenanthreneetc were also attacked. This was successful desulphurization, but the cost was too much of the fuel value of the oil. It was clear then that, further development work was meaningless until an enzymatic system that specifically attacked the sulphur atom in the PASHs in oil could be identified.
Kargi and Robinson (1983), had isolated a thermophilic bacterial strain*, Sulfolobusacidocaldarius* and they found out that sulphate ions were released into the medium, as the oxidation product. The kinetics of the sulphur oxidation had been investigated by them, was on the basis of sulphate released as a result of oxidation. Atlas and Mormile (1988) observed that, the degradation product of dibenzothiophene (DBT), like 3-hydroxy-2-formyl benzothiophene and dibenzothiophene sulfone could be mineralized with the release of CO_2. However, even though carbon in the ring structure of DBT was mineralized to CO_2, there was no release of sulphur from the thiophene ring under aerobic conditions.
Jorgensen and Bak (1991) studied the reductive and oxidative pathways of the sulphur cycle in a marine sediment by parallel radiotracer experiments with $^{35}SO_4^{2-}$, $H_2{}^{35}S$, and $^{35}S_2O_3^{2-}$ injected into undisturbed sediment cores. The distributions of viable populations of sulphate and thiosulphate reducing bacteria were concurrently determined. They observed that, oxidative and reductive cycling of sulphur occurred in all sediment layers with an intermediate “thiosulfate shunt” as an important metabolism regulating the electron flow.
Kilbane and Jackowski (1992) used water-soluble coal-derived material for their biodesulfurization experiments with *Rhodococcusrhodochrous* strain IGTS8. The results of their experiments revealed that, the microbial removal of significant amounts of organic sulfur from water soluble coal derived material with treatment times as brief as 24 hours were possible. Moreover, the carbon content and calorific value of

biotreated products were largely unaffected. Biotreatment, however resulted in increased hydrogen and nitrogen content and a decreased O_2 content of the coal derived material.They also found out that the aqueous supernatant obtained from biodesulphurization experiments, had not contained sulfate, sulfite or other forms of soluble sulphur at increased concentrations. Hence they concluded that sulphur removed from the coal materials might be incorporated into biomass.

Kayser et al. (1993) performed a variety of growth assays which revealed that *Rhodococcusrhodochrous* IGTS8 could use a wide range of organosulfur compounds as the sole source of sulfur, but none of the compounds served as carbon sources. Further, a specific spectrophotometric assay (Gibb's assay) was developed, and used in conjunction with GC/MS analyses to examine the kinetics of DBT metabolism by axenic and mixed cell cultures of *Rhodococcusrhodochrous* IGTS8. Their experiments revealed that the desulphrization activity, on a per cell basis, is higher in mixed cultures than in axenic cultures.

Young et al. (1994) were successful in the identification and cloning of genes involved in specific desulphurization of dibenzothiophene. They mutagenized IGTS8 strain and designated it as UV-1, and the UV-1 phenotype lacked the ability to desulphurize DBT. Then the genomic library of IGTS8 which was constructed in a cosmid vector pLAFR5, was transferred into UV-1 and several colonies, that had regained the desulphurization phenotype were isolated. When the origin of replication from a *Rhodococcus* plasmid was inserted, the efficiency, with which these clones transformed UV1, increased 20 to 50 folds and they could be retrieved as free plasmids. Further, the restriction mapping and sub cloning indicated that the desulfurization genes resided on a 4 kb DNA fragment. Finally, the phenotype was transferred to *Rhodococcus*fascians D 188-5, a species normally incapable of desulfurizing DBT.

Wang and Steven Krawiec (1994) isolated, a gram positive, non-spore forming, non-acid fast, rod-shaped, aerobic bacteria with ability to desulfurize dibzenzothiophene or dibenzothiophene-sulfone (DBT02) were isolated from soil samples contaminated with fossil fuels. Modified fluorescence and calorimetric assays were used for the initial detection of 2-hydroxybiphenyl (COH-BP) in microtiter plates. Confirmation of the presence of OH-BP was achieved with HPLC, UV-absorbance and mass spectrometry. They had identified the strains as *Rhodococcus*erythropolis by nutrient utilization and fatty acid composition, by Biology plates and Gas chromatography, respectively. It was found that, the strain Rhodococcus sp. could not use OH-BP as a carbon source.

Izumi et al. (1994) isolated a dibenzothiophene degrading bacterium, *Rhodococcuserythropolis*D-1, which utilized DBT as a sole source of sulphur, from soil. It was observed that 2-HBP was almost stoichiometrically accumulated as the dead end metabolite of DBT degradation. They had reported that DBT, at a concentration of 0.125 mM was completely degraded within 2 days of cultivation. They concluded that, the strain *Rhodococcuserythropolis* D-1 had a higher DBT-desulfurizing ability than any other microorganism reported previously.Izumi et al. (1995) isolated a bacterium, from soil which could utilize dibenzothiophene as the sole sulphur source in the presence of hydrocarbon. It was identified as *Rhodococcuserythropolis* and the strain was able to produce 2-HBP stoichiometrically, within a day, when grown on medium containing 0.27 mm DBT.

Lau et al. (1997) established the DNA-relatedness in six new rhodococcal isolates by the cloned sulphur oxidation (Sox) genes for DBT from the *Rhodococcus*sp strain IGTS8 using southern hybridization and PCR experiments. Those six isolates were capable of utilizing DBT as a sole sulphur source for growth. It was found that, the ability of these strains, to desulphurize, appears to be an exclusive property of a 4-kb gene locus on a large plasmid of ca 150 kb in IGTS8 and ca 100 kb in the other strains. They distinguished IGTS8 from the other strains, by the copy number of the insertion sequence IS1166, which was found to be associated with sox genes.

Fedorak (1997) et al., investigated the transformations of 1, 2, 3, 4 – tetrahydrodibenzothiophene (THDBT) with pure cultures of hydrocarbon degrading bacteria. The metabolites were extracted with dichloromethane (DCM) and analyzed by gas chromatography (GC) with flame photometric, mass and Fourier transform infrared detectors, and their approach of quantifying the degradative pathway intermediates (Kodama pathway) was the first of its kind.

Chang et al. (2000) revealed that the desulphurization activity of the resting cells of Gordona sp. CYKS1 was strongly dependant on harvest time and the highest value, when the cells had been harvested in the early growth phase. They also found out that, for the model oil, hexadecane containing dibenzothiophene, the specific desulfurization rate decreased as the reaction proceeded. They concluded that the diesel oils, light gas oil and a middle distillate unit feed were desulfurized at higher rates than the model oil.

Grossman et al. (2001) tried extensive desulfurization of hydrodesulruzied middle distillate oil by *Rhodococcus* sp. strain ECRD-1. They proposed that Dibenzothiophene and in particular substituted DBTs, were resistant to hydrodesulphurization (HDS) and could persist in fuels even after aggressive HDS treatment. They found out that upon treatment with *Rhodocossu* sp. strain ECRD-1 of a middle distillase oil, whose sulphur content was virtually all substituted DBT's produced extensive desulphurization and a sulphur level of 56 ppm.

Conclusion

Recent judicial interventions in our country for the introduction of low sulphur fuel oil specially in diesel (sulphur in diesel 0.05% w/v) and further the target for ultra-low sulphur (0.005%) in diesel has prompted hydrodesulphurization process. However, certain sulphur containing compounds such as alkylated dibenzothiophenes (which are major source of sulphur in diesel) are not possible to remove from fuel oil by current hydrodesulphurization process. Currently worldwide many research laboratories are engaged in development of Biodesulphurization process. These alkylated dibenzothiophene can be removed from diesel and heavy fuel oil by using bacterial enzymes such as dibenzothiophene monooxygenase and hydroxybiphyeny-2 sulfinatesulfinolyase.

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