BIO-DESULFURIZATION:THE EMERGING POTENTIAL TECHNOLOGY FOR DESULFURIZATION OF PETROLEUM PRODUCTS.

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Abstract

The stringent government policies over the regulation of sulfur discharge in the environment has enforced oil and chemical industries to make huge investment in bringing down this sulfur content in the discharge and petroleum products to the desired levels. Crude oil contains a large no. of sulfur containing molecules amongst which main sulfur containing molecules are alkylated dibenzothiophene (DBT). The conventional approach of desulfurization revolves around the hydrodesulfurization technique, in which sulfur is catalytically converted to hydrogen sulfide in the presence of hydrogen gas. The kinetics of this reaction is favored at high temperature and pressure conditions henceforth hiking the capital cost as well as the operating cost. As a surrogate method biodesulfurization (BDS) is an sophisticated and non-invasive approach to remove sulfur under mild conditions and it can be potentially used in industrial desulfurization. BDS in generally carried out in the presence of a anaerobic bacteria known as *rhodococcus erythropolis* which finally degrade the DBT to hydroxybiphenyl (HBP). This article comprehensively reviews and discusses key issues, advances and challenges for a competitive biodesulfurization process.

KEYWORDS: biodesulfurization, dibenzothiophene, hydrodesulfurization, hydroxybiphenyl, rhodococcus erythropoils

I. Introduction

Nonrenewable resources like oil, coal and gas are still the by far sources of energy in the current century. Most of the hydrocarbons being mined form the underlays of the earth's crust are used for in fact we should say burned for the energy production in one way or the other. And since most of the reserves of these hydrocarbons are contaminated by sulfur, direct combustion of these fuels will lead to the release of large quantities of sulfur oxides in the atmosphere [1]. Amongst all the sulfur oxides SO_2 is the most abundant and is released in the lower atmosphere where it reacts with the moisture present in the air and cause acid rain or low pH fogs. Moreover it has also been found that the total particulate matter emissions from the combustion of diesel fuel are directly proportional to the amount of sulfur present in it [2-6, 8].

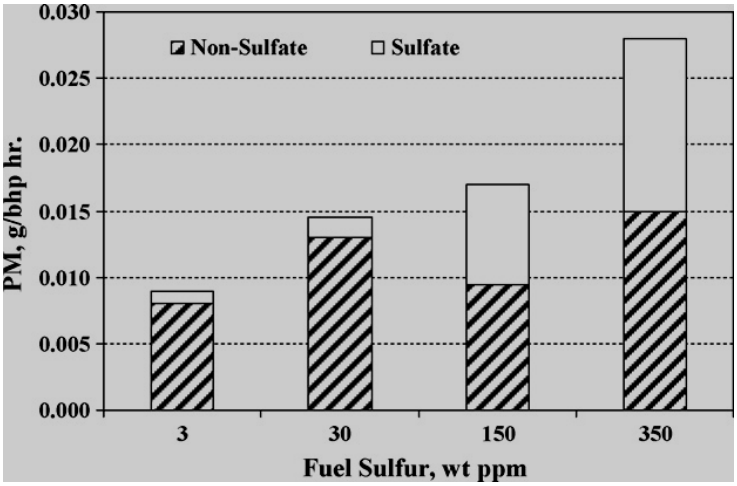

Fig: Particulate material (PM) emissions after diesel oxidation catalyst (DOC) as a function of diesel fuel sulfur level [8]

US EPA claimed that approximately 2 % of the sulfur present in the diesel is converted to the particulate matter that gets emanated on the combustion of diesel fuels. The main constituents of the PM are a carbonaceous core, a soluble organic fraction (SOF) and a mixture of SO_x and water, and it has been proved to be carcinogenic for humans [7-8].

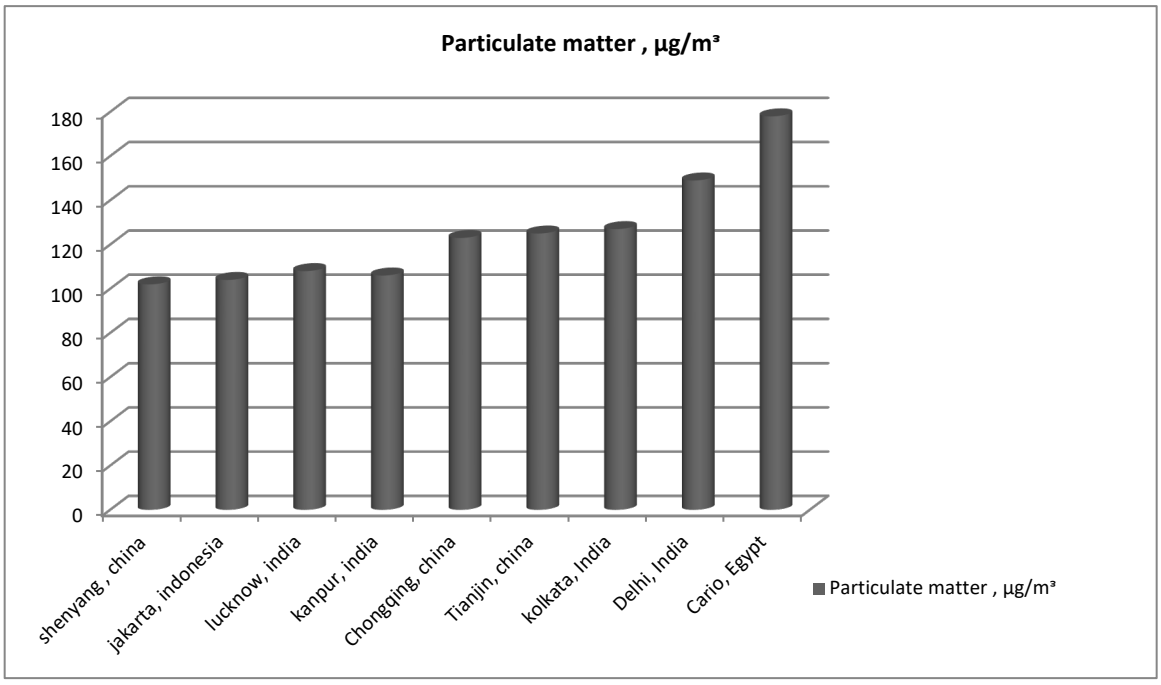

Fig: Particulate matter present in the atmosphere of some highly populated cities [8]

Several emission control devices installed in the vehicles to curb the various pollutants from release into the environment like Diesel Oxidation catalysts (DOC), NO_x absorbers , PM filters and selective catalyst reduction (SCR) systems, they also gets affected by the increased sulfur content adversely. These converters are responsible for the combustion of unburnt hydrocarbons in the engine exhaust that conduce to the automobile pollution [11]. Oxidation catalyst oxidize CO, HC and the soluble organic fraction of PM to CO_2 and H_2O in oxygen rich exhaust current in diesel engines [4,8]. Presence of sulfur also increases the rate of oxidation of SO_2 and high levels of harmful sulfates are emitted in result. Moreover sulfur presence poisons and reduces the effectiveness of the oxidation catalysts, consequently hazardous SOF, CO and HC also get increased in the exhaust stream [8-9].

Furthermore most of the times SO_2 is the cause of sulfate aerosol formation, these aerosol particles have an average diameter of order 2.5 µm that gets into the lungs and cause breathing problems[1,10]. As the consequences of the anticipation of hazardous effects of sulfur oxides in the atmosphere, International organizations have already stringent the policies and regulation to curb the ebbing increment in the sulfur percentage in the hydrocarbons being combusted directly. According to the published and the unpublished data several developed nations for instance Canada, United States and the other European countries have already signed many agreements to minify the sulfur dioxides emission in their countries. Most of the agreements were leaned towards the monitoring of the SO_2 emission in the transport fuel combustion as it is considered as one of the radical source of the SO_2 in the atmosphere. In 1993, the clean air pact interdicted the sales and supply of diesel oil with sulfur concentration more than 500 mg/kg. In the same series in 1998 the European Union defined the anticipated target for the sulfur content in the diesel fuel at the grade of 350 and 50mg/kg for the years 2000 and 2005 respectively. Similarly from June1, 2006 Canada and U.S. adjudicated to reduce the sulfur concentration in on-road diesel fuel and gasoline from 500 mg/kg and 350 mg/kg to 15 mg/kg and 30 mg/kg respectively [8, 10, 12]. In South or Central America including countries like Argentina, Chile, Brazil, Mexico Peru, Uruguay also implemented strict regulations to curb the sulfur emissions by controlling down the percentage of sulfur content present in fuels. In Mexico where the upper limit of sulfur content was 500 wppm in year 2005, it was reduced down to 15 wppm by the government authorities in the year 2009. Whereas these limits for Argentina, Brazil and Peru was set to be 50wppm in the year 2008, 2009 and 2010 respectively. The maximum prescribed sulfur content in diesel was aimed at 10 mg/kg by 2010 in US. Same trend of decreasing down the sufur content in the fuels also followed in Asian pacific countries including India, China and Singapore. Where the sulfur content allowed in the fuel was 500 and 350 wppm in the year 2005 in China and India respectively, it was reduced to 50wppm in the year 2010 for India and Singapore and 2012 for china. In Australia also govt. authorities reduced the limit from 500 wppm (2002) to 10 wppm (2009). Now let us talk about Middle East countries like Saudi Arabia, Russia and Iran.

Russia and Iran have also proposed the sulfur content allowable in the fuels at the levels of 50 wppm and implemented the policies regarding this in the year 2008 and 2010 respectively, where Saudi Arabia has anticipated the levels to be down to 10 wppm in the year 2013. Technically forward European countries have already pushed these levels under 10 wppm in the recent years [8,13-14]. And positively they have drawn very close to their aimed sulfur concentration [10].

Currently in refineries diesel and some other hydrocarbons are treated thermo-chemically following hydrudesulfurization (HDS) method. The kinetics of this method is favored by high temperature and pressure conditions. Inspite of the fact that this method is very efficient in removing the organic sulfur load to 100mg/dm^3 level but with the available range of catalyst (CoMo, NiMo etc). This process is not suitable for the dismissal of polyaromatic sulfur compounds like alkylated dibenzothiophene, napthothiophenes etc. present in diesel in ultra-low level (10 mg/dm^3) as required by the new US and European norms. Henceforth a new and ingenious technique of sulfur removal was required that induced intensive research. Consequently bio-desulfurization came into the picture replacing the higher pressure-temperature conditions and novel catalyst with milder conditions and better results [15-17]. Frequent efforts in microbial screening and development have traced out several microorganisms capable of petroleum desulfurization. In BDS biocatalyst being used are the microorganisms (*rhodococcus erthyropolis, thiobacillus forroxidans, Sulfolobus acidocaldarius*) that convert refractory sulfur content in organic compounds (DBT into HBP) [18-19].

Biological desulfurization may occur in two ways namely oxidative and reductive. Oxidative process proceeds with the conversion of sulfur into sulfate which may be dismissed in process water [19-24], whereas in reductive desulfurization, organic sulfur is converted to hydrogen sulphide which is converted to elemental sulfur catalytically [19,25-26]. Apart from the mode of desulfurization, prime factors affecting the economics of these processes are biocatalyst activity and cost, differential in products selling price, sale or disposal of co-products or wastes from the treatment process, and the capital and the operating costs of the treatment scheme [19].

II. Sulfur content in petroleum

Sulfur containing compounds present in crude oil and its derivatives can be broadly relegated under two divisions: inorganic sulfur and organic sulfur. Sulfur is the most abundant element in crude oil after hydrogen and carbon. The concentration of sulfur content can be estimated by the density of the crude oil, as the density increases the amount of sulfur content also increases. Moreover distillation fractions with higher boiling points contain higher sulfur concentration. The sulfur content in the crude oil ranges between 0.03 wt. % and 7.89 wt. % [10, 27]. However sulfur ingredient in the crude from Persian gulf and Venezuela are particularly high [27-29] .
Inorganic sulfur- containing compounds in crude are elemental sulfur, H_2S, Pyrites and are mainly found in dissolved or suspended form. Organic sulfur compounds include aromatic or saturated form of thiols, sulfides, disulfides, thiophenes substituted benzo- or dibenzo- thiophene and hetrocycles and many other complexes [1,8,10,11,19,27]. Amongst them DBT or its derivatives are of prime attention as they have higher boiling points (more than 200˚C). And hence they are difficult to be removed from atmospheric tower outlet streams (e.g. middle distillates) [10,30]. The order of sulfur content in crude oil fraction commonly increases as: saturates < aromatics < asphaltenes [27].

S-compounds present in the petroleum oils can be classified as

- Lighter fractions: mercaptans, sulfides, disulfide ,thiophene derivatives
- Middle fractions: sulfides, disulfides, benzothiophenes, dibenzothiophenes
- Heavier fractions: Multi-Ring S-Compounds [31]

Lighter fractions like thiols present in crude oils at boiling temperature below 200~ and can be easily removed during the refinery processing. Aliphatic sulfides (cyclic or acyclic) are another principal components of the sulfur containing petroleum products have boiling point above 200~. Sulfides having lower molecular wt. are easily removed from the crude oil in the pretreatment and the refining process whereas the heavy and bulkier alkyl- aryl, mono and disulfides are left back with the crude.

Heavier fractions are generally aromatic sulfides having lower concentration comparatively but possess large molecular weight [27]. Derivatives of thiophene such as benzothiophene, dibenzothiophene, napthobenzothiophene, they all form an integral composition in the high-sulfur oils. Moreover the amount of these compounds in distillates and residuals, like heavy oil and bitumens are the upper most. According to the published data, the Texa crude oil has been reported to have 70% of the DBT as the sulfur containing compounds whereas in the Middle East countries substituted benzo and dibenzohiophenes constitute more than 40% of the sulfur concentration [27,32]. Now, as

mentioned above DBT and substituted DBT are some of the most fractious organic sulfur compounds when subjected to hydrodesulfurisation. These refractory compounds are highly stable aromatic sulfur containing compounds, hence need a more incursive way of desulfurization to dismiss the sulfur content they possess. The fractious portion of diesel fuel is imputed to the thiophenic compounds which further can be subdivided as BTs (benzothiophene) and DBTs (dibenzothiophenes). BTs with alkyl substituent contain 1-7 carbon atoms where DBTs with alkyl substituent contains 1-5 carbon atoms. The distribution of these sulfur containing compounds in different gas oils (SRGO, LCO, CGO) is different and this dispersion is attributed to the origin of the petroleum [8].

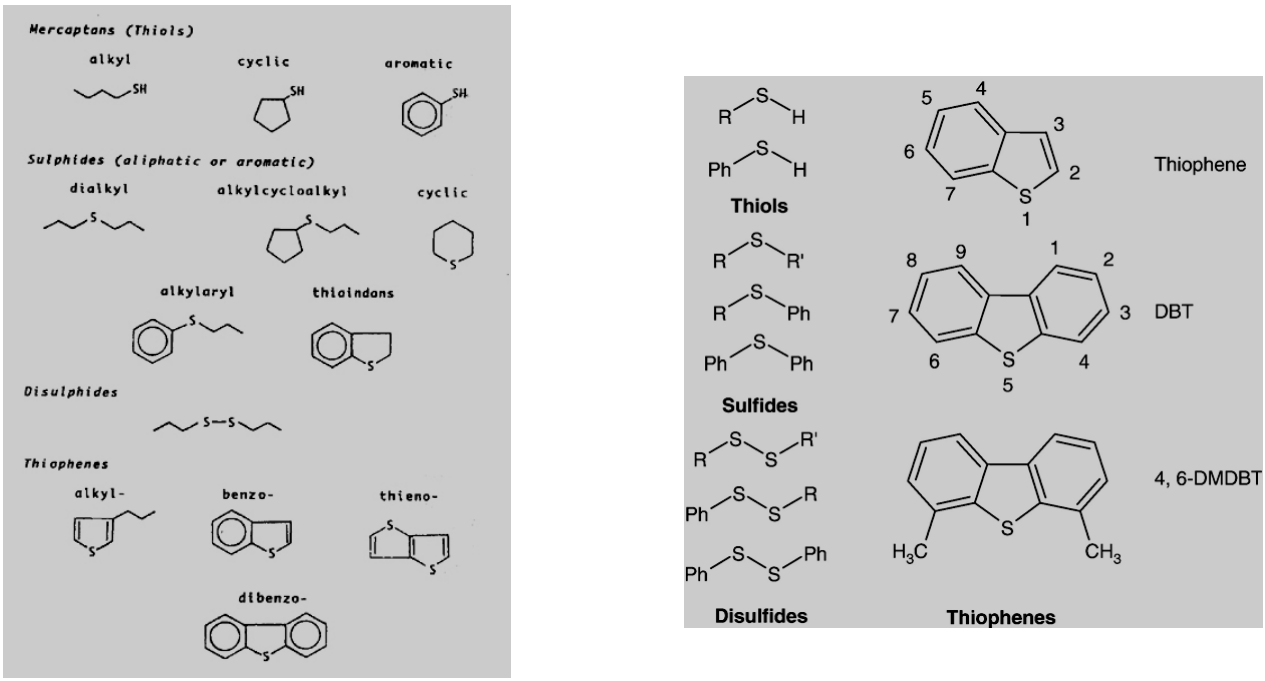

Fig: various S-containing compounds found in crude oils [1, 35]

III. Methods of desulfurization

Now, let us come to the methodologies and techniques available to desulfurize the various oil and gas products to the desired levels and to abide by the policies of the government of different nations.

There are basically two modes of desulfurization in general. They are: pre-combustion and post-combustion. Pre-combustion of the fossil fuel reduces the sulfur oxide emanation irrespective of the type of combustion. On the other hand post combustion deals with the hot and corrosive effluents and it is pretty expensive altogether. Therefore this method has limited scope of application and hence avoided over pre-combustion techniques having wider scope of the usability [10].

Now, most of the sulfur entrapped in the compounds including sulfides, disulfides, mercaptans, thiols, thiophenes etc. can be removed easily. But the refractory organic sulfur is the one which is very difficult to remove [27-32]. The processes being used currently include hydro treatment, operate under very extreme conditions of temperature and pressure and hence are very costly to carry out. Moreover these processes are emanating large amounts of CO_2 in the atmosphere leading to global warming. Therefore there is a need of some alternate ways of desulfurization hence a overview of master processes of desulfurization is discussed below.

1. Hydrodesulfurization

HYDRODESULFURIZATION is the method currently being used by many industries and refineries to carve out the sulfur content in the oil and gas fuels. As discussed above removal of organic sulfur from the refractory organic compounds of crude or fossil fuels is difficult. And this is so, because sulfur is attached to various other atoms in an organic molecule. Now to get this sulfur atom off that particular molecule, there is a need of large amount of energy to break all the bonds sulfur atom is linked with [33-34]. In HDS, by the use of several selective catalysts, sulfur atom in sulfur compounds is reduced to H_2S in the presence of H_2 gas. The catalysts used are Co/Al_2O_3 or $NiMo/Al_2O_3$ generally. The H_2S produced is then air oxidized catalytically to the elemental sulfur. The temperature

and pressure conditions of the HDS may vary in the range of 200-425°C and 150-250psi H_2. Because of the fact that BTs and DBTs concentrations are considerably decreased by HDS and it is being used commercially for a long time [10,33]. It has several disfavors also listed below are [1, 8, 10, 11, 27, 19, 32-35]:

1. This method requires higher temperature, pressure, and longer residence time conditions for refractory sulfur compounds to reduce to hydrogen disulfide gas.
2. The installation, operating and maintenance of this process are very expensive as they are designed to bear extreme conditions.
3. HDS is inefficient in the removal of several aromatic compounds such as 4- and 4,6-Substituted DBT, and polyaromatic sulfur heterocycles (PASHs). Whereas it is efficient in the removal of paraffinic sulfur such as thiols, sulfides and disulfides effectively.
4. The hydrogen atmosphere we use to in the process to produce H_2S has a side effect as olefinic compounds are hydrogenated and hence reduces the calorific value of the fuel. Now to makeover the reduced calorific value HDS treated stream is sent to the fluid catalytic cracking (FCC) which again adds to the cost.
5. The cost of reduction of sulfur content from 200 mg/kg to 50mg/kg Is approximately four times higher than to reduce the sulfur content from 500 mg/kg to 200 mg/kg.
6. The amount of CO_2 emanated is very large.

Hence to economize the desulfurization process and to overcome the above mentioned drawbacks, a milder desulfurization is required.

2. Desulfurization by extraction

2.1 Desulfurization using conventional liquids

The main theme idea behind this concept is the face that organosulfur compounds are more soluble in any appropriate solvent with respect to any other hydrocarbon. Here the key for the effective desulfurization is the selection of appropriate extractants and optimization of the conditions in a way so that maximum extraction of organosulfur compounds is possible. Different solvents like acetone, ethanol [36], polyethylene glycol [37-39] and nitrogen-containing solvents [39] have been tested in the same regard and showed the results with 50-90% of sulfur removal. According to the studies conducted by Bailes [40] , where sulfur compounds along with aromatic hydrocarbons are extracted from a light oil using extractants such as dimethyl sulfoxide (DMSO), acetonitrile and tetramethylenesulfone at room conditions. The study revealed that the extraction process reached equilibrium between organic solvents and light oil in less than five minutes and phase separation took place in about just 10 seconds. The light oil is once washed with equal volumes of water in order to remove the dissolved polar solvents. Further Petkov [41] demonstrated that the aromatic content of a hydrotreated middle distillate feed can be reduced 3-fold (from 27.1% to 8%) and sulfur content to 7-fold (from 0.2% to 0.0029%) using extractants like methanol, furfural, ethylene glycol. Various other extractants like acetonitrile, lactones like gamma butyrolactone, DMF, N-containing solvents like amines and pyrrolidones, or sulfur containing solvents like DMSO and sulpholane. Recently, according to the studies of Toteva and Topalova [42], it was revealed the diminuation in the sulfur content from 2.0% to 0.33% by a two stage extraction technique with dimethylformamide as the solvent used.

Cons of this process include the incapability if this method to reduce the sulfur levels to ultra-low levels as prescribed by the government policies. Moreover co-extraction of large amount of aromatic HC molecule leading to the loss in calorific value of the fuel [8].

2.2 Desulfurization by ionic liquids.

An ionic liquid (IL) is a salt in the liquid state below some random temperature (generally its) 100°C (212 °F) [8,10]. Ionic liquids are anticipated to replace organic solvents because they have no measurable vapor pressure below their decomposition temperature and can be fashioned to have different properties depending upon their structure. Ionic liquids can be used for desulfurization by extraction theories and moreover it's a mild process unlike HDS. Numerous number of ILs can be prepared by designing organic ions in different varieties and combining them together.

Amongst several ionic liquids possible, imidazolium based ILs have shown highest selective partitioning for the refractory organic compounds such as DBTs, single β and di-β methylated DBTs [44]. This nature of ILs can be used in desulfurizing various fuels. Imidazolium based ionic liquids can be used for the same purpose are [BMIM][PF6], [EMIM][BF4],[BMIM][MeSO4], [BMIM][AlCl4], [BMIM][OcSO4] [8,10-44].

Now selecting ions for these ionic liquids being used for sulfur removal is very critical and important. For instance some of the chlorometallate ionic liquids like [BMIM][$AlCl_4$] demonstrate very high selectivity for sulfur removal but

side-by-side they are highly sensitive to air and moisture and lead to the alkene polymerization in the fuel. Another important attribute in the selection of ions for the ILs for sulfur removal is the size of anions being chosen. Larger anions like $[OcSO_4]^-$ is more likely to extract DBTs effectively then smaller anions such as $[PF_6]^-$ or $[CF_3SO_3]^-$ [43]. According to the published data it has already been validated that imidazolium ions having larger alkyl substitution groups are better solvents for DBT removal [45]. [BMIM][$OcSO_4$] showcased a high partitioning for DBTs , but at the same time it dissolves non-sulfur organic molecules such as cycloalkanes and aromatics [10]. The ILs is seen to have the potential of being a commercial method for desulfurization and this is the sole reason of the commencement of extensive research on in the same field. But even after offering mild conditions of desulfurization and sweeping away the backlogs offered by HDS this method also lags at some points and they are:

1. During the desulfurization process recovery and recycle of ILs is very hard[46].
2. Loss of solvents during the extraction process is unavoidable is totally undesired.

3. Oxydesulfurization

Oxydesulfurization is yet another process for defulfurization and side by side the nonconventional too. It as a potential substitute for the conventional hydrotreatment of the fuels. In this process the refractory or the organic sulfur is oxidised to their corresponding sulfones in the presence of various oxidizing agents for instance H_2O_2, ozone, t-butyl hydroperoxide, t-butyl hypochlorite (t-BuOCl) [8, 47]. H_2O_2 is comparatively a slow oxidizing agent in the absence of a catalyst, but it becomes extremely effective in the presence of catalyst. The catalyst that increase the effectiveness of H_2O_2 include two sub categories: homogenous catalyst (organic acids, Polyoxometallic acids and their salts in aqueous solution); heterogeneous catalyst (transition metal compounds, supported–transition metal oxides etc.) [47-49]. The sulfone thus produced need further processing to be removed completely. The various methods being used to dismiss sulfonic compounds include extraction, decomposition, distillation and adsorption methods.

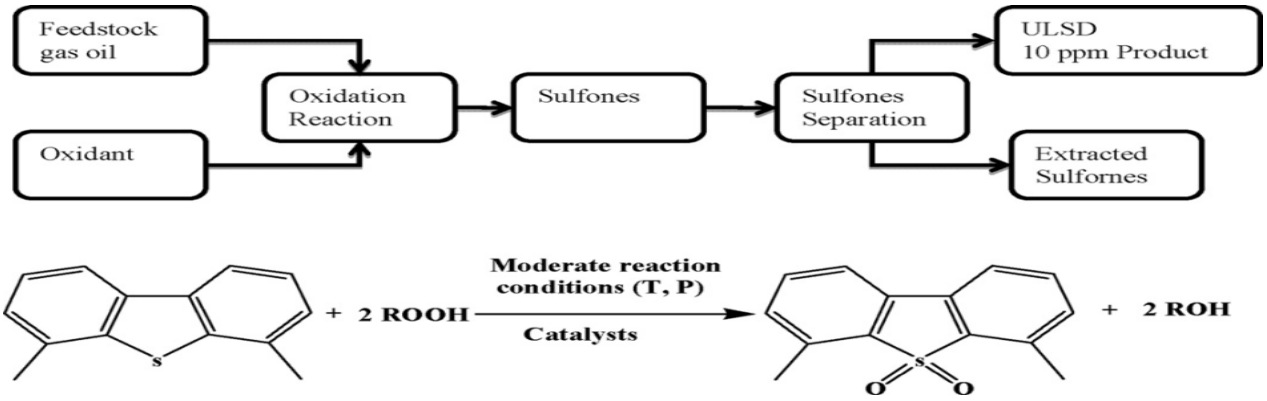

Fig: General flow diagram of 4,6-DMDBT oxidation by hydroperoxides at mild conditions in presence of a solid catalyst[8]

In ODS (oxydesulfurization) the reactivity of the organosulfur compounds to oxidation depends widely upon their local environment and structure of the sulfur atom. The following order has been found in the H_2O_2–formic acid system for the oxidation of some of the organosulfur compounds [47,50].

Methyl phenyl sulfide>thiophenol>diphenylsulfide> 4, 6,-DMDBT> 4-MDBT > DBT > BT

Now here we can see an interesting fact that the oxidative reactivity of 4-6- DBT molecule is more than the DBT molecule, which is reverse of that in HDS. Electrophilic addition mechanism for the oxidation of sulfur explains this behavior. So in this way the higher reactivity of the alkylated or hindered DBT offers an advantage of carrying out the desulfurization process under mild conditions unlike the conventional HDS process. Moreover in this method expensive hydrogen is not being consumed as in the HDS process [8].

These advantages catalyzed various researches in the stream of ODS to procure the diesel feeds with minimum amount of sulfur percentages. Oxidation of DBT and 4-6- DBT in hydrotreated light gas oil was studied by Otsuki [51]. The hydrotreated sample taken in this investigation comprised 150 ppm of DBT and 145 ppm of 4-6-DBT applying ozone as oxidant. Here it was found that the oxidation of 4-6-DBT was more apace than DBT. In another experiment conducted by the same researchers H_2O_2-formic acid was taken as the oxidant to carry out the oxidative

desulfurization of straight-run light gas oil (SR-LGO) and it was found that the sulfur content of the input feed has been reduced to 1.35 wt.% to 0.65 wt.%. Then Wang [52.a] declared through his research the complete transformation of refractory sulfur into sulfones present in a hydrotreated diesel having total sulfur content as 39 ppm by oxidation in the presence of MoO_3/Al_2O_3 as catalyst with t-butyl hydroperoxide. Amazing results were reported by Nanoti [52.b] recently, with the complete conversion of sulfur compounds present in diesel fuel having a total sulfur content of 500 ppm by the use of H_2O_2-formic acid reagents. The SCD chromatogrmas of the light gas oil incurred before and after the oxidation is complete as shown below, here we can clearly see that the peaks of sulfur compounds has moved towards higher retention times indicating the heavier molecular weights.

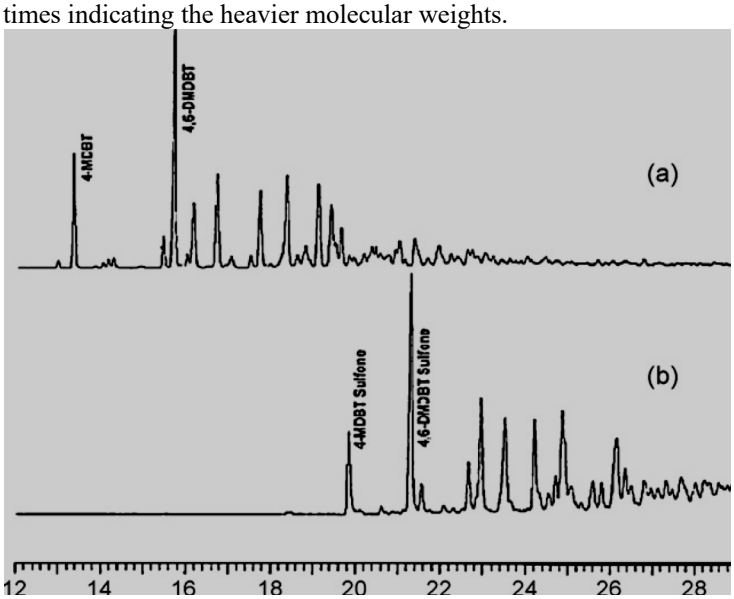

Fig: GC–SCD chromatograms of (a) diesel feed and (b) oxidized diesel [8]

The peaks representing DBT has almost disappeared where the appearance of corresponding DBT sulfone peaks consolidate the oxidative conversion of DBT to DBT sulfones. These sulfones so produced can be removed by a secondary treatment using adsorption and extraction techniques.

Several other modes of ODS were also practiced by various researchers, Chica et al.[53] performed ODS for partially hydrotreated light crude oil containing sulfur content comprising of mono-, di-, and trimethyl DBTs summing to a total of 330 ppm of sulfur content. The ODS process was carried out in a fixed bed reactor employing Ti-MCM-41C (calcined) and Ti-MCM-41S (sililated) catalysts in the presence of t-butyl hydroperoxide. A complete conversion of sulfur to sulfones has been reported using Ti-MCM-41S catalyst.

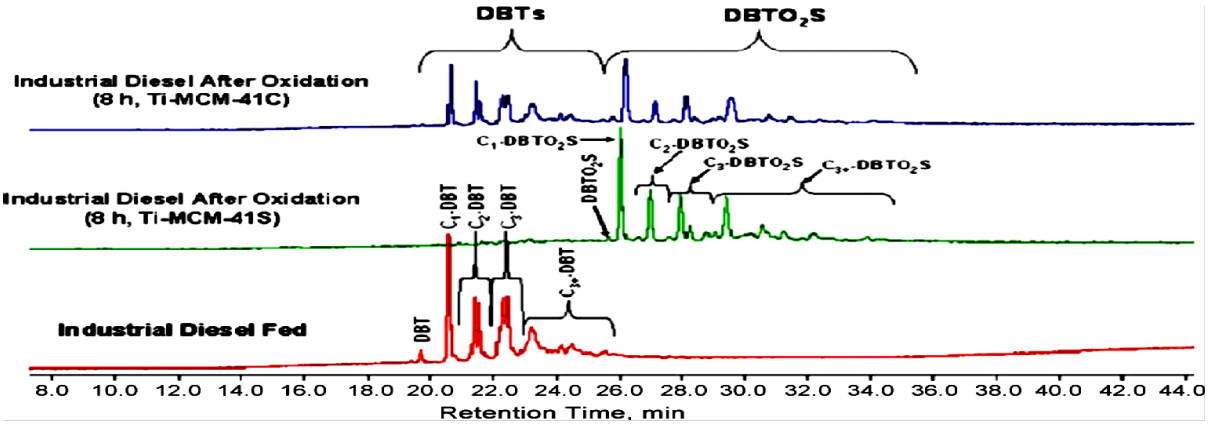

Fig: Sulfur-specific GC–PFPD chromatograms of industrial diesel fed and industrial diesel in the reactor outlet after 8 h of reaction time with Ti–MCM-41C (calcined) and Ti–MCM-41S (silylated) catalysts. Reaction conditions: industrial diesel, 373 K, atmospheric pressure, 0.1 g of catalyst, WHSV of 51.5 h−1, and oxidant/S ratio of 6 mol mol−1 [8]

Another work conducted by Mei et al. [54] revealed the ebbing increment in the rate of oxidation on the application of ultrasound employed during the oxidation process.

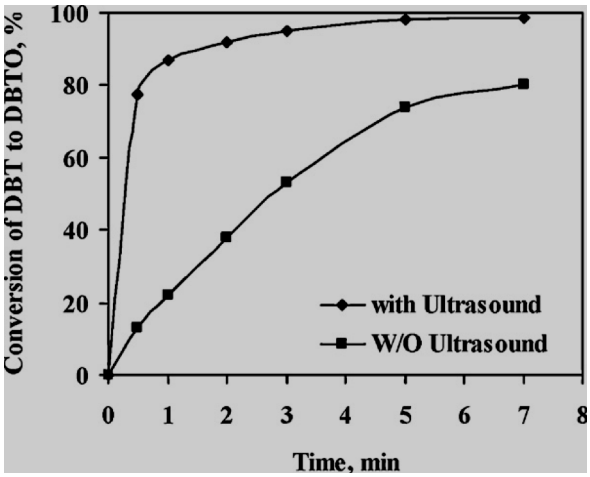

Fig: Conversion of DBT to DBTO with and without the use of ultra sound [8]

Then Sampanthar et al.[55] studied the diminution of sulfur content from 430 ppm to 40-60ppm in a diesel fuel by oxidation using molecular oxygen in air in the presence of Co- and Mn- containing oxide catalysts supported on –Al_2O_3, this is further followed by the extraction by a polar solvent.

Now let us take the secondary process that is the removal of sulfones from the oxidized fuels into the limelight [47-55]. Extraction and adsorption are the two main techniques been used for the purpose. Extraction of sulfones with various solvents has been studied critically and it revealed that the sulfur amount in any fuel can be taken down to the level of 1 ppm by oxidation followed by extraxtion technique. Sovents with higher polarity (e.g. Acetonitrile) supports the extraction process of sulfones. Garcia- Gutierrez et al. [56] used Mo/Al_2O_3-H_2O_2 system for the deep desulfurization of the diesel fuel. The sulfur content was found to be reduced from 320 wppm to 10 wppm under mild temperature conditions of 60˚C and atmospheric pressure. Another technique of sulfone removal is adsorption, according to Otsuki et al. [57] silica-alumina and silica gel are better adsorbents comparatively for the sulfone removal from the oxidized diesel feeds reducing the sulfur content from 730 ppm to 10 ppm. Various other adsorbents are also used for the removal of sulfone includes activated carbon, molecular sieves, -Al_2O_3, zeoloites and ZSM-5. Recent studies conducted by Ma et al.[58] that conflated the oxidation of sulfur present in the feed with the molecular oxygen in the presence of Fe(III) salts at normal conditions, followed by the adsorptive removal of sulfone using activated carbon. This reduced the sulfur content of a model jet fuel from 412 ppm to 2 ppm. Now a days ODS technology is all set to substitute the conventional HDS techniques, it is evident from the fact that around 30 process patents have already been issued under this technology some of them include SulphCo process, Enichem/UOP process, Lyondell chemical process, Unipure process, Petrostar process [8]. One of the main problem in carrying out this process is the consumption of expensive catalysts like hydrogen peroxide, t-butyl peroxide which is anti to the cost–effectiveness factor.

4. Desulfurization by adsorption

Desulfurization of oganosulfur compounds present in various fuel feeds can be carried out by the sue of adsorption mechanism. It is based on the capability of several solid adsorbents that can effectively adsorb the refractory organo sulfur compounds over their surface from the stream. Further desulfurization by adsorption can be subdivided into two groups depending upon the mode of interaction of adsorbent with sulfur containing compounds. The two groups are desulfurization by physical adsorption and reactive adsorption desulfurization [8].

4.1 Physical Adsorption

In desulfurization by physical adsorption organosulfur compounds present in the stream are adsorbed by the solid adsorbent without any conversion. This is solely a physical method in which no side reaction takes place between the constituents of adsorbent and sulfur containing compound. Here adsorbent with high sorption capacity, selectivity and regenerability are required for an efficient desulfurization process, hence the development of such adsorbents is the key task in this mode of desulfurization. According to the studies conducted by Song et al. [58-62] and his co-workers demonstrated various adsorbents based on transition metal complex supported in porous materials, zeolites, supported

transition metals, activated carbon, mixed metal oxides etc. in order to execute the adsorptive desulfurization of jet fuel, gasoline and diesel under ambient conditions.

4.2 Reactive Adsorption

In reactive adsorption the sulfur present in organosufur compounds is first converted to H_2S and then it is subsequently adsorbed by the adsorbents. Materials comprising a combination of sorbent and transition metal catalyst are usually used for the reactive adsorption of organosulfur compounds [63-68]. In case of diesel, the reaction takes place at the temperature of the range 300-400˚C and pressure of 275- 500 psig in the presence of hydrogen. Various catalysts used for the reactive adsorption process include adsorbent–catalyst combination such as Cu-ZnO, Ni-Al_2O_3, Ni-ZnO, Ni/Al-SiO_2, NiP/SiO_2, Ni-SiO_2, Ni-SBA-15 have been validated. Amongst all of them Ni-ZnO has been proven the best for the reactive adsorption. The mechanism of Ni-ZnO involves the contribution of both Ni and ZnO, here nickel reacts with sulfur to form NiS under in presence of hydrogen which then extend s to ZnO to frorm ZnS and restore Ni.

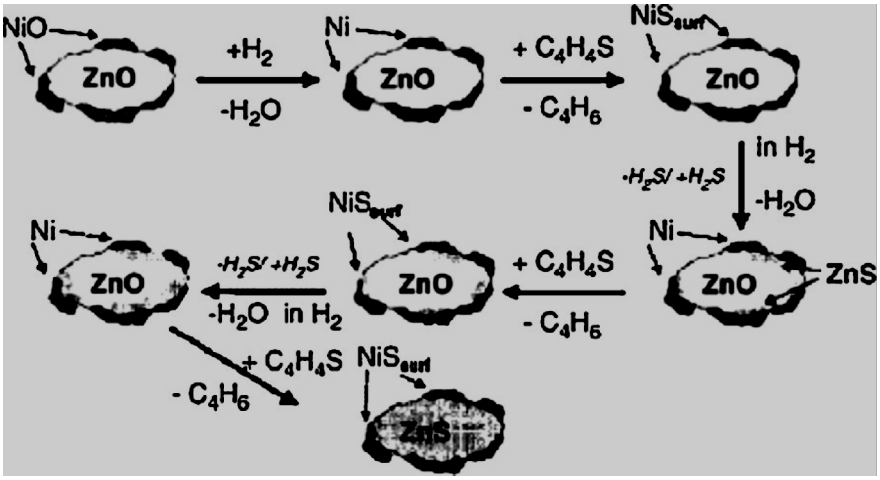

Fig: Mechanism of reactive adsorption desulfurization [8,123]

In regard to this Philips petroleum company (Conoco- phillips) has developed a technology called S-Zorb SRT for the purpose of deep desulfurization via reactive adsorption technique.

As nitrogen containing compounds are the strongly inhibits the desulfurization process of DBT, various techniques have also been evolved to pretreat the feed to remove these nitrogen containing compounds including (aniline, pyridine, acridine and quinolineand their alkyl substituent derivatives, pyrrole, indole, carbazole and their alkyl substituent derivatives) [67-69].

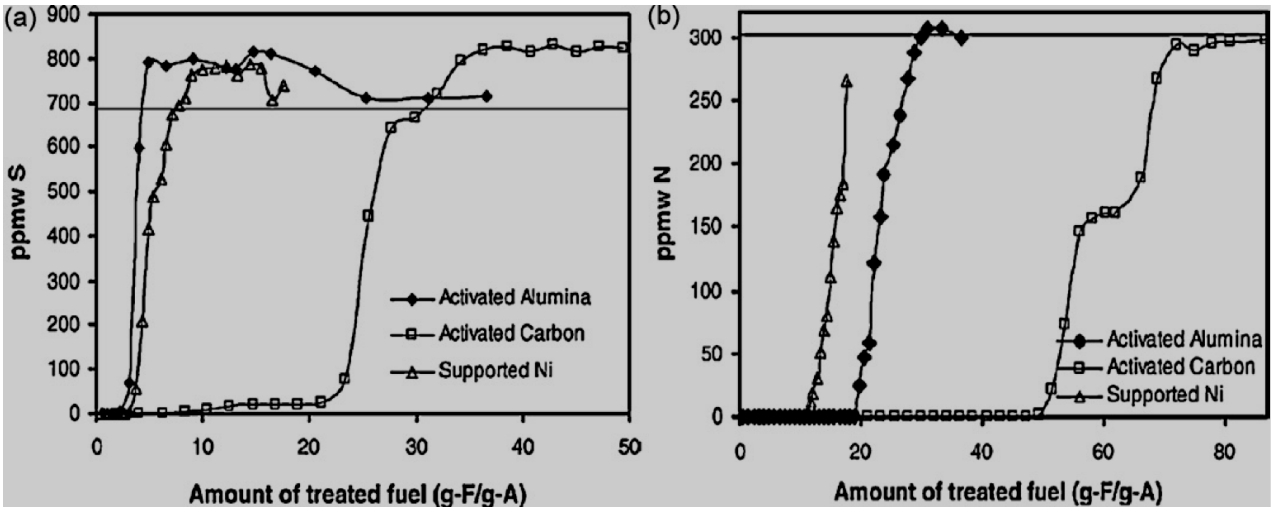

Fig: Breakthrough curves for (a) total sulfur and (b) total nitrogen over the three different adsorbents [8].

5. Biodesulfurisation

Now to surmount the drawbacks of HDS , desulfurization by ionic liquids , ODS, and extraction methods we are hooked to biodesulfurization , as biodesulfurization is the only method that removes sulfur from refractory organic hydrocarbons most effectively and that too under mild conditions without tempering the calorific value of the fuel. Now let us go deep into the science which deals with the BDS and make it such a viable method.
Sulfur is an integral part of the entire living organism, in small quantities every organism some sort of sulfur compounds in it. Studies have revealed that sulfur atom constitutes around 0.5 to 1% of bacterial cell dry weight. Hence every microorganism requires sulfur for their growth and metabolic activities. The general existence of sulfur is in the form of some enzyme cofactors, for instance biotin, thiamine and coenzyme A, in amino acids and proteins like cystine, methionine and disulfur bonds [10,70]. Different microorganism consumes sulfur from their proximities via different pathways depending upon metabolism. Those organisms that consume sulfur from the thiophenic compounds such as DBT are of our keen interest as these microorganism can be used to remove refractory organic sulfur compounds from fuels leading to the sulfur free hydrocarbons so as to meet the government policies.
This paper mainly focuses upon three different pathways of biodesulfurization namely Destructive, Anaerobic and specific. Amongst them specific biodesulfurisation is the most effective of all. There is one more way of clasifyiong the desulfurization process similar to that of discussed above, this method relies upon the pathway chosen for the degradation of the refractory sulfur present. These pathways are as 1.) Oxidative C-C cleavage 2.) Reductive C-S cleavage 3.) Oxidative C-S cleavage.
Let us take every pathway one by one, firstly let us talk about oxidative c-c cleavage pathway

5.1 Destructive biodesulfurization (Oxidative C-C cleavage)

To commence this process firstly, those species of microorganism that use DBT as their sulfur source were isolated. Further it was found that some of the isolated microorganisms are not able to carry out the BDS process as they cannot specifically remove sulfur from the DBTs. Microorganisms were using thiophenic compounds as their carbon and sulfur source altogether [71-73]. Whereas some other microorganism in the same series converted DBT in to several water-soluble compounds through a series of oxidizing steps [74]. Furthermore these water soluble end products itself came up as a problem as the assemblage of these compounds interdicted the DBT oxidation and microbial growth. In this process the attacked phenyl rings undergoes the breakage of one bond or a fragment from the phenyl ring. Hence carbon atoms are also being targeted instead of sulfur atoms, this process cannot be considered as a sole sulfur removal process. Aromatic compounds which do not bear any sulfur atoms are also the target of this process and ended with the cleavage of aromatic bonds. Due to this unwanted breakage of carbon-carbon bonds in benzene rings, this mode of desulfurization is known as destructive desulfurization [10].
The attack of these microorganisms on the carbon atoms of a DBT molecule can be studied by a specific pathway, which consist a series of oxidative and carbon-destructive enzymatic actions. This pathway was originally proposed by Kodama , here DBT is degraded by hyroxylating one of the benzoid rings to DBT–diol and DBT-di hydrodiol, cleaving the ring between the diol substituents and then leading to produce 4-2-(3-hydroxy)-thionapthenyl–oxo-3-butenoic acid and 3-hydroxy-2-formylbenzothiophene (HFBT) [75]. Kodama pathway comprises mainly three steps namely 1.) Hydroxylation 2.) Ring cleavage 3.) Hydrolysis [76-77].

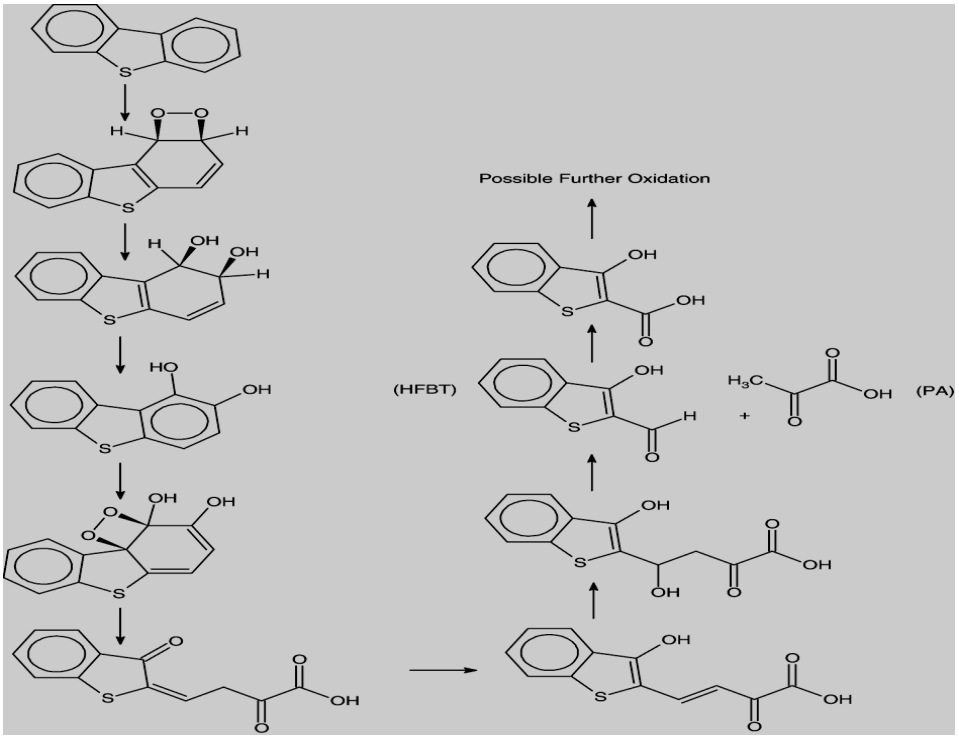

Fig: Kodama enzymatic pathway on dibenzothiophene. The oxidation in most cases reaches the step where 3-hydroxy-2-formyl-bnzothiophene (HBFT) and pyruvic acid (PA) are produced. The steps after production of HFBTare not fully known. HFBT is chemically unstable and it is probably mineralized in nature [78].

In the year 1970 two of the microorganisms named pseudomonas jijani and P. abikonesis were reported that demonstrated the DBT degradation wchich later on became the basis of kodama pathway. In these microorganisms degradation of DBT is plasmid encoded (55-MDa plasmid). But it was found that the product of this DBT degradation was repressive to both , further DBT degradation and cell growth. Other than this an another pathway was detected being followed by *P. putida* , in which DBT was converted to sulfone. This organism first follows kodama pathway to degrade DBT and then take alternate DBT degradation pathway to form sulfone as the end product. Various other microorganism including *Cunninghamellaelegans , Pleutorisostreatus , rhizobium melioti, Beijerincika sp.* Were found to produce DBT siulfone via the shown alternate pathway. It was further found that kodama pathway enzymes preferred to cleaver the unsubstitued homocyclic rings, in comparison to methylated derivatives [11, 27]. But in this process there was production of CO_2 gas and hence this process is not preferred as the degradation of aromatic compounds was there.

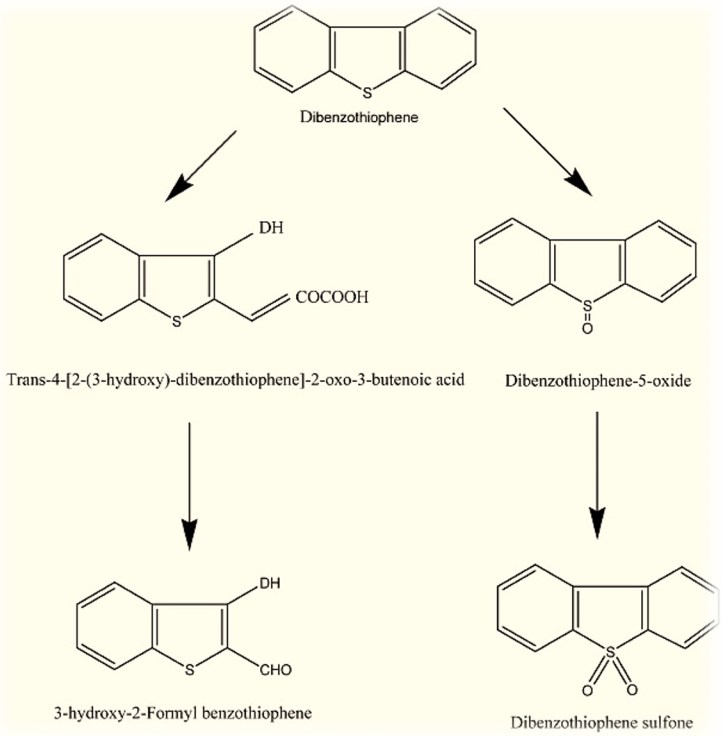

Fig: Two pathways of DBT degradation in P. putida[11]

Generally desulfurization through DBT carbon-destructive method is carried out by several different genera but most of the studies have converged to Pseudomonas cultures.

5.2 Anaerobic desulfurization or reductive C-S cleavage

Many of the anaerobic strains have shown the potential to delete the organic sulfur from refractory organic sulfur containing compounds like DBTs. Studies have shown that several anaerobic strains like desulfovibrodesulfuricans M6 has the potential to demean BTs and DBTs upto 96 and 42 % respectively and converts them into biphenyl and H_2S. Other anaerobic microorganisms like Desulfomicrobiumscambium and Desulfovibriolongreachii have been investigated to degrade only upto 10 % of the dissolved DBTs in kerosene [10,79]. Gas chromatography of several samples has shown unknown metabolites, emphasizing that bacteria had perhaps followed a pathway different from the conventional pathway for the anaerobic degradation [80].

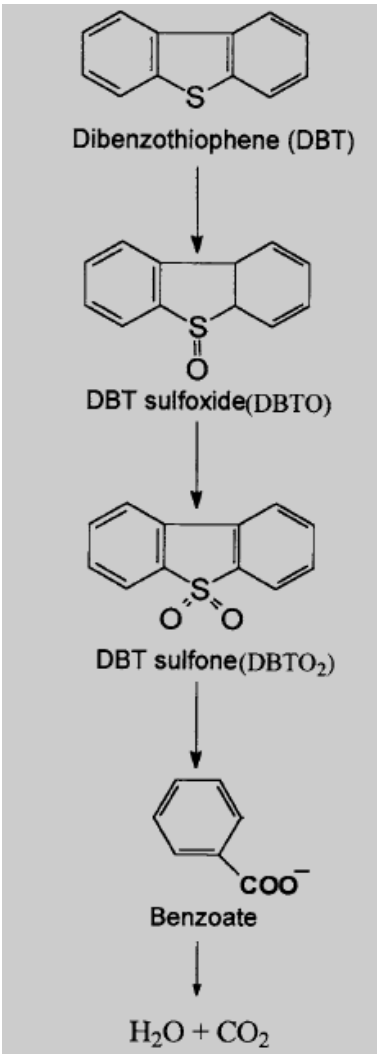

Fig: Metabolic pathway for the degradation of DBT by *Brevibacterium* sp. [27]

Now let us have a look at the pros and cons of the method. The yield of unwanted products like colored and gum forming compounds in the final product is very less. But on the other hand maintenance of anaerobic process is very difficult. Moreover the specific activity of the majority of the isolated anaerobic strains has been accounted to be peanut for the DBTs [76, 81].

5.3 Specific oxidative desulfurization

The process of sulfur removal specifically without tempering the carbon structure was first proposed by Gallagher et al. [82] for Rhodococcus rhodocorus IGTS8. In this desulfurization process when DBT was converted to 2-hydroxybiphenyl four different molecules were formed, hence this pathway was named as 4S pathway [11]. This microorganism degraded DBT to 2-HBP and sulfate, and it was also found that the extent of degradation was proportional to the concentration of bacterial cells present and corresponding to the minimum amount of sulfur required for the bacterial growth (0.1 mM sulfur allows growth of 10^9 cells.cm^{-3}) [27]. The 4S pathway continues through two cytoplasmic monooxygenases (Dsz C, Dsz A) backed by flavinreductase (Dsz D) and a desulfinase (Dsz B) [11].

A number of microorganisms were reported to follow this pathway for the sulfur degradation like R. erythropolisD1, RhodococcusECRD1, RhodococcusB1, RhodococcusSY1, RhodococcusUM3, GordonaCYKS1, Xanthomonas, Nocardiaglobelula, Paenibacillusstrain, and Mycobacterium. The process of sulfur removal from kodama pathway was reported to be destructive as it was targeting the carbon atoms too along sulfur atoms present in DBT rings. Therefore an extensive research work was done in attempts to isolate a variety of aerobic and anaerobic strains that

could perhaps carry out the desulfurization process nondestructively. Many attempts were made in the same sequence but all were in vain [83]. Consequently a hypothetical oxidative desulfurization process was proposed that could specifically remove sulfur from DBTs non-destructively and it was named as 4S pathway. In this pathway the consecutive oxidation of sulfur present in DBTs to sulfoxide (DBTO), sulfone (DBTO2), sulfinate (HPBS) and hydroxybiphenyl (HBP) [84].

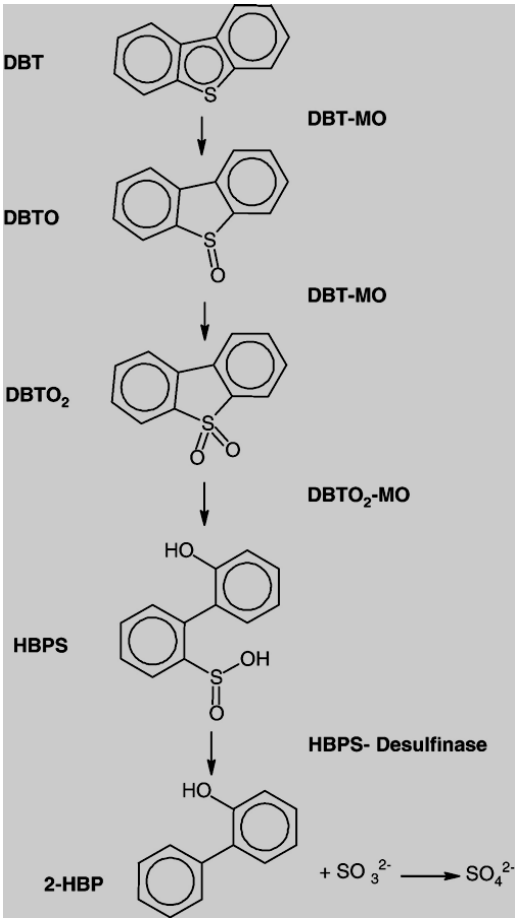

Fig: Proposed sulfoxide–sulfone–sulfinate–sulfate (4S) pathway. All the metabolites are practically immiscible in water. DBT has the lowest (1.0 mg/L) and DBTO has the highest water solubility (320 mg/L) at 25 °C. The released sulfate is consumed by the cell through sulfur assimilation pathways [10].

Several researches converged their studies to propose a nondestructive method of sulfur removal. In 1990 Afferden et al. [85] proposed a Brevibacterium sp. DO, which uses DBT s their sulfur source. The metabolism carried out by this microorganism to degrade the sulfur atoms present in DBT was somehow similar to the 4S pathway. But it was still carbon destructive as the aromatic compounds were also being degraded via this desulfurization process. In the same series another microorganism was reported to have the properties of extracting sulfur from refractory organic molecules. It was Arthrobacter sp. K3b (also known as DBTS2) it was studied that this microorganism also acted similarly to the Brevilbacterium sp. DO and but it also acted in the same way and the process came out to be carbon destructive. After that an assortment of fungi (for example cunnighamellaelegans) was detected to have the power to convert sulfur present in DBT to DBTO and then to DBTO2 oxidatively. But these fungal strains didn't shown any further degradation and sulfur could not be detached [86-88].

After such futile researches in 1990 the institute of gas technology, IL developed new strains by unnatural selective mutation. In this effort researchers of IGT investigated upon sulfur contaminated mixed culture soil sample which was then fed to a continuous coal bioreactor and exposed to mutagen (NTG; 1-methyl-3-nitrosoguanidine). It was noted that only a certain group of microbial species was able to survive in bioreactor after several months. This species demonstrated a specific Carbon-Sulfur incision activity and has the potential of removing upto 90% of the refractory sulfur and was named IGTS7 [89]. Furthermore it was detected that IGTS7 comprises of a minimum of seven different colonies formed with different populations. Amongst them two strains of Rhodococcus rhodochrous and Bacillus sphaericus having lowest abundance established desulfurization properties. Henceforth these strains were named as R. rhodochorus IGTS8 (ATCC 53968) and B. sphaericus IGTS9 (ATCC 53969) [90].

Till date several microorganism genera have been reported to have the capabilities of desulfurization but majority of them belongs to rhodococcus genus. The rhodococcus genus belongs to the phylum and to the class of Actinobacteria, order of Actinamycetales and family of Nocardiaceae [91]. These species possess a mixture of plasmids from large to linear and circular ones [92]. And comparatively they are enveloped in a thicker envelope unlike most bacterial cells. This thick cell envelope provides a higher immunity for the accumulation of the essential compounds [93]. Due to the presence of peptidoglycan layer of large aliphatic mycolic acids chains in their cell walls these rhodococci cells show hydrophobicity and hence taking its advantage these microorganisms attach themselves to oil and water interface and grow in hydrocarbon-aqueous system [94]. Rhodococci requires a standard cultivation media with a optimum temperature range of about 30 °C and need one to three days to form colonies on solid media that are visible properly. Rhodococci possess oxidative metabolism, moreover they are chemoorganotrophic. General features of rhodococci includes that they are catalase-positive , obligate aerobes, Gram- positive, non-conidia forming, non-motile, non-endospore and partially lysosome sensitive bacteria [10].

5.3.1 Rhodococcus erythopolis

Rhodococcus erythoppolis IGTS8 primarily isolated from a soil sample and classified as saprophyte rhodococcus, having no aerial hyphae an it was found to be an aerobe [95-97]. Amongst many competent desulfurization microorganism for instance IGTS8, N1-43, D-1, KA2-5-1, and I-19, which are the strains of R.erythopolis, IGTS8 is the one upon which extensive research has already been conducted attributed to its higher capability to desulfurize the crude. Kilbane and Bielaga [89] isolated the IGTS8 in 1990 and then energy biosystems corporation used these strains for the evolution of commercial biodesulfurization process. According to the conducted studies it was found IGTS8 was a gram-positive and rod shaped bacterium having length of 0.5 μ approximately. IGTS8 forms cream colored colonies over nutrient agar medium which turn peach I color after some time. Now as far as the desulfurization capability of this strain is concerned it was detected that genes responsible for desulfurization are located on a plasmid in an IGTS8 strain. Heat treatment of this strain has shown no considerable loss of the plasmid , whereas the UV treatment (5 to 20s of UV emission [254 nm at 3.5 cm distance]) has demonstrated adverse effects over the desulfurization potential of IGTS8 strain. Sub culturing is the way by which desulfurization trait can be fully preserved.

5.4 MOLECULAR BIOLOGY

5.4.1 Molecular biology of kodama pathway

Microbial degradation of the sulfur containing compounds present in the fuel feed such as DBT via proposed kodama pathway which is also called the ring destructive pathway was found to be plasmid mediated ending up with water soluble products DBT2 and DBT4 in Pseudomonas sp. Strain [29]. Studies showed that the two isolates harbored a 55-megadalton plasmid, and in the presence of novobiocin plasmid along with the capability to oxidize DBT was lost [98]. In the studies conducted by Denome et al. [99], an 9.8kb DNA was isolated from a soil sample of a Pseudomonas sp. C18 strain , further it was cloned and sequenced such that it was encoded with biodegradation genes. It conferred the DBT-metabolizing phenotype on *Pseudomonas putida* and *Escherichia coli*. This DNA was found to have ten open reading frames (ORFs) having length greater than over 100 amino acids and were designated as dox ABCDEF GHIJ. The nucleotide analysis revealed that naphthalene dioxygenase-encoding Pseudomonas putida genes ndoA–ndoC was identical to three of the ORFs (doxA, doxB, doxD). It was found that these bacteria are capable of using a variety of other Aromatic HCs, like methyl DBTs, benzene, biphenyl and naphthalene [11,100]. Perhaps there may not be a separate set of enzymes or genes for DBT degradation through the Kodama pathway. The resemblance of the dox genes with the ndo genes and the capability of the naphthalene dioxygenase from the Pseudomonas strain NCIB 9816-4 to oxidize DBT, infer that DBT can serve as an alternate substrate for naphthalene degrading enzymes [101].

5.4.2 Molecular biology of 4S pathway.

The elementary genes involved in the metabolism of DBT called dsz or sox, have already been cloned, sequenced and fairly characterized. The sox designation was used firstly but due to several other irrelevant genes were also labelled as sox, the dsz (desulfurization) designation was acquired, and is being generally accepted to avoid any confusion with the gene designations [11]. The dsz genes are arranged in a 4-kb preserved region of a mega-plasmid in a operon-regulated system [102]. The dsz gene is a bunch of three genes named dsz A,B,C transcribed in the same direction which encode enzymes Dsz A, Dsz B and Dsz C respectively which are sufficient for the effective conversion of DBT to 2-HBP [103]. According to the published data it has been reported that Dsz B is present in several times less concentration in cytoplasm as compared to the other two enzymes (Dsz A and Dsz C) [104]. In case of rhodococcus rhodochorus IGTS8 this dsz operon was found on a plasmid of 150kb. Whereas in other strains it was found to be on a 100kb plasmid. The initiation codon for dszB and termination codon for dszA overlaps but there is a band gap of 13-bp between the codons of dszB and dszC. Further subclone study revealed that DszC is involved in the conversion of DBT to $DBTO_2$ and DszA along with DszB converts $DBTO_2$ to 2-HBP [103,105]. It was further found that the

enzymes are repressed in the presence of bioavailable sulfur like sulphate, sulphide, methionine and cysteine, the phenomenon is somehow similar to that of responses to other sulfur compounds under sulfur starvation [104]. Assimilation of 2-HBP also have inhibitory effects on the growth and the desulfurization process. According to the studies conducted by Monticello et al. [33], it was demonstrated that the repression of enzyme synthesis happens at the transcription of enzyme, but 2-HBP doesn't have inhibitory effects over the enzymes. In order to increase the desulfurization rate recombinant strains have been taken into consideration. These recombinant strains have been reported to have better desulfurization activity in comparison to other wild-type strains, reason being the production of surfactant by the host organism. Recombinant pseudomonas strains have been fashioned in view of enhancing the desulfurization potential by the insertion of dsz gene cluster in their chromosome. Studies conducted by Rambosek et al. [106] infer that the reconstruction of various promoters containing the R. rhodochorus IGTS8 dsz gene , with dszD gene increases the rate of DBT desulfurization. The enzyme aspect can also be alleviated by using transposons for generating high-activity desulfurizing enzymes(for instance R. erythropolis KA2-5-1 constructed using a transposon showed desulfurization ability even in the presence of sulphate) [107-108].

5.5 Enzymology

The Dsz enzymes are reported to be purified from R.rhodochorus IGTS8 [109], R. erythropolis D-1 [110] and paenibacillus sp. Strain A11-2[111]. The Dsz enzymes named Dsz A, B, C are responsible for the conversion DBT to 2-HBP. Let us take these enzymes one at a time into consideration.

The Dsz A enzyme can be purified from R. rhodochorus, R. erythropolis D-1,and Paenibacillus sp. Strain A11-1. Dsz A is a monooxygenase which is responsible for the oxidation of DBT sulfone to 2-(2-hydroxyphenyl) benzene sulfinate (HPBS). Paenibacillus strain A11-2-is an thermophile and therefore the enzyme isolated from this strain behave differently from those of mesophiles [11,111]. The enzyme from paenibacillus A11-2 strain demonstrate a higher enzyme activity towards heavier substrates than its mesophilic counterparts but on the other hand it loses its activity in the presence of thiol reagents [11]. In a general trend shown by monooxygenase it has been inferred that these enzyme show a 1.7- fold alleviated activity towards 4,6-dimethyl DBT sulfone (which is difficult to degrade due to hinderance effects) as compared to DBT sulfone [110]. Presence of chelating agent for instance EDTA inhibits the enzyme activity of R.erythropolis upto 50% when the amount EDTA present was around 1mM but sideways the in case of R. rhodochorus IGTS8 showed no inhibition effect even in the presence of 10 mM EDTA [109].

The second enzyme DszB or disulfinase catalyzes the transformation of HPBS to HBP and is a rate–limiting enzyme. As mentioned above it is present in very less quantities demonstrates the enzyme activity in the temperature range of (25-50˚C) and the optimum temperature being 35˚C. Where the pH ranges from 6.0 to 7.5 for the proper working of this enzyme [112].

The third enzyme is Dsz C or DBT monooxygenase, it catalyzes the transformation of DBT to DBT sulfone via two-step process . Here DBT sulfoxide is the intermediate compound. The rate constants for the two processes are 0.006 min^{-1} and 0.5 min^{-1} respectively. According to Gray et al. [109] Dsz C shows homology to the acyl coenzyme A enzyme and is reported to be a homotetramer with subunit molecular weight of 50 kDA. Ohshiro et al. [113] isolated Dsz C from R.erythropolis D-1 and accounted Dsz C as a homohexamer with a subunit molecular weight of 45kDA. The activity of this enzyme has been reported to be maximum at 40˚C temperature and 8.0 pH. This enzyme is functional over derivatives of DBT i.e. 4,6-dimethyl DBT, 2,8-dimethyl DBT, 3,4-benzo-DBT but doesn't show any activity on carbazole , fluorene and dibenzofuran [11].

The Dsz D enzymes (reductase) are related monooxygenase as a matter of fact monooxygenase cannot be active in the absence of reductase. Dsz D has been purified from paenibacillus sp. Strain A11-2 (thermophilic), and has been accounted as a homodimer having subunit molecular weight of 25kDa [114]. The optimum working conditions for this enzyme include 55˚c of temperature and pH 5.5. flavin reductase is an essential component required in the equimolar quantities for the oxygenation reactions carried out by monooxygenases [115].

IV. Feasibility and economy

The removal of inorganic sulfur from the feed stokes have been reported to be best carried out by Thiobacillus Ferro oxides and even other physical methods known are efficient and economical [116]. But the case is different for the removal of organic sulfur from the fuels. Organic sulfur is divided into two parts, one part can be easily removed by procedures like hydro treating and adsorption etc. but the second part known as refractory organosulfur is difficult to be dismissed from the fuel feedstokes. Currently desulfurization of refractory sulfur is carried by HDS under high temperature and pressure conditions , which makes it a cost ineffective procedure. Moreover HDS is incapable of taking the sulfur content to the ultra-low levels without tempering the calorific values of the fuel. Hence to overcome all these drawbacks BDS has been taken into consideration. BDS process having advantage of mild process conditions, economizes the desulfurization energy consumption and produces lower amounts of pollutants [10].

Kilbane et al. [117-118] introduced the first bacterial strain R.erythropolis IGTS8 which can remove sulfur specifically without breaking C-C bonds. Generally biological or biotechnological process are considered as expensive and are meant for the production of lower volumes of high value product, but in BDS output generated has to be a high volume and contains low value of sulfur product unlike other biological processes. According to the kinetics of BDS studied, it was found that the biological sulfur removal is a slow process and requires large amounts of water [119]. So due to the non-economic conditions generated attributed the above mentioned fact, enzymes are involved in the bio desulfurization process. Enzymes in comparison to microorganisms need less amount of water to function hence several enzymes like NADH, $FADH_2$ are involved to carry out the process. After that the elimination or reduction of water required for the BDS process is also a challenge. Now, for microbial desulfurization either resting cells can be used or the microorganisms might be grown in an aqueous/oil system. But cultivating the living microorganisms in a two phase (aq. /oil) system is too slow and would yield very low desulfurization, makes the process practically non-viable hence desulfurization by resting cells is explored. Development of resting cells may be cross contaminated by the other microorganisms that can attack carbon bonds or might consume nutrients. Moreover the production of resting cells and to maintain their biocatalyst activity requires huge facilities[10,120]. The steps involved in a BDS process from commercialization point of view include

1.) Preparation of the feed stokes
2.) Microorganism/biocatalyst preparation
3.) Desulfurization in bioreactor
4.) Separation and recovery [10].

Amongst them to produce a biocatalyst with higher specific activity and long half-life is very important. Even now, the main concern of the BDS processes in industries is to isolate a strain with higher biodesulfurization activity [121]. Along with this to obtain higher desulfurization specific activity by increasing the driving force from one phase to another and preventing the accumulation of inhibitor species is of major concern. In comparison with the conventional HDS process BDS is expected to offer 70-80% less CO_2 emission. Moreover the installation capital cost of BDS process plant is expected to be $2/3^{rd}$ of a HDS process plant and also operating cost of a BDS process is also expected to be 10-15% less than that of HDS process [119,122].

V. Conclusion

The paper presents an overview of the technologies available of the desulfurization process emphasizing biodesulfurization process to be the potential substitute. Different technologies have been developed across the globe in order to produce ultra-clean fuel in order to comply with the regulations imposed by the government agencies. Many microbial methods of desulfurization has been developed using different strains but most effective being Rhodococcus genus. However the reaction rates and the specific activities of these biocatalysts needs to be improved for the effective commercialization and considering the pace of researches being done under this label, we can expect the production of microbial cultures that could remove the organic sulfur efficiently from the fuel feeds.

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