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Faculty of Engineering

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M. Sc. Thesis

Biological Desulfurization of Crude Oil and Its Cuts

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Abstract

A new DBT degrading bacterial consortium was gained from oil contaminated soil samples gathered from oil sources of Naftshahr, Kermanshah, and vicinity of oil refinery of Kermanshah. All of species exist in this consortium, path Kodama pathway for degrading DBT, that is a nonspecific C-S degrading rout, and C-C bonds be cleaved with cells. The growing cells, consumed 0.5 mM DBT completely after 84 h. But the activity of resting cells was very better. They were thermophile and hydrophobia. It causes they consumed DBT from oil phase directly. The best operating condition of these cells was calculated as 43°C, pH 7.6, and O/A (V/V) 70% using response surface methodology. The predicted activity of cells in this condition, calculated using MODDE 8.0, was 2.699 gDBT/kgDCW.h in two first hours of bioreaction. While the experiment showed that the real amount is 2.784. The resting cells in this condition consumed 0.5 mM DBT completely approximately after 3 h.

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Chapter One

Introduction

1-1 Sulfur-Containing Compounds of Petroleum and Their Disadvantages

Obviously the energy consuming is increasing throughout the world rapidly. Oil cuts, as energy sources, are consumed more than other fuels, so that cover about 82% of all consuming fuels (Ayala *et al.*, 1998). The crude oil has many contaminants like nitrogen and sulfur containing compounds, and they should be treated before consuming.

Petroleum is construct of many components, and after carbon and hydrogen, sulfur is considered as the most abundant element in it (Marcelis, 2002), so that sulfur constructs about (0.05-8)wt% of crude oil (Rall *et al.*, 1972) which it depends on petroleum sources. Crude oil with higher density contains more sulfur compounds (Marcelis, 2002). An overview of sulfur contents of crude oil from various sources is given in Table1-1. The Middle East and Venezuela have the most oil reserves with high sulfur contents (De Krom, 2002).

In a major classification, the sulfur-containing compounds can be classified into two major groups: inorganic compounds *e.g.* hydrogen sulfide and pyrite, and organic compounds *e.g.* thiophenes, sulfides and mercaptans that are the most constituents of petroleum (Tissot *et al.*, 1984). Among these, aromatic compounds such as dibenzothiophene (DBT) and its derivatives are of significant importance because they have higher boiling points than others (more than 200°C) and it is difficult to remove them from outlet stream of atmospheric tower (*e.g.* middle distillates) (Kawatra and Eisele, 2001). The molecular structure of some organic sulfur-containing compounds is presented in Figure 1-1.

There is one question: Why desulfurization is important? The answer of this question is stupendous! Combustion of Sulfur-containing compounds in fossil fuels causes emission

Table 1-1 Organic sulfur contents in petroleum of various sources (De Krom, 2002)

source	wt.% sulfur
Argentina	0.06 - 0.42
Australia	0 - 0.1
Canada	0.12 - 4.29
Cuba	7.03
Denmark	0.2 - 0.25
Egypt	0.04 - 4.19
Indonesia	0.01 - 0.66
Iran	0.25 - 3.23
Iraq	2.26 - 3.3
Italy	1.98 - 6.36
Kuwait	0.01 - 3.48
Libya	0.01 - 1.79
Mexico	0.9 - 3.48
Nigeria	0.04 - 0.26
Norway	0.03 - 0.67
Russia	0.08 - 1.93
Saudi Arabia	0.04 - 2.92
United Kingdom	0.05 - 1.24
USA	0.29 - 1.95
Venezuela	0.44 - 4.99

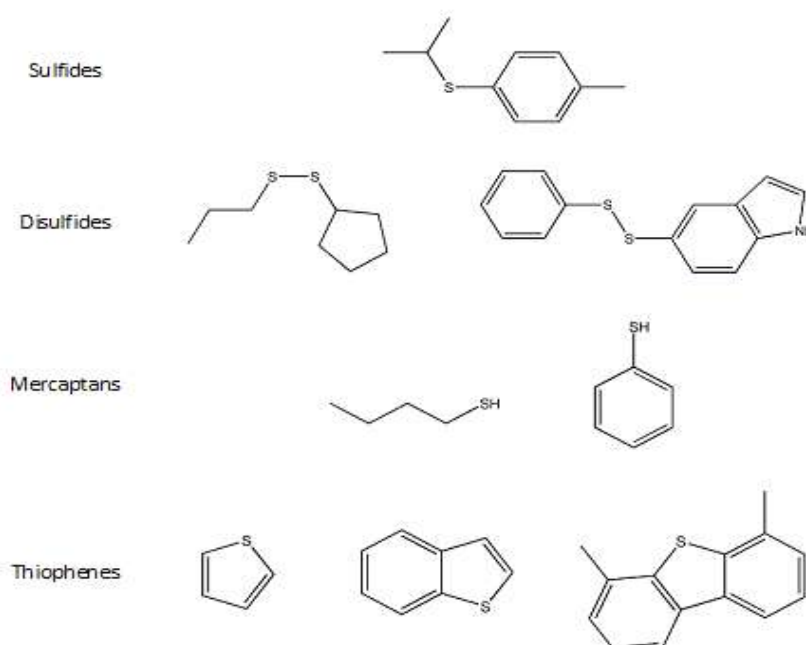


Figure 1-1 Molecular structure of some sulfur-containing compounds of petroleum

sulfur oxides which can cause many various problems. Between them SO_2 is abundant and produced in the lower atmosphere. It's aerosol particle has an average diameter of $2.5\mu\text{m}$

that can be transported into the lungs (Atlas *et al.*, 2001), and causes harsh problems for human respiratory system like asthma and exacerbating lung disease when it be inhaled over long periods of time. In addition, SO_2 reacts with the moisture in the air, and leads to acid deposition, which known as acid rain or low pH fogs, and some destructive results of it are damaging the foliage, depressing the pH of lakes and soils that threat the life of marines and microorganisms, damaging the buildings and eroding the surface of structures, and ultimately reducing the visibility (Bookhart and Zien, 2003).

The results of investigations of Consumer Energy Council of America (CECA) in this regard demonstrated that the fuels by lower amount of sulfur have very sensible advantages in compare with ordinary fuels, and they are obvious in environmental, economical, and sanitary problems. However their price is high, it can be compensated by increasing the instruments life time, increasing the fuel stability, and decreasing the maintenance costs, *etc* (Bookhart and Zien, 2003).

The relationship between the sulfur content of oils and the emission of SO_2 is shown in Figure1-2. Clearly there is a linear relationship between them. Approximately 99% of sulfates that be produced during oxidization, is consisted of SO_2 and remaining 1% of it is SO_3 which forms sulfuro acid when it comes in contact with water (Bookhart and Zien, 2003).

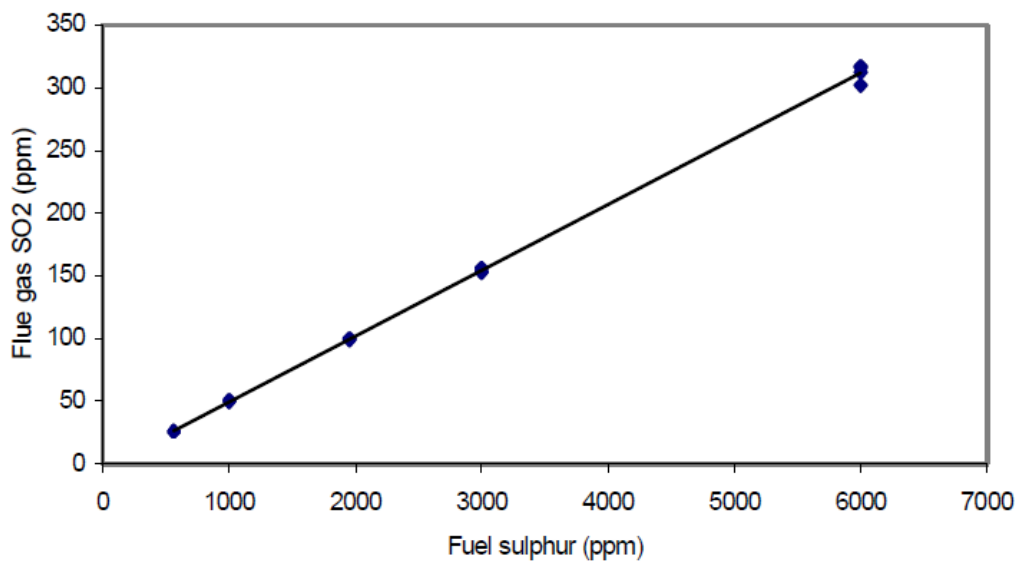


Figure 1-2 Relationship between heating oil sulfur contents and SO_2 emissions (Marcelis, 2002)

These problems are impetus to announce stringent legislation. In 1993, the Clean Air Act proscribed the sales and supply of diesel oil with sulfur concentration more than 500 ppm. This value decreased to 350 ppm at 2000 and 50 ppm at 2005 (Knudsen *et al.*, 1999), and ultimately less than 10 ppm for after than 2010 (Kilbane, 2006). These laws are executed in many countries such as United States, Canada, Japan and European nations (Marcelis, 2002). On account of it rules, the objectionable quantities of sulfur must be removed to fuel become acceptable as refinery product.

1-2 Hydrodesulphurization as Current Method for Desulfurization

Hydrodesulphurization (HDS) is an established physico-chemical technology to remove organically bound sulfur down to specified levels (Speight, 1981), and converts them to hydrogen sulfide and some hydrocarbons (Babich and Moulijn, 2002). In order to comprehend the principles of HDS, an understanding of chemistry of this process is valuable. In hydrotreating, much of hydrogen is supplied from an external source, and hydrogenation¹ and various hydrogenolysis² reactions consume the hydrogen with resulting reduction in the molecular weight of the starting material. Decomposition of model compounds to yield unsaturated hydrocarbons ($R-CH=CH-R^1$) and H_2S and decomposition of alkyl sulfides to yield thiols ($R-SH$) and olefins ($R-CH=CH-R^1$) are some examples of this reaction. The different reactivity of molecules that contain sulfur can be explained by the relative strength of the carbon-sulfur bonds, with respect to the bond strength in aromatic and saturated systems (Speight, 1991) which are shown in Table1-2. Bond energies offer some guidance about the preferential reactions that occur at high temperature, and for the most part can be an adequate guide to the thermal reactions of the constituents of petroleum. However, often the bond energy data fail to include the various steric effects that are a consequence of complex molecules containing three-dimensional structures. Furthermore, the complexity of the individual reactions occurring

¹ The chemical reaction that results from the addition of H_2 that typically constitutes the addition of pairs of hydrogen atoms to a molecule (Hudlicky, 1996).

² A chemical reaction whereby a carbon-carbon or carbon-heteroatom single bond is cleaved or undergoes lysis by hydrogen (Connor and Adkins, 1932)

in an extremely complex mixture and the interference of the products with those from other components of the mixture is unpredictable. Or the interference of secondary and tertiary products with the course of a reaction, and hence with the formation of primary products, may also be cause for concern. Hence, caution is advised when applying the data from model compound studies to the behavior of petroleum, especially the molecularly complex heavy oils. These have few, if any, parallels in organic chemistry (Speight, 1991).

Table 1-2 Bond strength of various C-S bonds (Bressler *et al.*, 1998)


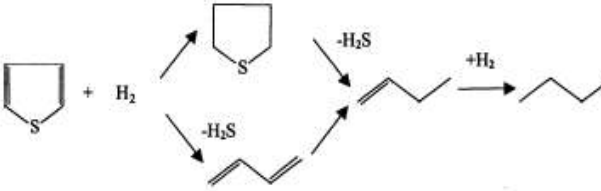
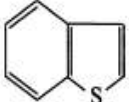
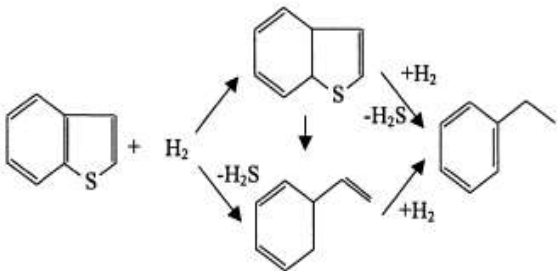
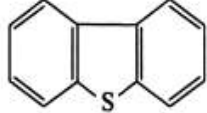
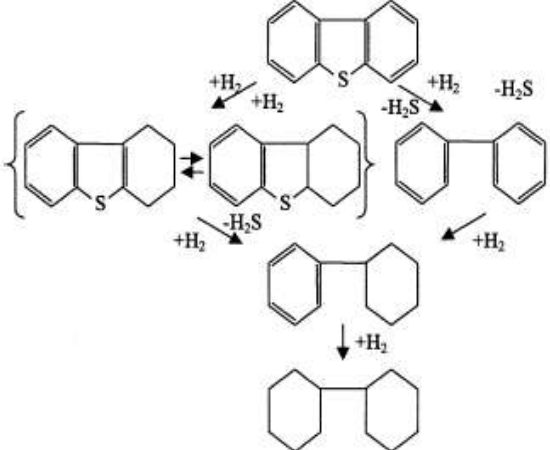
C-S bonds	Strength (kJ/mol)
C-S in thiophene	341
C-S in benzothiophene	339
C-S in dibenzothiophene	338
HS-CH ₃	312
H ₃ C-SCH ₃	308
H ₃ C-SO ₂ CH ₃	280
H ₃ C-SCH ₂ C ₆ H ₅	257
H ₃ C-SO ₂ CH ₂ C ₆ H ₅	221

Some reactions that occur during HDS are shown in Table1-3. Both reaction pathways (hydrogenation and hydrogenolysis) can be seen in this table. For example, in degradation of thiophenic compounds, during the first pathway the sulfur is removed after hydrogenation of the aromatic ring and via the second rout the sulfur atom is directly removed from the molecule (hydrogenolysis pathway). This situation can be seen in desulfurization of benzothiophene (BT) and dibenzothiophene (DBT) too.

In the very simplified processes, the feedstock is pressurized and mixed with hot recycle gasses and preheated to the temperature of the reactor inlet. Then the hot feed is introduced to the catalysts in the reactor where temperature between 290 to 455°C and pressure in the range (1500- 3000) psi prevail (Speight, 1991). It should be mentioned that more sever conditions result not only in a higher level of desulfurization, but also in

undesired side reactions (Babich and Moulijn, 2002). Usually at the range of temperatures that HDS proceeds on them, the logarithms of the equilibrium constants are positive, so the reaction can proceed to completion if hydrogen is present in the stoichiometric quantity, however the hydrogen requirement for HDS differs by the nature of the feedstock (Figure 1-3).

Table 1-3. Hydrotreating pathway of some organosulfur compounds of oil (Speight, 1991)

Type of organic sulfur compound	Chemical structure	Mechanism of hydrotreating reaction ^a
Mercaptanes	$R-S-H$	$R-S-H + H_2 \rightarrow R-H + H_2S$
Sulfides	R^1-S-R^2	$R^1-S-R^2 + H_2 \rightarrow R^1-H + R^2-H + H_2S$
Disulfides	$R^1-S-S-R^2$	$R^1-S-S-R^2 + H_2 \rightarrow R^1-H + R^2-H + H_2S$
Thiophene		
Benzothiophene		
Dibenzothiophene		

^a Reaction pathway for alkylated thiophene, benzothiophene and dibenzothiophene is similar to the reaction of nonalkylated counterparts.

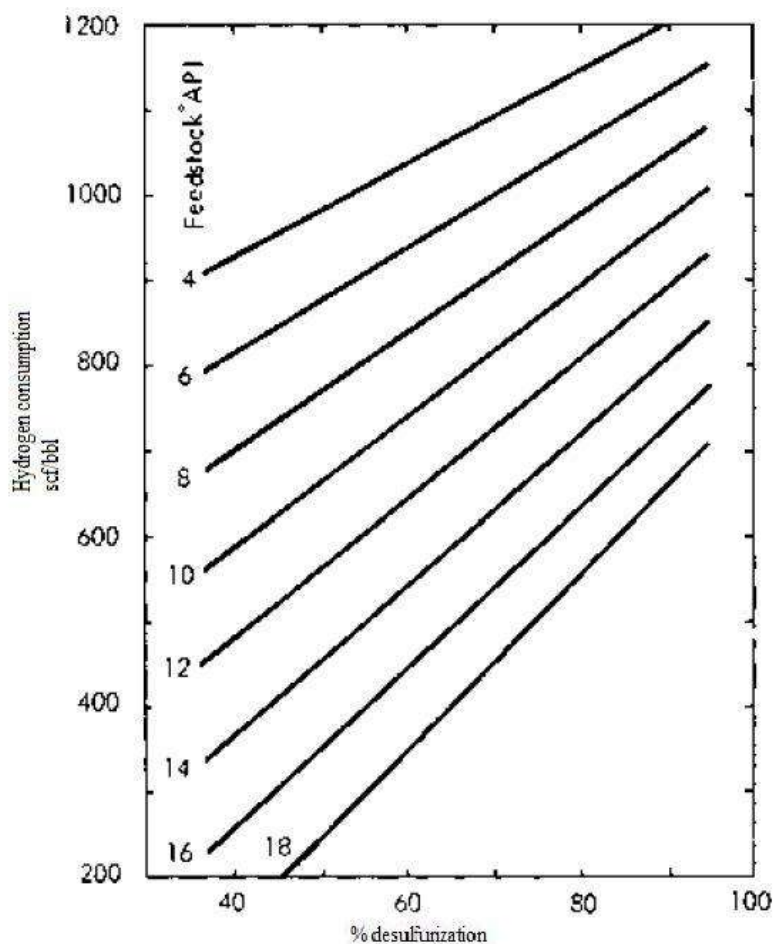


Figure 1-3 Variation of hydrogen consumption with the nature of feed and degree of desulfurization (Speight, 1991)

Heat exchangers are employed to cool the reactor effluent and the desulfurized liquid product is separated from the recycle gas at a pressure somewhat lower than that of the reactor section. Hydrogen sulfide and any light hydrocarbon gases are removed from the recycle gas which is then mixed with fresh (makeup) hydrogen, compressed, and mixed with further hydrocarbon feedstock (Speight, 1991). A schematic diagram of a HDS unit is presented in Figure 1-4.

Industrial HDS processes are usually carried out on supported sulfided molybdenum (Mo), nickel (Ni), cobalt (Co) and tungsten (W) (Szymczycha-Madeja and Mulak, 2009; Ren *et al.*, 2008). Their performance in terms of desulfurization level, activity and selectivity depends on the properties of the:

- specific catalyst used, *i.e.*, active species concentration, support properties, and synthesis route,

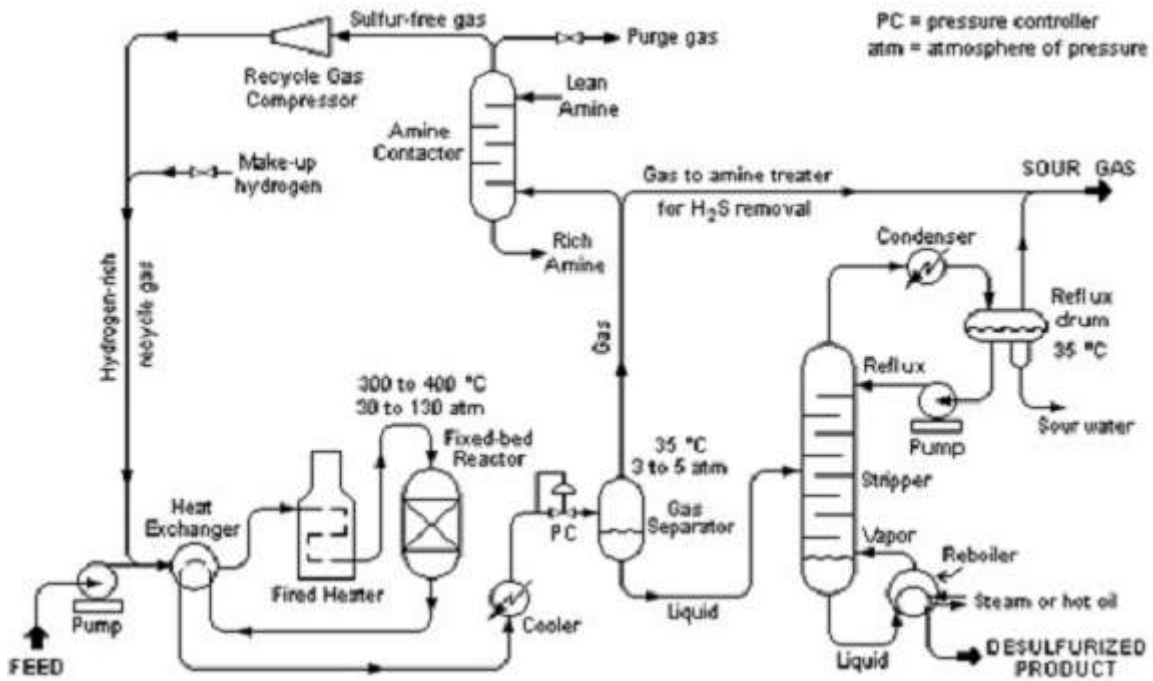


Figure 1-4 Schematic diagram of a HDS unit or a crude oil refinery (Gary and Handwerk, 1984)

- the reaction conditions, *i.e.*, sulfiding protocol, temperature, and partial pressure of hydrogen and H₂S,
- nature and concentration of the sulfur compounds presented in the feed stream, and
- reactor and process design.

It should mention that since from study to study the parameters of the HDS processes differ, the reported values of catalyst activity and selectivity vary a lot (Babich and Moulijn, 2002).

As an important component of HDS catalysts, the support has a direct interaction with the metal species, and has an indirect role in determining the promotional effects of the secondary metal species (Ren *et al.*, 2008). Alumina is the most widely used support material for commercial HDS catalysts due to its good mechanical and textural properties and ability to provide high dispersion of the active metal components (Yu *et al.*, 2008). However some other materials are examined and used as support too. Yu *et al.* (2008) compared alumina, fishbone and platelet carbon nanofibers as supports and concluded that MoO_x be dispersed as monolayer on the alumina, but as small crystalline particles on the

carbon nanofibers. There are no obvious differences between fishbone and carbon nanofibers in terms of the resulting catalyst phases and alumina supported catalysts are much difficult to reduce than others, due to the strong interaction between the alumina and metal particles. Cross-linked polystyrene-PPh₃ resins are used as heterogeneous supports for nickel catalysts by Torres-Nieto and Garcia (2009). They emphasized that two important disadvantages of homogeneous catalysts with respect to their heterogeneous counterparts are related with the separation and recovery procedures that are required for them at the end of each process.

Some other heterogeneous catalysts that used for HDS are CoMo catalyst that supported on B₂O₃-Al₂O₃ that is a binary mixed oxide that prepared by Saih and Segawa (2009), and Ni-Mo sulfides catalyst that supported on mixture of mesoporous MCM-41 and microporous HY zeolite that prepared by Ren *et al.* (2008). In addition of these supports, silica, titania, zirconia, TiO₂-Al₂O₃, SiO₂-TiO₂ and ZrO₂-Al₂O₃ are named as support too (Saih and Segawa, 2009).

As be seen in earlier examples, usually Co and Ni have been added to Mo for preparing better catalysts in compare by them that prepare by Mo or Co or Ni separately, but in addition of this combination, sometimes using other promoters results better performance, for example Navarro *et al.* (2009) added Pd and Ru to commercial Ni(Co)Mo/ γ -Al₂O₃ catalysts to enhance their hydrogenation function.

Anyway, the conventional reaction model of hydrodesulfurization of fuel oil does not work effectively in the ultra-deep desulfurization range down to sulfur content 100 ppm or less. The catalyst volumes must be three times more in the case of 50 ppm, and four times more if the aim is to reach the final sulfur content of 30 ppm (Rang *et al.*, 2006). In addition, the reactivity of sulfur compounds in HDS follows this order (from most to least reactive): thiophene > alkylated thiophene > BT > alkylated BT > DBT and alkylated DBT without substituents at the 4 and 6 positions > alkylated DBT with one substituent at either the 4 or 6 position > alkylated DBT with alkyl substituents at the 4 and 6 positions (Babich and Moulijn, 2002). The low reactivity of refractory DBT derivatives is generally

attributed to the steric hindrance of alkyl groups, present in the sulfur neighborhood. They reduce the interaction between the sulfur atom and the active sites of catalysts (Saih and Segawa, 2009).

For overcoming to this problem and achieving ultra low sulfur fuels, new desulfurization methods have been introduced, *e.g.*

- oxidation (oxidation of S-containing compounds in presence of catalysts like Alumina-supported vanadium oxide (Cedeno-Caero *et al.*, 2008)),
- adsorption (chemical adsorption of S-containing compounds in the presence of hydrogen and modified zinc oxide on a carrier that is named Phillips S Zorb process (Babich and Moulijn, 2002), and physical adsorption on some adsorbant like activated carbon (Selvavathi *et al.*, 2009)),
- extraction (extraction of S-containing compounds by using some solvents like acetonitrile (Ramirez-Verduzco *et al.*, 2004), and some ionic liquids like N-ethyl-N-ethyl-imidazolium diethylphosphate ([EEIM][DEP]) (Jiang *et al.*, 2008)), and
- biodesulfurization that will be introduced in the next section. The final purpose is using one of these processes as complementary method for HDS.

1-3 Biodesulfurization

Biodesulfurization (BDS) offers an attractive alternative to conventional HDS due to the mild operating conditions and reaction specificity offered by the biocatalysts. It is an environmentally friendly method that can remove sulfur from refractory organic compounds under ambient temperature and pressure without lowering the calorific value of the fuel (Soleimani *et al.*, 2007).

Sulfur atoms form 0.5-1% of bacterial cell dry weight and microorganisms require sulfur for their growth and biological activities, so depend on their enzymes and metabolic pathways they may able to provide their required sulfur from different sources (Kertesz, 1999). There are two major pathways for metabolizing the S-containing compounds and specially DBT as a model compound (Kim *et al.*, 1996): oxidative pathways that aerobic