

CHAPTER II LITERATURE REVIEW



2.1 Transportation Fuels and Sulfur Specifications

2.1.1 Transportation Fuels

The transportation fuels comprise three major types: gasoline, diesel, and jet fuel. The compositions of these fuels vary widely depending on the crude oil compositions, the refining process, the product demand, and the product specifications. The approximate compositions of gasoline, diesel, and jet fuel are given in Table 2.1. Branched and n-alkanes are the main ingredients of these fuels, typically 70-80%. The major alkanes in gasoline is n-hexane and the main branched alkanes are C₅ and C₆ compounds. The aromatics are mainly benzene, toluene, xylenes and alkyl benzenes, totaling about 20-30%.

Table 2.1 Typical compositions of transportation fuels (vol %) (Yang, 2003)

	Gasoline ^a	Diesel ^b	Jet Fuel ^c
Boiling range (°C)	40-204	232-350	330-510
Aromatics	30.5	17	18
Olefins	1.8	5	2
Normal alkanes	17.3	-	-
Branched alkanes	32	-	-
Cycloalkanes	5	-	-
Saturates	-	78	-
Paraffins	-	-	60
Naphthenes	-	-	20

^a Sciences International, Inc., "Toxicological Profile for Gasoline," Report to Department of Health and Human Services, June, 1995.

^b Ma *et al.*, 1994.

^c Ma *et al.*, 2002.

2.1.2 Sulfur Specification

Due to the increasingly stringent environmental regulations on sulfur concentration in transportation fuels, ultra-deep desulfurization of diesel fuel has become a more and more important research subject. This is because the sulfur compounds in the fuel are converted to SO_x during combustion, which not only results in acid rain, but also poisons catalysts in catalytic converters for reducing CO and NO_x . Consequently, the sulfur level in diesel fuel must be reduced from current maximum 500 to 15 ppm by 2006 in the US (Kim *et al.*, 2006), and the sulfur level in diesel fuel required by European Emission Standards decreases gradually from EURO 2 (500ppm) to EURO 3 (350ppm) and rapidly decreases from EURO 3 (350ppm) to EURO 4 (50ppm). For EURO 5, the sulfur level is reduced to 10 ppm in 2009. In Thailand, the sulfur level in diesel is regulated to decrease gradually from 350 ppm to 50 ppm in 2012 (Department of energy business, Ministry of Energy, Thailand, 2008). The regulated sulfur levels are illustrated in Figure 2.1.

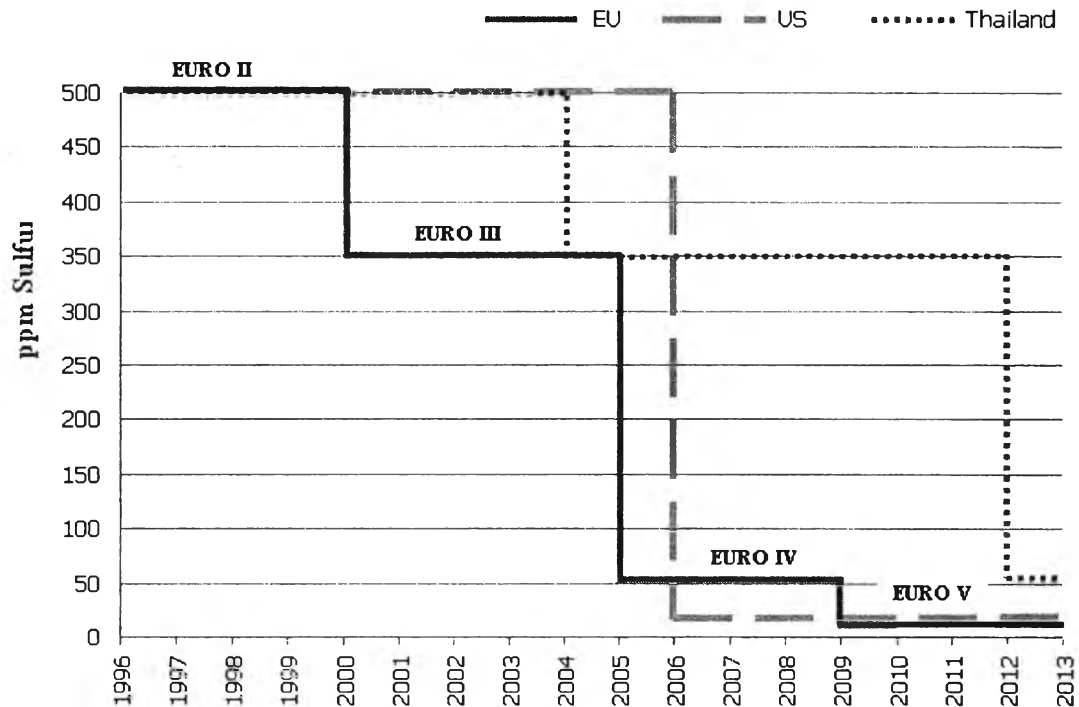


Figure 2.1 The regulated sulfur levels in diesel fuel in EU, USA and Thailand.

2.2 Organosulfur Compounds

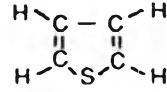
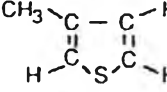
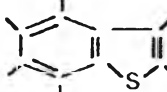
Organosulfur compounds are organic compounds that contain sulfur. They are often associated with foul odours, but ironically many of the sweetest compounds known are organosulfur derivatives. Nature abounds with organosulfur compounds sulfur is essential for life. Two of the twenty common amino acids are organosulfur compounds. Fossil fuels, coal, petroleum, and natural gas, which are derived from ancient organisms, necessarily contain organosulfur compounds, the removal of which is a major focus of oil refineries (http://en.wikipedia.org/wiki/Organosulfur_compounds).

Sulfur is a divalent element associated with hydrogen and carbon in 4 types of principal compound: hydrogen sulfide, mercaptans, sulfides, and thiocyclic compounds (containing sulfur in a ring). The physical constants of the principal sulfur compounds are shown in Table 2.2.

The sulfur content of liquid fuels can vary from virtually zero to as high as 7 or 8 wt%. There are many common types of sulfur compounds in liquid fuel (Figure 2.2) which can be analyzed with X-ray fluorescence spectroscopy or by gas chromatography equipped with a capillary column plus a flame photometric detector:

- *Gasoline range*: naphtha, fluid catalytic cracking (FCC)–naphtha, etc.
 - Mercaptanes (RSH); sulfides (R₂S); and disulfides (RSSR);
 - Thiophene and its alkylated derivatives;
 - Benzothiophene.
- *Jet fuel range*: heavy naphtha, middle distillate,
 - Benzothiophene (BT) and its alkylated derivatives.
- *Diesel fuel range*: middle distillate, light cycle oil (LCO),
 - Alkylated benzothiophenes;
 - Dibenzothiophene (DBT) and its alkylated derivatives.
- *Boiler fuel feeds*: heavy oils and distillation residues,
 - ≥3-ring polycyclic sulfur compounds, including DBT, benzonaphthothiophene (BNT);
 - Phenanthro[4,5-b,c,d]thiophene (PT), and their alkylated derivatives.

Table 2.2 The physical constants of the principal sulfur compounds

	Chemical formula	Structural formula	Molecular weight	Normal boiling point °C	Sp gr ₄ ¹⁵ (liquid)
hydrogen sulfide	H ₂ S	H-S-H	34.1	-60.3	
MERCAPTANS					
methylmercaptan	CH ₃ SH	$\begin{array}{c} \\ -\text{C}-\text{S}-\text{H} \\ \end{array}$	48.1	6.0	0.873
ethylmercaptan	C ₂ H ₅ SH	$\begin{array}{c} \quad \\ -\text{C}-\text{C}-\text{S}-\text{H} \\ \quad \end{array}$	62.1	35.0	0.845
n-propylmercaptan	C ₃ H ₇ SH	$\begin{array}{c} \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{S}-\text{H} \\ \quad \quad \end{array}$	76.2	67.6	0.847
n-butylmercaptan	C ₄ H ₉ SH	$\begin{array}{c} \quad \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{C}-\text{S}-\text{H} \\ \quad \quad \quad \end{array}$	90.2	98.5	0.847
SULFIDES					
dimethylsulfide	C ₂ H ₆ S	$\begin{array}{c} \quad \\ -\text{C}-\text{S}-\text{C}- \\ \quad \end{array}$	62.1	37.3	0.854
ethylmethylsulfide	C ₃ H ₈ S	$\begin{array}{c} \quad \quad \\ -\text{C}-\text{S}-\text{C}-\text{C}- \\ \quad \quad \end{array}$	76.2	66.6	0.848
diethylsulfide	C ₄ H ₁₀ S	$\begin{array}{c} \quad \quad \quad \\ -\text{C}-\text{C}-\text{S}-\text{C}-\text{C}- \\ \quad \quad \quad \end{array}$	90.2	92.1	0.841
methyl n-propylsulfide	C ₄ H ₁₀ S	$\begin{array}{c} \quad \quad \quad \\ -\text{C}-\text{S}-\text{C}-\text{C}-\text{C}- \\ \quad \quad \quad \end{array}$	90.2	95.5	0.847
DISULFIDES					
dimethyldisulfide	C ₂ H ₆ S ₂	$\begin{array}{c} \quad \\ -\text{C}-\text{S}-\text{S}-\text{C}- \\ \quad \end{array}$	94.2	109.6	1.069
diethyldisulfide	C ₄ H ₁₀ S ₂	$\begin{array}{c} \quad \quad \quad \\ -\text{C}-\text{C}-\text{S}-\text{S}-\text{C}-\text{C}- \\ \quad \quad \quad \end{array}$	122.2	152.6	0.998
dipropyldisulfide	C ₆ H ₁₄ S ₂	$\begin{array}{c} \quad \quad \quad \quad \quad \\ -\text{C}-\text{C}-\text{C}-\text{S}-\text{S}-\text{C}-\text{C}-\text{C}- \\ \quad \quad \quad \quad \quad \end{array}$	150.3	126.5 at 100mm of Hg	0.964
THIOPHENIC COMPOUND					
thiophene	C ₄ H ₄ S		84.1	84	1.070
methylthiophene	CH ₃ C ₄ H ₃ S		98.2	119	1.069
benzothiophene	C ₈ H ₆ S		134.2	220	1.165



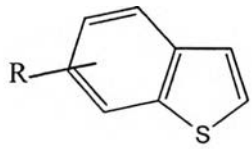
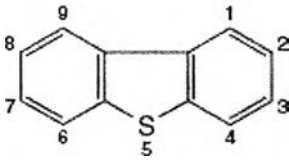
H_2S	Hydrogen sulfide
S_8	Elemental sulfur
$R-SH$	Mercaptan
$R-S-R'$	Sulfide
$R-S-S-R$	Disulfide
	Cyclic sulfide (tetrahydrothiophene)
	Thiophene
	Benzothiophene
	Dibenzothiophene (with alkyl groups at the 4- and 6-positions, that is, 4-MDBT and 4,6-DMDBT, are the refractory sulfur compounds that are most difficult to remove by HDS or sorbents aiming at bonding with S due to steric hindrance.)

Figure 2.2 Examples of sulfur compounds in petroleum.

Ma *et al.* (2002) showed GC-FPD chromatograms of a sample each of gasoline, diesel, and jet fuel in Figure 2.3. The FPD detects only sulfur compounds. The dominant sulfur compounds in the gasoline were (in decreasing order) 3-MT, BT, T, 2-MT, and 2,4-DMT. No mercaptans, dialkyl sulfides and dialkyl disulfides were detected. In diesel, the dominant sulfur compounds were 4-MDBT, 4,6-DMCBT, 2,4,6-TMDBT, 3,6-DMDBT, DBT, 2,3,7-TMBT, 2,3,5-TMBT, 2,3-DMBT, and others. The sulfur compounds found in the jet fuel were 2,3,7-TMBT, 2,3-DMBT, and the minor species 2,3,5-TMBT and 2,3,6-TMBT. All these MBT have two methyl groups at 2- and 3-positions, respectively, implying that the BT with two methyl groups at 2- and 3-positions are more difficult to be removed than other sulfur compounds in hydrotreating of jet fuel.

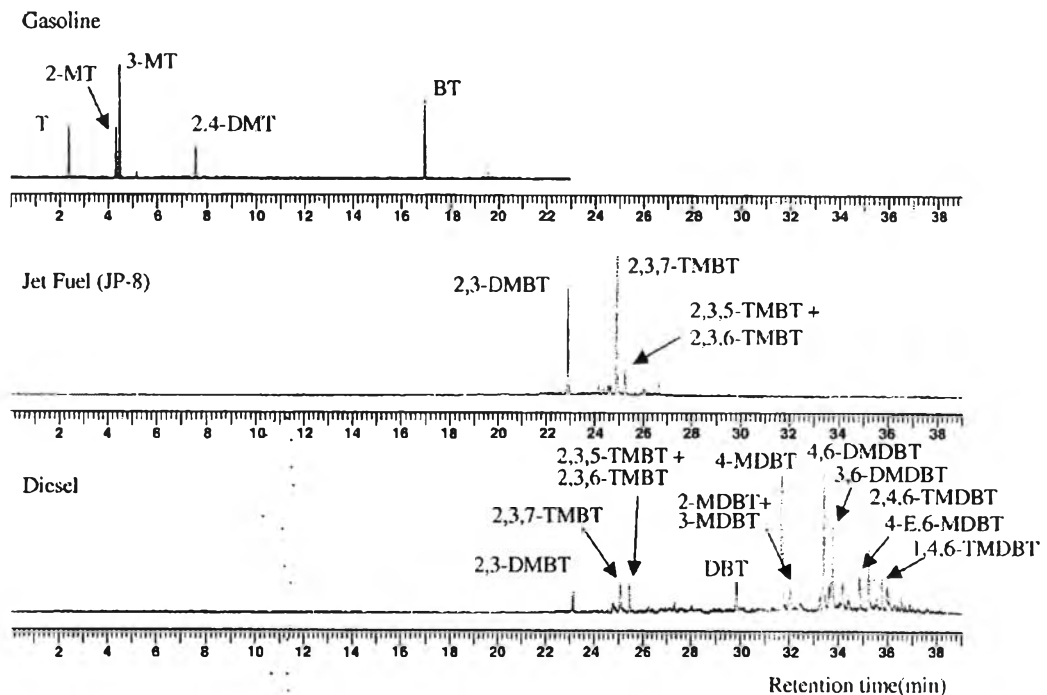


Figure 2.3 GC-FPD chromatograms of gasoline, jet fuel and diesel for identification of sulfur compounds (Ma *et al.*, 2002).

2.3 Desulfurization Process

There are several processes that can be used to remove the sulfur compounds in the liquid fuel. The classification of desulfurization technologies, according to Babich and Moulijn (2003), can be based on the fate of the organosulfur compounds during desulfurization, the role of hydrogen, or the nature of the process used (chemical and/or physical).

Based on the way in which the organosulfur compounds are transformed, the processes can be divided into three groups depending on whether or not the sulfur compounds are decomposed separately from the refinery stream without decomposition, or whether they are both separated and then decomposed (Figure 2.4). When organosulfur compounds are decomposed, gaseous or solid sulfur products are formed and the hydrocarbon part is recovered and remains in the refinery streams.

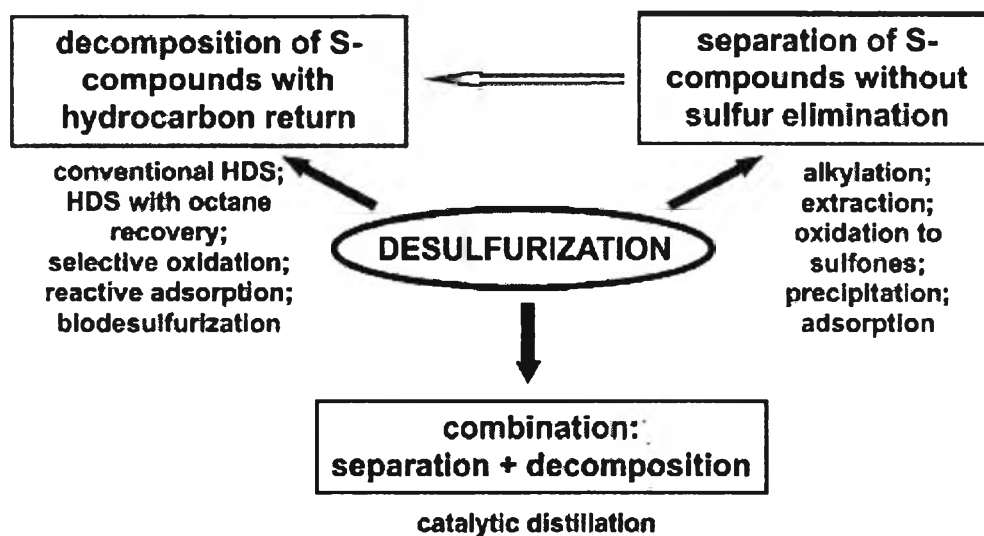


Figure 2.4 Classification of desulfurization processes based on organosulfur compound transformation (Babich and Moulijn, 2003).

Depending on the role of hydrogen in removing sulfur, desulfurization processes can be also classified into two groups: ‘HDS-based’ and ‘non-HDS-based’. In HDS-based processes, hydrogen is used to decompose organosulfur compounds and eliminate sulfur from refinery streams, while non-HDS-based processes do not require hydrogen.

Finally, desulfurization processes can be classified based on the nature of the key physico-chemical process used for sulfur removal (Figure 2.5). The most developed and commercialized technologies are those which catalytically convert organosulfur compounds with sulfur elimination. Such catalytic conversion technologies include conventional hydrotreating, hydrotreating with advanced catalysts and/or reactor design, and a combination of hydrotreating with some additional chemical processes to maintain fuel specifications.

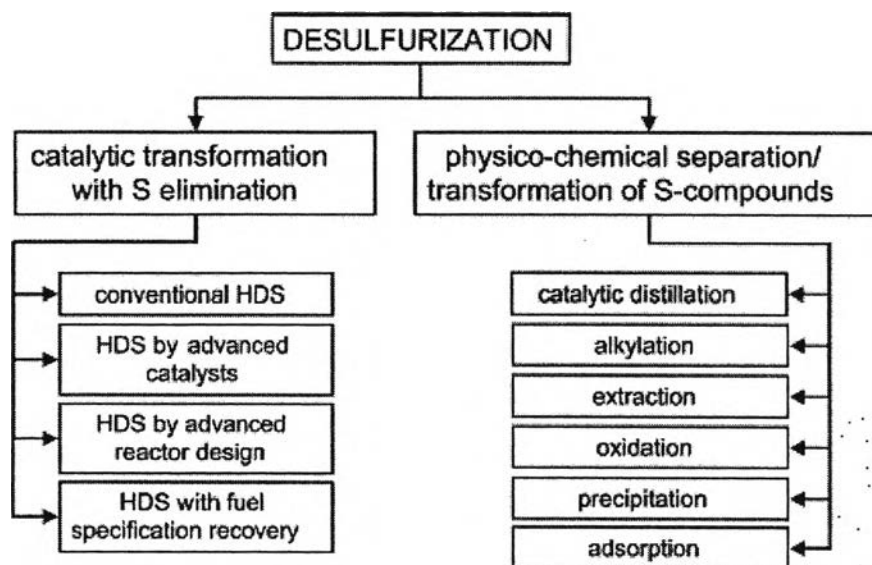


Figure 2.5 Desulfurization technologies classified by nature of a key process to remove sulfur (Babich and Moulijn, 2003).

2.3.1 Conventional Hydrodesulfurization (HDS)


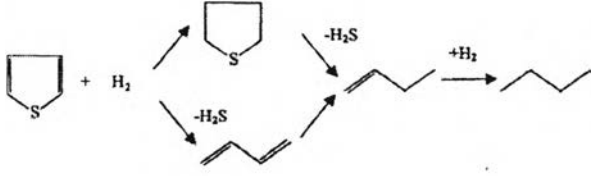
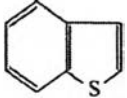
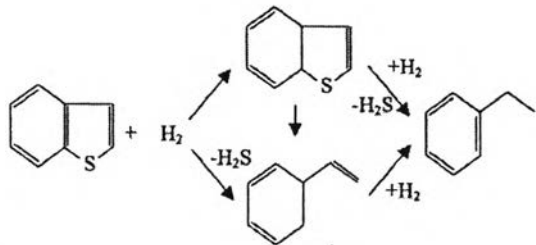
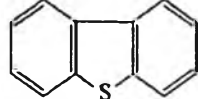
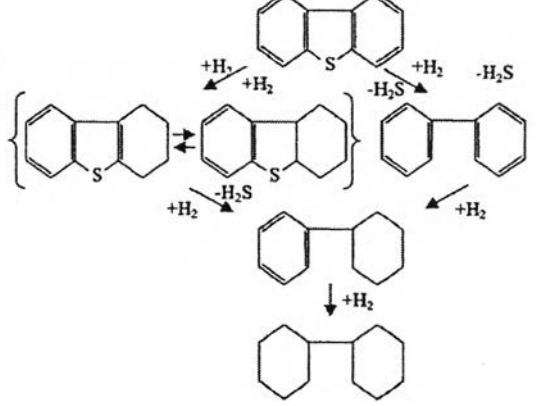
Conventional hydrodesulfurization (HDS) process is an efficient method of sulfur removal from gasoline and diesel with high sulfur concentrations, and is used worldwide (Xue *et al.*, 2005). The hydrodesulfurization process involves catalytic treatment with hydrogen to convert the various sulfur compounds present to hydrogen sulfide at elevated temperatures (300-340 °C) and pressures (20-100 atm H_2) using Co-Mo/ Al_2O_3 or Ni-Mo/ Al_2O_3 catalysts (Hernandez *et al.*, 2004a). The hydrogen sulfide is then separated and converted to elemental sulfur by the Claus process. Their performance in terms of desulfurization level, activity and selectivity depends on the properties of the specific catalyst used (active species concentration, support properties, synthesis route), the reaction conditions (sulfiding protocol, temperature, partial pressure of hydrogen and H_2S), nature and concentration of sulfur compounds present in the feed stream, and reactor and process design (Babich and Moulijn, 2003). However, these catalysts are poisoned by H_2S and metals in feedstock. There is generally no method for regeneration other than running straight hydrogen through the reactor.

The HDS process is effective to remove thiols, sulfides and disulfides, but it is difficult to remove thiophene, benzothiophene (BT), dibenzothiophene (DBT) and their derivatives (most importantly, 4,6-DMDBT) (Zhang *et al.*, 2008). The reactivity of organic sulfur compounds varies widely depending on their structure and local sulfur atom environment. The low-boiling crude oil fraction contains mainly the aliphatic organic sulfur compounds: mercaptans, sulfides and disulfides. They are very reactive in conventional hydrotreating processes and they can easily be completely removed from the fuel. For high boiling crude oil fractions, the organic sulfur compounds pre-dominantly contain thiophenic rings. These compounds include thiophenes and benzothiophenes and their alkylated derivatives. These thiophene containing compounds are more difficult to convert via hydrotreating than mercaptans and sulfides as they are more stable. Thus, because of this problem, the sulfur compounds that remain in the transportation fuels are mainly thiophene, benzothiophene, dibenzothiophene, and their alkylated derivatives (Hernandez *et al.*, 2004a). The organic sulfur compounds and their hydrotreating pathway are shown in Table 2.3.

It has been reported that for the removal of these sulfur compounds by the HDS process to the desired levels would demand more than three-fold increase in the catalyst volume/reactor size resulting in enormously high cost of operation of this high temperature and high pressure process. In view of the complex nature of sulfur reduction in the existing HDS process, the requirement of stringent process conditions and also energy and cost-intensive operation, it is desirable to search for alternate solutions to this problem (Bhandari *et al.*, 2006).

Table 2.3 The organic sulfur compounds and their hydrotreating pathway (Babich and Moulijn, 2003)

Typical organosulfur compounds and their hydrotreating pathway

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.

2.3.2 Desulfurization by Adsorption.

Due to the high complexity of HDS process for removal of sulfur compound to comply with the new regulations, thus it is necessary to consider the different technologies. As an alternative or supplement to the HDS process a number of other approaches are being tested. These include oxidative microbial desulfurization, oxidative chemical desulfurization and adsorption which is the majority interesting technique (Reut *et al.*, 2006; Bhandari *et al.*, 2006).

Adsorption processes consist of the selective concentration of one or more components of either a gas or a liquid at the surface of a solid (adsorbent). The attractive forces causing the adsorption are generally weaker than those of chemical bonds, and by increasing the temperature of the adsorbent or reducing as an adsorbate's partial pressure (or concentration in a liquid), the adsorbate can be desorbed (Rousseau, 1987).

There are two types of adsorption: physical adsorption and chemical adsorption. The physical adsorption involves only relatively weak intermolecular forces. These forces include van der Waals forces (dispersion-repulsion) and electrostatic interactions comprising polarization, dipolar and quadrupolar interactions. The chemical adsorption involves, essentially, the formation of chemical bonds between the sorbate molecule and the surface of the adsorbent (Ruthven, 1984).

Adsorptive separation is achieved by one of three mechanisms: steric, kinetic, or equilibrium effect. The steric effect derives from the molecular sieving properties of zeolites and molecular sieves. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecule. A large majority of processes operate through the equilibrium adsorption of mixture and hence are called equilibrium separation processes (Yang, 2003).

Desulfurization by adsorption is based on the ability of a solid sorbent to selectively adsorb organic sulfur compounds from refinery steams. Based on the mechanism of the sulfur compound interaction with the sorbent, desulfurization by adsorption can be divided into two groups: adsorptive desulfurization and reactive

adsorptive desulfurization. Adsorptive desulfurization is based on physical adsorption of organic sulfur compounds on the solid sorbent surface. Regeneration of the sorbent is usually done by flushing the spent sorbent with a desorbent, resulting in a high organic sulfur compound concentration flow. Reactive adsorption desulfurization employs chemical interaction of the organic sulfur compounds and the sorbent. Sulfur is fixed in the sorbent, usually as sulfide, and the S-free hydrocarbon is released into purified fuel stream. Regeneration of the spent sorbent results in sulfur elimination as H_2S , S, or SO_x , depending on the process applied. Efficiency of the desulfurization is mainly determined by the sorbent properties: its adsorption capacity, selectivity for the organic sulfur compounds, durability and regenerability (Babich and Moulijn, 2003)

2.3.3 Adsorbents for Desulfurization

Commercial adsorbents are divided into four major types: activated carbon, molecular-sieve zeolites, silica gel, and activated alumina. As the adsorption is a surface-related phenomenon thus the useful adsorbents are all characterized by large surface area per unit of weight (or volume). The typical range of area covers from about 100 to over 3000 m^2/g , however, the most common commercially useful materials exhibit surface areas ranging from about 300 to 1200 m^2/g (Rousseau, 1987). Table 2.4 shows examples of commercial applications of these sorbents (Yang, 2003).



Table 2.4 Adsorbents in commercial adsorption separations (Yang, 2003)

Separation	Adsorbent
Gas Bulk Separations	
Normal paraffins/isoparaffins, aromatics	Zeolite
N ₂ /O ₂	Zeolite
O ₂ /N ₂	Carbon molecular sieve
CO, CH ₄ , CO ₂ , N ₂ , Ar, NH ₃ /H ₂	Activated carbon followed by zeolite (in layered beds)
Hydrocarbons/vent streams	Activated carbon
H ₂ O/ethanol	Zeolite (3A)
Chromatographic analytical separations	Wide range of inorganic and polymer resin agents
Gas Purification	
H ₂ O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite (3A)
CO ₂ /C ₂ H ₄ , natural gas, etc.	Zeolite, carbon molecular sieve
Hydrocarbons, halogenated organics, solvents/vent streams	Activated carbon, silicalite, others
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite, activated alumina
SO ₂ /vent streams	Zeolite, activated carbon
Odors/air	Silicalite, others
Indoor air pollutants—VOCs	Activated carbon, silicalite, resins
Tank-vent emissions/air or nitrogen	Activated carbon, silicalite
Hg/chlor-alkali cell gas effluent	Zeolite
Liquid Bulk Separations	
Normal paraffins/isoparaffins, aromatics	Zeolite
p-xylene/o-xylene, m-xylene	Zeolite
Detergent-range olefins/paraffin's	Zeolite
p-Diethyl benzene/isomer mixture	Zeolite

Table 2.4 (Cont.) Adsorbents in commercial adsorption separations (Yang, 2003)

Separation	Adsorbent
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymer, and affinity agents
<i>Liquid Purifications</i>	
H ₂ /organics, oxygenated organics, halogenated organics, etc., dehydration	Silica, alumina, zeolite, corn grits
Organics, halogenated organics, oxygenated organics, etc./H ₂ O—water purification	Activated carbon, silicalite, resins
Inorganics (As, Cd, Cr, Cu, Se, Pb, F, Cl, radio nuclides, etc.)/H ₂ O—water purification	Activated carbon
Odor and taste bodies/H ₂ O	Activated carbon
Sulfur compounds/organics	Zeolite, alumina, others
Decolorizing petroleum fractions, syrups, vegetable oils, etc.	Activated carbon
Various fermentation products/fermentor effluent	Activated carbon, affinity agents
Drug detoxification in the body	Activated carbon

2.3.3.1 Activated Carbon

Activated carbon material is a hydrophobic porous material with very high surface area and large pore volume. It has been widely used in deodorization, decolorization, purification of drinking water, treatment of waste water, adsorption and separation of various organic and inorganic chemicals. Haji and Erkey reported using carbon aerogels as adsorbents for desulfurization of a model diesel (DBT in n-hexadecane) (Haji and Erkey, 2003). They found that the saturation adsorptive capacity of a carbon aerogel with pore size of 22 nm was 15 mg

of sulfur per gram of adsorbent (mg-S/g-A) and the carbon areogel selectively adsorbed DBT over naphthalene. Mochida and co-workers reported an interesting work on adsorptive desulfurization of real gas oil over activated carbon materials with surface area from 683 to 2972 m²/g (Mochida *et al.*, 2004). They found that using the activated carbon materials can remove sulfur and nitrogen species from gas oil (Kim *et al.*, 2006).

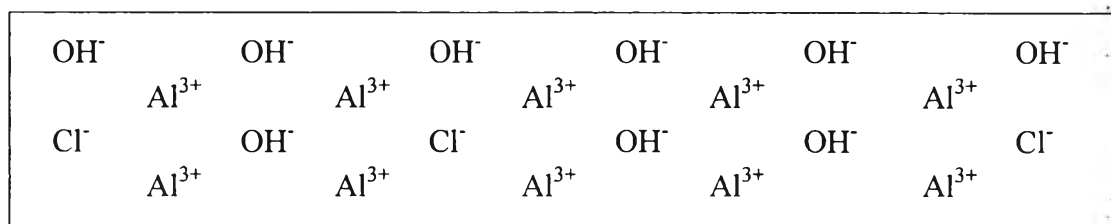
Activated carbon is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700-1000 °C). The structures of activated carbon are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The porosity yields the surface area that provides for the ability to adsorb gases and vapors from gases, and dissolved or dispersed substances from liquids. The actual distribution and the total pore volume associated with each pore size range are however sensitive to the conditions of the initial pyrolysis and activation procedures. Typical ranges are given in Table 2.5, but by special procedures, it is possible to prepare activated carbons with even higher porosity, surface area, and adsorptive capacity.

Table 2.5 Pore sizes in typical activated carbon (Ruthven, 1984)

Properties	Micropore	Mesopore or Transitional Pores	Macropores
Diameter (Å)	< 20	20-500	>500
Pore volume (cm ³ /g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m ² /g)	100-1000	10-100	0.5-2
(Particle density 0.6-0.9 g/cm ³ ; porosity 0.4-0.6)			

2.3.3.2 Activated Alumina

Activated alumina is a porous high-area form of aluminum oxide, prepared either directly from bauxite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) or from the monohydrate by dehydration and recrystallization at elevated temperature. The surface area is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal (Ruthven, 1984). The surface acidity is the most important property for both adsorption and catalysis. Unlike silica, Lewis acid sites are usually abundant on aluminas. These are the Al^{3+} sites on the surfaces. There are both tetrahedral and octahedral Al^{3+} sites. The acidity of the surface can be increased with acid, such as HCl and HF. Partial conversion of a fully hydrate alumina surface by the acid treatment would form a surface that contains both Cl^- and OH^- groups:

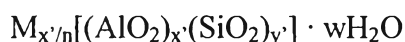


Activated alumina is a versatile sorbent that can be tailored for many special applications. New applications continue to be developed, mainly by aluminum companies. The following are proven applications of various tailored alumina (Yang, 2003):

- Removal of HCl and HF from gases and liquids
- Removal of acidic gases (COS , CO_2 , H_2S , CS_2) from hydrocarbons
- Removal of oxygenates and Lewis Bases
- Removal of polar organic compounds
- Removal of As^{5+} , PO_4^{3-} , Cl^- , and F^- from water
- Scavenger for organic process liquids
- Alkalized alumina for SO_2 removal

2.3.3.3 Molecular-Sieve Zeolites

The zeolites that are in commercial use today are mainly the types in Milton's invention; that is types A, X, and Y. Zeolites are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium, and calcium, and are represented by the chemical composition:



where n is the valence of cation M , w is the number of water molecules per unit cell, x' and y' are the total number of tetrahedral per unit cell, and x'/y' usually has values of 1-5.

The zeolites of most interest in catalysis are those having medium to large pore sizes, consisting of 10- or 12-ring oxygen atoms, and having relatively high Si/Al ratios. The latter may stem from the initial synthesis method or from subsequent treatments. Zeolites of high current interest industrially include zeolite Y and mordenite, which have a 12-ring system, and zeolite ZSM-5, which has a 10-ring system (Ruthven, 1984; Rousseau, 1987).

2.3.3.4 Silica Gel

Silica gel is a partially dehydrated form of polymeric colloidal silicic acid. The chemical composition can be expressed as $SiO_2 \cdot nH_2O$. The water content, which is present mainly in the form of chemically bound hydroxyl groups, amounts typically to about 5 wt.%. The surface area is generated by the very fine size of the colloidal particles. They exhibit surface areas from as low as $100 \text{ m}^2/\text{g}$ for the "aerogels" to over $800 \text{ m}^2/\text{g}$. The product is provided both in granular and spherical forms. The silica-gel surface has an affinity for water and organics, although water is preferred. The surface of the silica gel can be in a fully hydroxylated form (Si-O-H) or in a dehydrated siloxane form (Si-O-Si).

The primary adsorptive application of silica gel is in the dehydration of gases and liquids. Until the advent of the application of cryogenic technology in the natural gas industry, silica gel was commonly used to recover hydrocarbons from natural gas streams.

2.3.4 Previous Studies on the Use of Adsorbents for Sulfur Removal

At PPC, there have been several studies on sulfur adsorption using various kinds of adsorbents. In 2007, Ho studied the desulfurization of transportation fuels by adsorption process using the ion-exchanged zeolites which prepared by exchanging NaX and NaY zeolites with Ni^{2+} and Cu^+ cations using both LPIE and SSIE methods. These adsorbents were evaluated for their efficiency in removing 3-MT and BT in both binary and ternary systems of isooctane and benzene (or toluene) as model fuels. In the static adsorption, the sulfur adsorption capacity increased in the order $\text{NiY (LPIE at } 135\text{ }^\circ\text{C)} < \text{NiX (LPIE at } 45\text{ }^\circ\text{C)} < \text{NiY (SSIE)}$ for both sulfur compounds. Furthermore, the adsorption data of sulfur compounds in isooctane and benzene revealed that the removal rate and the overall sulfur uptake capacity of the adsorbents were significantly reduced when benzene was used, which can be attributed to the competitive π -complexation forming with the adsorbent between the aromatic (benzene) and sulfur compound. The equilibrium capacity under dynamic conditions for 3-MT adsorption increased in the order of $\text{NaY} < \text{NiY} < \text{NiX} < \text{NaX} < \text{Cu(I)Y}$; while the selectivity for 3-MT over toluene exhibited the following trend $\text{NaY} < \text{NiY} < \text{NaX} < \text{NiX} < \text{Cu(I)Y}$. In addition, the pre-adsorbed water was found to have detrimental effect on the π -complexation bonding between adsorbent and sulfur compounds.

Prateepamornkul (2008) studied the adsorptive capacity and selectivity of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in simulated diesel fuels containing polyaromatic or nitrogen compounds on activated carbon and alumina, modified with Cu^+ and Ni^{2+} using different preparation methods. Direct impregnation by using $\text{CuCl}/\text{CH}_3\text{CN}$ was found to be unsuitable due to the stability and low solubility of Cu^+ . Impregnation was therefore performed with an aqueous solution of CuCl_2 following by a reduction step of CuCl_2 into CuCl using H_2 . For Ni^{2+} , an aqueous solution of NiCl_2 was used. A suitable feed flow rate and granulometry of the adsorbent was found to be $0.4\text{ cm}^3/\text{min}$ and 100 to $400\text{ }\mu\text{m}$, while the optimum temperature was $60\text{ }^\circ\text{C}$ and $90\text{ }^\circ\text{C}$ for Ni^{2+} and Cu^+ impregnated alumina, respectively. The adsorption capacity at the sulfur breakthrough followed the order non-impregnated macroporous alumina $<$ Cu^+ /macroporous alumina $<$ non-impregnated mesoporous alumina $<$

Cu^+ /mesoporous alumina < Ni^{2+} /macroporous alumina < Ni^{2+} /mesoporous alumina < Cu^+ /AC < non-impregnated AC. The breakthrough capacity of DBT was higher than 4,6-DMDBT for both of Ni^{2+} and Cu^+ /mesoporous alumina. Moreover, the breakthrough capacity of DBT without polyaromatic and nitrogen compounds was higher than that with polyaromatic and nitrogen compounds.

2.3.5 π -Complexation

The π -complexation bond is typically a weak bond that can be formed between the sorbent and sorbate. The sorbents that are used for separation and purification based on π -complexation are called π -complexation sorbents. Development of π -complexation sorbents began only recently. A number of sorbents have already been used commercially, and tremendous potential exists for future applications in separation and purification, both for the chemical/petrochemical industry and environmental applications. All major industrial adsorption processes are based on van der Waals and electrostatic interactions between the sorbate and sorbent. Chemical bonds have yet to be exploited in a significant way. Chemical complexation has been studied and used on a large scale in a number of other separation and purification processes by using mass separating agents.

Chemical complexation bonds are generally stronger than van der Waals interactions (thus giving rise to higher selectivities), many of them are weak enough to be reversible (i.e., to be broken by simple engineering means). The π -complexation is a special class of chemical complexation. For π -complexation sorbents, it pertains to the main group (or d-block) transition metals (and there are 27 elements). When interact with a gas or solute molecule, these metals and their ions can form the usual σ bonds with their s-orbitals and, in addition, their d-orbitals can back-donate electron density to the antibonding π -orbitals of the molecule to be bonded (Yang, 2003).

During the last decade, π -complexation sorbents have been developed for many applications, including desulfurization, olefin/paraffin, diene/olefin, and aromatics/aliphatics separations. For desulfurization, transition-metal ion exchanged zeolites have used to selectively remove organosulfur molecules from commercial fuels like diesel and gasoline. In the complexation mechanism, the cation can form

the usual σ bonds with their s-orbitals and, in addition, their d orbitals can back-donate electron density to the antibonding p-orbitals of the sulfur ring (see Figure 2.6, 2.7 and 2.8). Molecular orbital calculations have shown that the π -complexation bonds between Cu^+ or Ag^+ and thiophene are stronger than that with benzene (Yang, *et al.*, 2001). Moreover, it was determined that the π -complexation bond was stronger for substituted thiophenes over non-substituted ones and thus π -complexation sorbents are selective for sulfur removal from transportation fuels (Hernandez *et al.*, 2005).

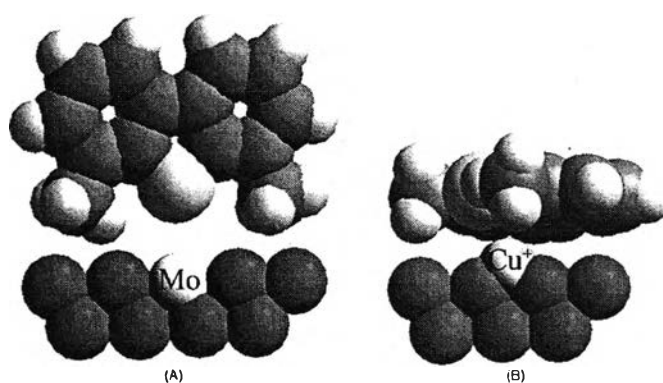


Figure 2.6 Schematic representation for desulfurization of 4,6-dimethyl-dibenzothiophene with molybdenum-based (A) and copper(I)-based (B) adsorbents. Case (B) corresponds to π -complexation (Hernandez *et al.*, 2005).

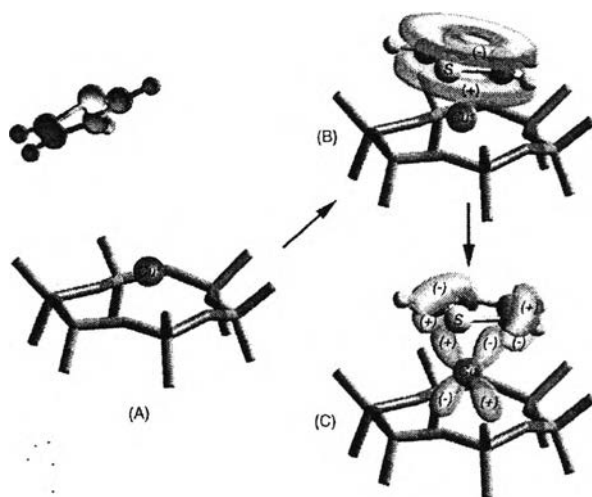


Figure 2.7 Copper ions occupying faujasite 6-ring windows sites (A); σ -donation of π -electrons of thiophene to the 4s orbital of copper(I) (B); $d-\pi^*$ backdonation of electrons from 3d orbitals of copper(I) to π^* orbitals of thiophene (C). Here 3d represents d_{xy} , d_{yz} , or d_{xz} , or 3 of the 53d orbitals (Hernandez *et al.*, 2005).

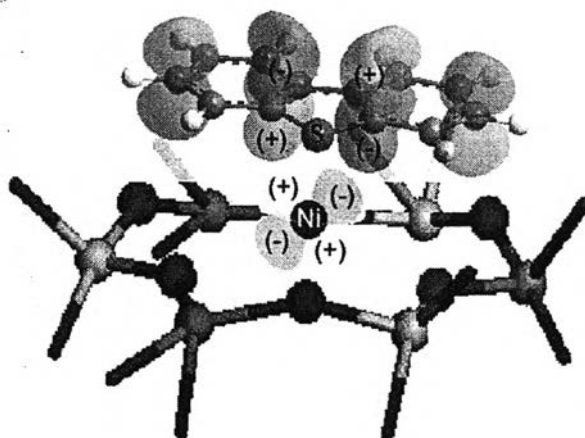


Figure 2.8 Means of interaction for a DBT molecule with NiY, corresponding to π -complexation (Juan *et al.*, 2009).



2.3.6 Regeneration of Adsorbent

Desorption or regeneration step is quite important in the overall process. First, desorption allows recovery of adsorbates in those separations where they are valuable; and second, it permits reuse of the adsorbent for further cycles. In a few cases, desorption is not practical, and the adsorbate must be removed by thermal destruction or another chemical reaction, or the adsorbent is simply discarded.

Wang and Yang (2007) studied the desorption of PdCl₂/activated carbon after saturated with the model jet fuel by using ultrasound-assisted sorbent regeneration. The desorption was conducted in a static bath of solvent at room temperature and 50 °C. The results showed that the amount of sulfur desorbed depended on the time and temperature. With increasing desorption time, the amount of sulfur desorbed reach a constant value. They also found that ultrasound was an effective technique for regenerating spent PdCl₂/activated carbon. Kaewboran (2005) investigated the desorption of NaX after desulfurized the sulfur compounds such as 3-MT and BT in simulated gasoline and DBT in simulated diesel by heating technique at 400°C. The result was not proper for DBT but 3-MT and BT. In addition, the recovered adsorption capacity of NaX that adsorbed with BT was a slightly lower than 3-MT. Xue *et al.* (2005) found that the regeneration of CeY-zeolite (Na) was accomplished by calcining at 450°C in air for 2 hours. More than 90% of that of the first adsorption was recovered. Hernandez-Maldonado *et al.* (2004) regenerated the layered adsorbents by using two techniques. In regeneration of AC/Cu(I)-Y zeolite by using solvents, the CCl₄ showed the highest capacity recovery when compared with DMF, methanol and toluene. When regenerated by flowing air at 350°C for 6 hours followed by autoreduction, the CDX/Cu(I)-Y can be fully regenerated while the AC/Cu(I)-Y can recover only 85%. Hernandez-Maldonado *et al.* (2004) reported that the regeneration of Ni(II)-Y (SSIE-500) was achieved by calcination in dry air at 350°C for 6 hours. Hernandez-Maldonado *et al.* (2004) demonstrated that Selexsorb CDX Cu(I)-Y (VPIE) was regenerated by using air at 350°C followed by reduction of the copper species in helium.

2.3.7 Fixed Bed Adsorption

Fixed bed adsorption processes are ubiquitous throughout the chemical process and other industries. The phenomenon of adsorption is an attraction of adsorbate molecules to specific interaction between adsorbate molecules (aromatic rings or specific atoms) and the adsorbent surface. Figure 2.9 illustrates the breakthrough curve used to represent the adsorption process.

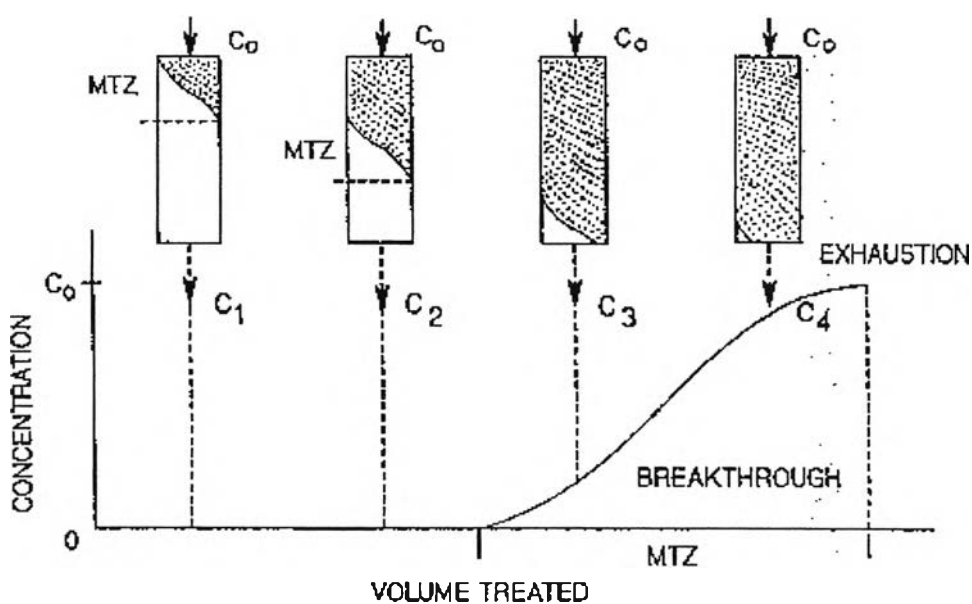


Figure 2.9 Idealized breakthrough curve of a fixed bed adsorber (<http://www.activated-carbon.com/solrec3.html>).

Figure 2.9 plots the relationship between outlet concentration of the adsorbate from the fixed bed adsorber and volume treated which is the function of time. The mass transfer zone (MTZ) is the area within the adsorbate bed where adsorbate is actually being adsorbed on the adsorbent. The MTZ typically moves from the influent end toward the effluent end of the adsorbent bed during operation. That is, as the adsorbent near the influent becomes saturated (spent) with adsorbate, the zone of active adsorption moves toward the effluent end of the bed where the adsorbate is not yet saturated. The MTZ is sometimes called the adsorption zone or critical bed depth. The MTZ is generally a band, between the spent zeolite and the fresh zeolite, where adsorbate is removed and the dissolved adsorbate concentration ranges from C_0 to C_e .

The length of the MTZ can be defined as LMTZ. When LMTZ = bed depth, it becomes LCRIT, or the theoretical minimum bed depth necessary to obtain the desired removal. As adsorption capacity is used up in the initial MTZ, the MTZ advances down the bed until the adsorbate begins to appear in the effluent. The concentration slowly increases until it equals the influent concentration. In cases where there are some very strongly adsorbed components, in addition to a mixture of less strongly adsorbed components, the effluent concentration very seldom reaches the influent concentration because only the components with the faster rate of movement through the adsorber are in the breakthrough curve.

Dynamic desorption capacity is influenced by many factors, such as flow rate, temperature, bed length, and concentration of the bed. The adsorption column may be considered exhausted when the effluent adsorbate concentration equals 95–100% of the influent concentration. As the concentration wave moves through the bed, most of the mass transfer is occurring in a fairly small region. This mass transfer zone moves down the bed until it breaks through. The shape of the mass transfer zone depends on the adsorption isotherm (equilibrium expression), flow rate, and the diffusion characteristics. Usually, the shape must be determined from the experiment. The shape of the wave front may change as it moves through the bed, and the mass transfer zone broadens or diminishes. Unfavourable and linear isotherms tend to broaden. Favourable Langmuir may broaden at first, but quickly achieve a constant pattern front, an asymptotic shape. This means that the mass transfer zone is constant with respect to both position and time (Ho, 2007).