



## CHAPTER II LITERATURE REVIEW

### 2.1. Transportation Fuels and Sulfur Compositions

The present transportation fuels comprise three major types: gasoline, diesel, and jet fuels. Their compositions vary widely depending on many factors such as type of crude oil used, refining process, and product specifications. In these fuels, branched and *n*-alkanes are the main ingredients, typically around 70–80%. For example in gasoline, the major alkane is *n*-hexane and the main branched alkanes are C5 and C6 compounds. Main aromatic compounds are benzene, toluene, xylenes, and alkyl benzenes, totaling about 20–30%. Table 2.1 shows the typical compositions of transportation fuels.

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

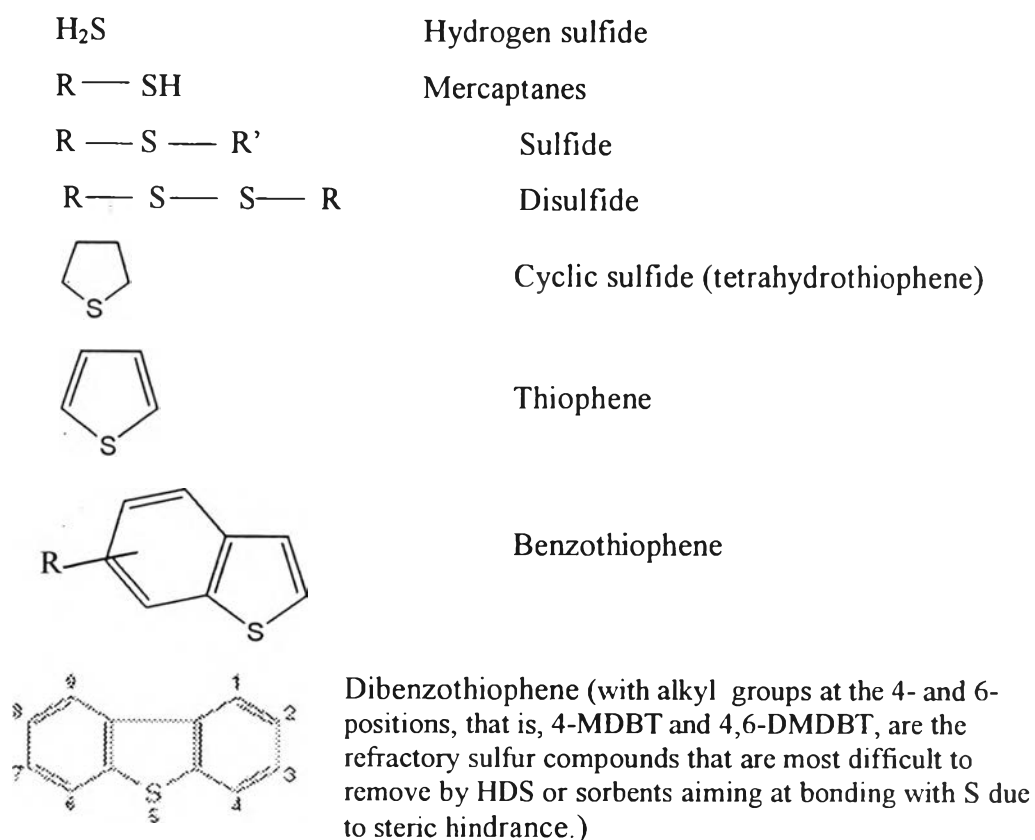
	Gasoline <sup>a</sup>	Diesel <sup>b</sup>	Jet Fuel <sup>c</sup>
Boiling range (°C)	40–204	232–350	330–510
Aromatics	30.5	17	18
Olefins	1.8	5	2
<i>n</i> -alkanes	17.3	—	—
Branched alkanes	32	—	—
Cycloalkanes	5	—	—
Saturates	—	78	—
Paraffins	—	—	60
Naphthenes	—	—	20

<sup>a</sup>Sciences International, Inc., “Toxicological Profile for Gasoline,” Report to Department of Health and Human Services, June, 1995, <sup>b</sup>Ma *et al.*, 2002a, <sup>c</sup>Ma *et al.*, 2002b.

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 (Figure 2.1) 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 (R<sub>2</sub>S); 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.

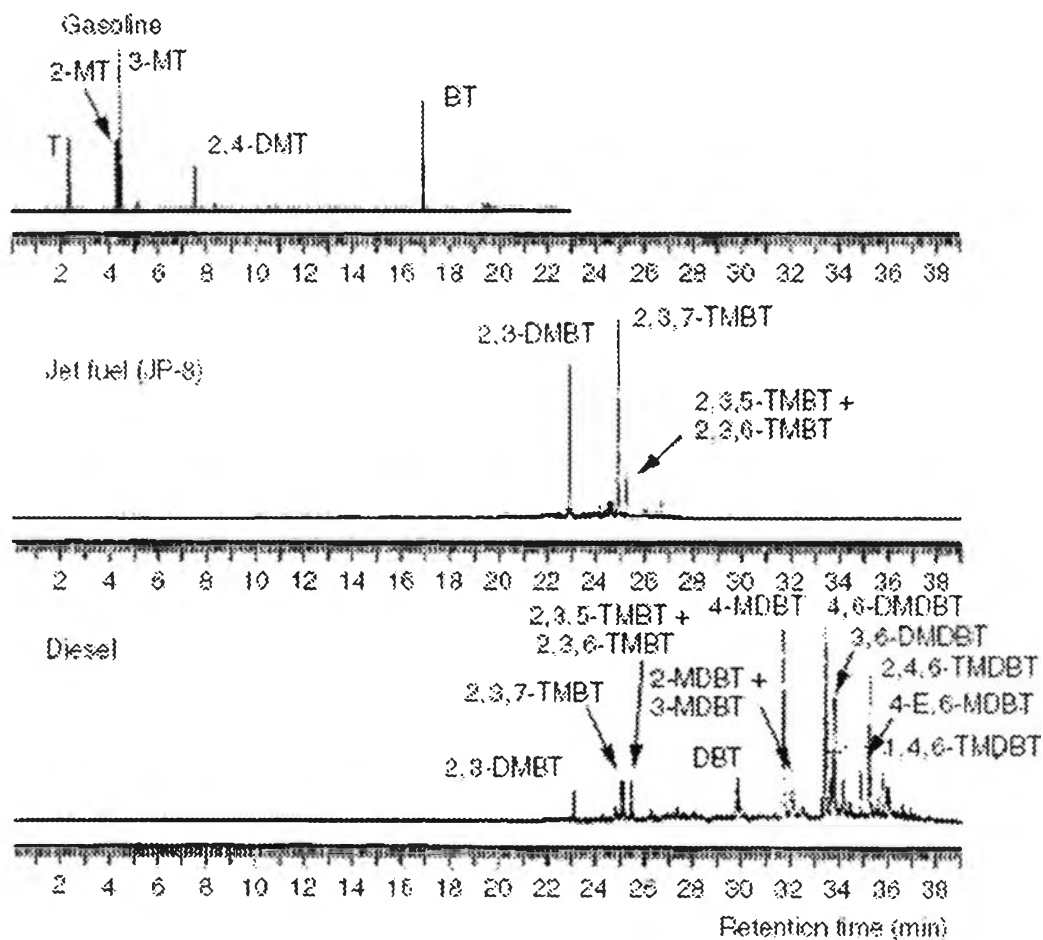


**Figure 2.1** Examples of sulfur compounds in petroleum.

Ma *et al.* (2001) showed GC-FPD (flame photometric detector) gas chromatograms of a sample each of gasoline, diesel, and jet fuel, reproduced in Figure 2.2. The FPD detects only sulfur compounds. The author reported that the major sulfur compounds in commercial gasoline were 3-methylthiophene (3-MT), benzothiophene (BT), thiophene (T), 2-methylthiophene (2-MT), and 2, 4-dimethylthiophene. Major sulfur compounds existing in jet fuel were 2, 3, 7-trimethylbenzothiophene (2, 3, 7-TMBT), 2, 3-dimethylbenzothiophene and the minor species 2, 3, 5-trimethylbenzothiophene (2, 3, 5-TMBT) and 2, 3, 6-trimethylbenzothiophene (2, 3, 6-TMBT). The sulfur compounds commonly found in the diesel fuel included 4-methyl-dibenzothiophene (4-MDBT), 4, 6-dimethyldibenzothiophene (4, 6-DMDBT), 2, 4, 6-trimethyldibenzothiophene (2, 4, 6-TMDBT), 3, 6-dimethyldibenzothiophene (3, 6-DMDBT), dibenzothiophene (DBT), 2, 3, 7-trimethylbenzothiophene (2, 3, 7-TMBT), 2, 3, 5-trimethylbenzothiophene (2, 3, 5-TMBT), 2, 3-dimethylbenzothiophene (2, 3-DMBT) and others. Among them, the 4, 6-DMDBT and the dibenzothiophenes with two alkyl substituents at 4- and 6- positions, respectively, were found to remain even after deep hydrodesulfurization (Kim *et al.*, 2006). An example of the sulfur composition of gasoline is given in Table 2.2.

**Table 2.2** Example of heteroatom contents in the FCC gasoline

Heteroatoms	Content, ppmw
Nitrogen	16.0
Oxygen	14.0
Mercaptan sulfur	24.2
Sulfide sulfur	7.3
Thiophene sulfur	61.9
C <sub>1</sub> thiophene sulfur	115.0
C <sub>2</sub> thiophene sulfur	130.6
C <sub>3</sub> thiophene sulfur	90.9
C <sub>4</sub> thiophene sulfur	88.0
Benzothiophene and dibenzothiophene sulfur	238.1
<b>Total</b>	<b>786.0</b>



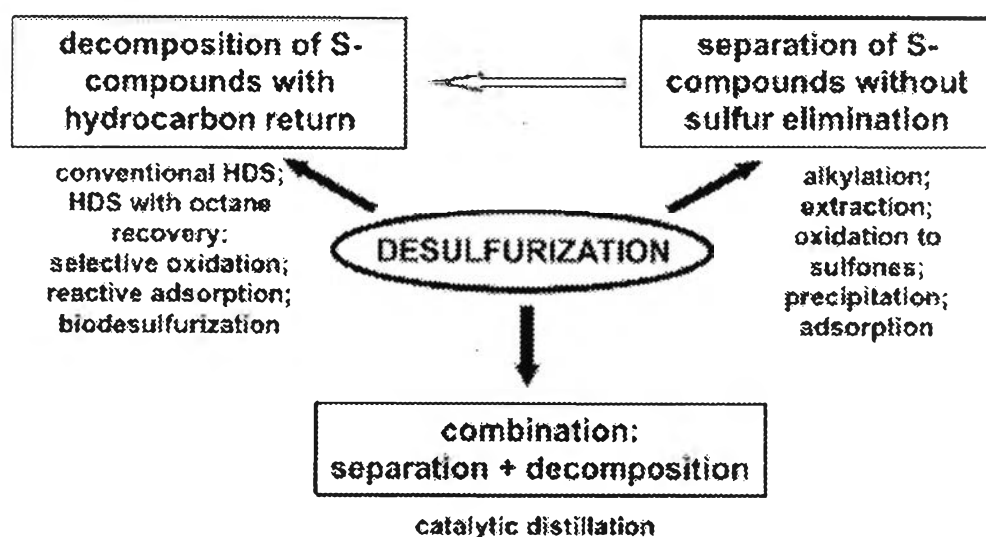
**Figure 2.2** GC-FPD (flame photometric detector-for sulfur only) chromatograms for three transportation fuels (Ma *et al.*, 2001).

## 2.2 Classification of Desulfurization Technologies

There are several processes available to decrease the sulfur content to acceptable levels. 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

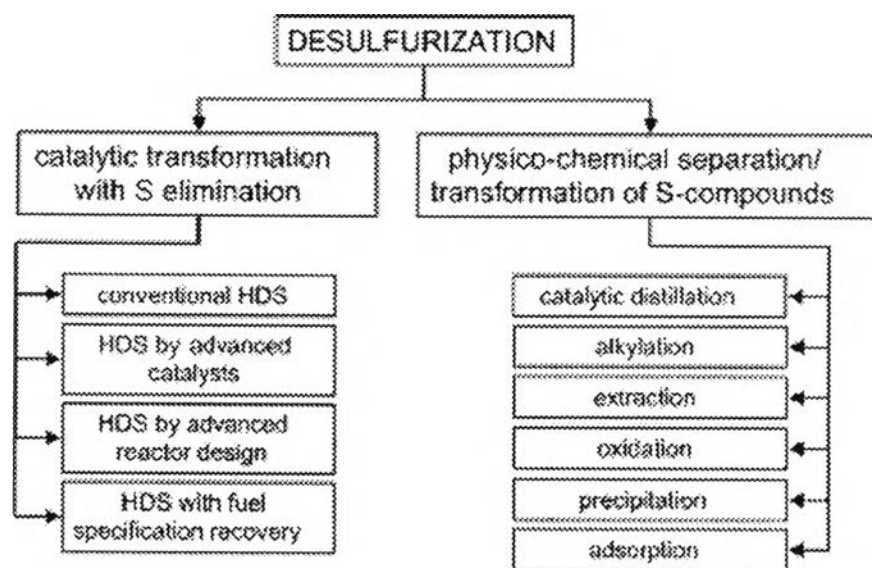
decomposition, or whether they are both separated and then decomposed (Figure 2.3). When organosulfur compounds are decomposed, gaseous or solid sulfur products are formed and the hydrocarbon part is recovered and remains in the refinery streams. Conventional HDS is the most typical example of this type of process. In other processes, the organosulfur compounds are simply separated from the refinery streams. Some processes of this type first transform the organosulfur compounds into other compounds which are easier to separate from the refinery streams. When streams are desulfurized by separation, some desired products can be lost and disposal of the retained organosulfur molecules is still a problem. In the third type of process, organosulfur compounds are separated from the streams and simultaneously decomposed in a single reactor unit rather than in a series of reaction and separation vessels. These combined processes, which provide the basis for many technologies currently proposed for industrial application, may prove very promising for producing ultra-low sulfur fuels. Desulfurization by catalytic distillation is a typical example of this type of process.



**Figure 2.3** 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 2.4). 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 2.4** Desulfurization technologies classified by nature of a key process to remove sulfur (Babich and Moulijn, 2003).


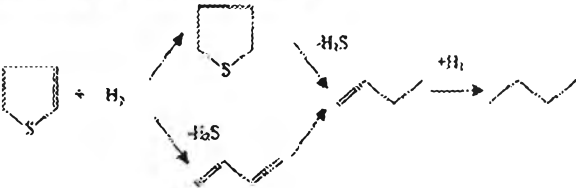

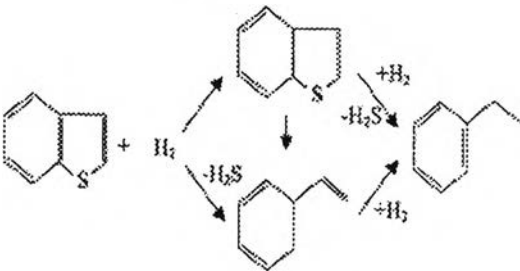
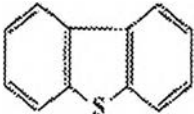
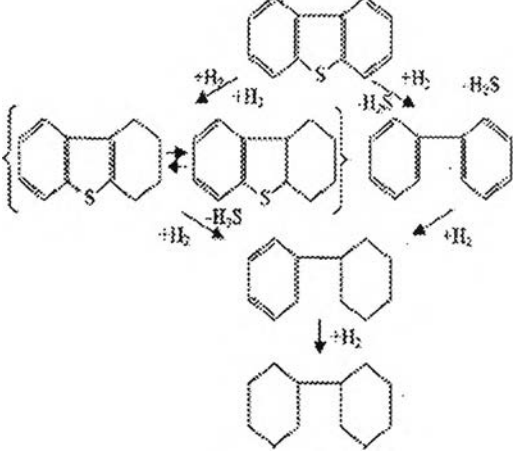
Among the processes mentioned above, conventional HDS, which has been widely used for the removal of sulfur compounds in refineries, will be discussed in more details subsequently.

### 2.2.1 Conventional HDS

The conventional HDS process is usually conducted over sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts with H<sub>2</sub> to remove organosulfur compounds as H<sub>2</sub>S, which is ultimately captured and converted to elemental sulfur. The catalyst 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<sub>2</sub>S), nature and concentration of the sulfur compounds present in the feed stream, and reactor and process design. This process requires H<sub>2</sub>, often at high pressure, and tends to saturate high-octane alkene and arene components in fuels, resulting in an undesirable loss of octane number. However, the metals in the feedstock are deposited on the catalyst in the form of metal sulfides, and cracking of the feedstock to distillate produces a lay-down of carbonaceous material on the catalyst; both events poison the catalyst as its activity and selectivity sulfur. As a result, hydrodesulfurization becomes less useful for gasoline than for diesel fuels, for which hydrogenation of unsaturated components can actually increase fuel quality (Chicacá *et al.*, 2004).

The reactivity of sulfur compounds varies widely depending on their structure and local sulfur atom environment. The hydrotreating pathway of sulfur compounds is shown in Table 2.3.

**Table 2.3** Typical organosulfur compounds and their hydrotreating pathway (Babich and Moulijn, 2003)

Type of organic sulfur compound	Chemical structure	Mechanism of hydrotreating reaction <sup>a</sup>
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		

<sup>a</sup> Reaction pathway for alkylated thiophene, benzothiophene and dibenzothiophene is similar to the reaction of nonalkylated counterparts.

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 (Barrio *et al.*, 2003).



### 2.2.2 Desulfurization by adsorption

The selective concentration of one or more components (adsorbates) of either a gas or a liquid at the surface of a microporous solid (adsorbents) is called the adsorption process. The bonds between the adsorbates and the adsorbents can vary in strength depending on the nature of compounds and of solid involved. They are weaker than those of chemical bonds but are easier to be desorbed by increasing the temperature of the adsorbent or reducing the adsorbate's partial pressure (or concentration of the liquid).

Adsorptive separation is achieved by one of three mechanisms: the 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 molecules. A large majority of processes operate through the equilibrium adsorption of the 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 organosulfur compounds from refinery streams. Depending on the mechanism of the sulfur compound interaction with the sorbent, we divide desulfurization by adsorption into two groups: 'adsorptive desulfurization' and 'reactive adsorption desulfurization'. Adsorptive desulfurization is based on the physical adsorption of organosulfur 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 organosulfur compound concentration flow. Reactive adsorption desulfurization utilizes the chemical interaction of the organosulfur compounds and the sorbent. Sulfur is fixed in the sorbent, usually as sulfide, and the S-free hydrocarbon is released into the 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 organosulfur compounds, durability, and regenerability (Babich, and Moulijn, 2003).

There are various correlations which are used to represent the adsorption isotherms, as shown in Table 2.4. However, the Langmuir isotherm is the most important model.

**Table 2.4** Correlations used to represent the adsorption isotherm (Pringprayong, 2006)

Name of isotherm	Equation
Langmuir	$Q_s = \frac{Q_{max} b C_s}{1 + b C_s} \quad (2.2.1)$
Langmuir-Freundlich	$Q_s = \frac{Q_{max} b C_s^n}{1 + b C_s^n} \quad (2.2.2)$

Where,  $Q_s$  = the amount adsorbed (mole g<sup>-1</sup> adsorbent)  
 $Q_{max}$  = the maximum amount the adsorbed (mole g<sup>-1</sup> adsorbent)  
 $C_s$  = the adsorbate amount in the mobile phase (mole m<sup>-3</sup>)  
 $B$  = the adsorption equilibrium constant (m<sup>3</sup> mole<sup>-1</sup>)  
 $N$  = Freundlich exponent (If  $n$  equal 1, the Freundlich isotherm reduces to the linear isotherm)

### 2.2.3 Adsorbents and their applications in sulfur removal

Only five types of generic sorbents have dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, and activated alumina, polymeric resins. The adsorbent may be used once and discarded, or, as is more common, it is employed on a regenerative basis and used for many cycles. Table 2.5 shows examples of commercial applications of these sorbents (Yang, 2003).

Table 2.5 Adsorbents in commercial adsorption separations (Yang, 2003)

Separation	Adsorbent
<b>Gas Bulk Separations</b>	
Normal paraffins/isoparaffins, aromatics	Zeolite
N <sub>2</sub> /O <sub>2</sub>	Zeolite
O <sub>2</sub> /N <sub>2</sub>	Carbon molecular sieve
CO, CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub> , Ar, NH <sub>3</sub> /H <sub>2</sub>	Activated carbon followed by zeolite (in layered beds)
Hydrocarbons/vent streams	Activated carbon
H <sub>2</sub> O/ethanol	Zeolite (3A)
Chromatographic analytical separations	Wide range of inorganic and polymer resin agents
<b>Gas Purification</b>	
H <sub>2</sub> O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite (3A)
CO <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> , 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 <sub>2</sub> /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
<b>Liquid Bulk Separations</b>	
Normal paraffins/isoparaffins, aromatics	Zeolite
p-xylene/o-xylene, m-xylene	Zeolite

Detergent-range olefins/paraffin's	Zeolite
p-Diethyl benzene/isomer mixture	Zeolite
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymer, and affinity agents
<i>Liquid Purifications</i>	
H <sub>2</sub> /organics, oxygenated organics, halogenated organics, etc., dehydration	Silica, alumina, zeolite, corn grits
Organics, halogenated organics, oxygenated organics, etc./H <sub>2</sub> O—water purification	Activated carbon, silicalite, resins
Inorganics (As, Cd, Cr, Cu, Se, Pb, F, Cl, radio nuclides, etc.)/H <sub>2</sub> O—water purification	Activated carbon
Odor and taste bodies/H <sub>2</sub> 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

Activated carbon has been used as an all-purpose sorbent. It is "hydrophobic" and consists of elementary microcrystallites of graphite, which are stacked together in random orientation. It is the spaces between the crystallite which form the micropores. This porosity yields the surface area that provides for the ability to adsorb gases and vapor from gases, and dissolved or dispersed substances from liquids. Its precedent, charcoal, was first used in the sugar industry in England in 1794 to decolorize sugar syrup. The major development of activated carbon took place during World War I for use in filters to remove chemical agents from air. Commercial activated carbon has taken its present form since the 1930s (Jankowska

*et al.*, 1991). Silica gel and activated alumina are used mainly as desiccants, although many modified forms are available for special purification applications. They have a high affinity for water, not as high as that of the molecular-sieve zeolites, but they can produce dried gases to less than 1 ppm moisture content.

Among four types of commercial adsorbents, synthetic zeolites, the youngest type (invented by Milton in 1959), was the most attractive adsorbent for the desulfurization.

### 2.2.3.1 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  $x$  and  $y$  are integers with  $y/x$  equal to or greater than 1,  $n$  is the valence of cation  $M$ , and  $z$  is the number of water molecules in each unit cell. The water molecule can be removed easily by heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with void fraction between 0.2 and 0.3. The zeolite framework concludes the tetrahedra of silicon and aluminum,  $SiO_4$  and  $AlO_4$ , which link together through shared oxygen atoms to form an open crystal lattice containing pores of the larger class of molecular sieves. The framework composition depends on the synthesis conditions. Post-synthesis modifications that insert Si or Al into the framework have also been developed. As the Si/Al ratio of the framework increases, the hydrothermal stability, as well as the hydrophobicity, increases. Figure 2.5 shows a comparison of pore sizes of different framework structures.

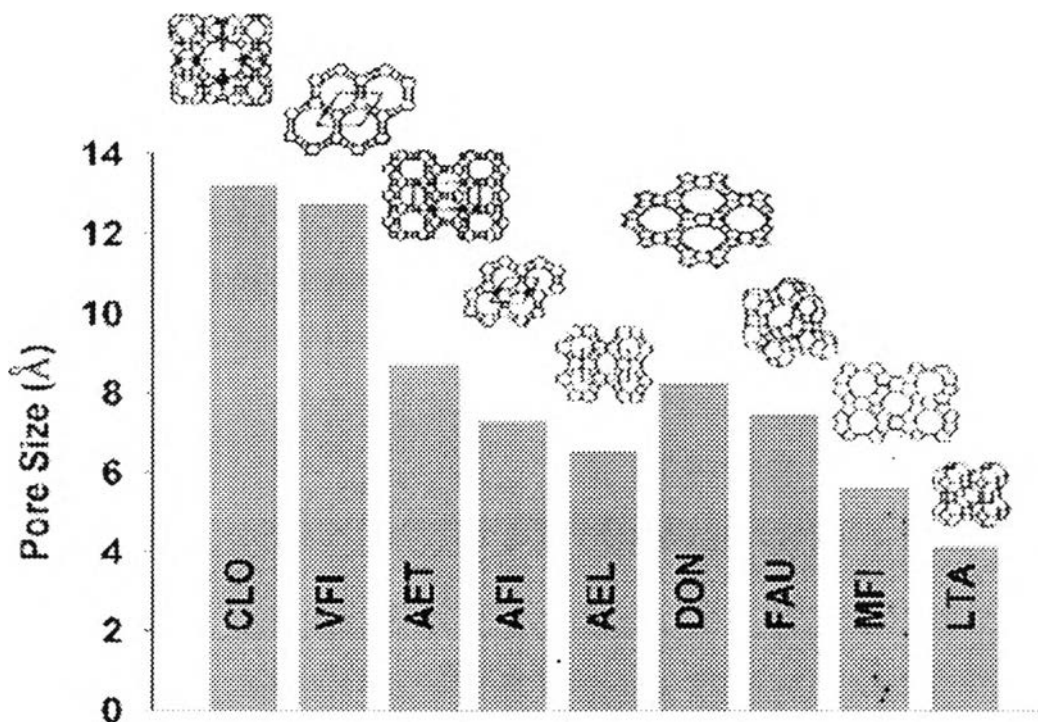


Figure 2.5. Comparison of pore sizes of different framework structures (Auerbach *et al.*, 2003).

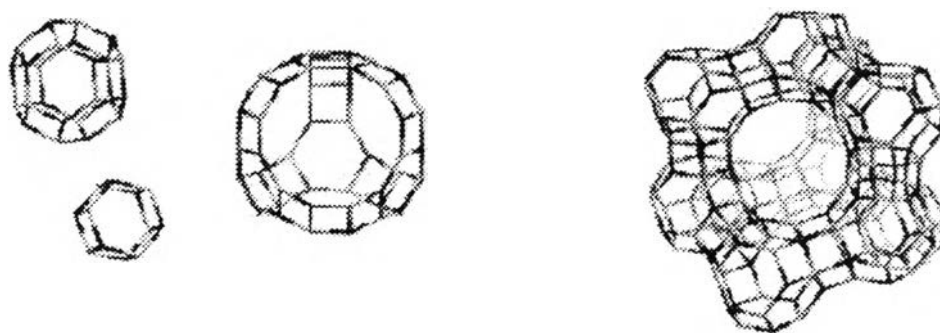
Zeolites are used for their special adsorption properties due to their unique surface chemistries and crystalline pore structures. Their diversity is due to the fact that zeolites not only have a high adsorption capacity but also show great selectivity, enabling substances to be separated or purified. Three effects contribute to the selectivity of a zeolite, and these can be influenced by the synthesis methods used to tailor it to requirements:

- ❖ Zeolites are characterized by regular pores with definite aperture sizes so that substances whose molecules are of different sizes can be separated.

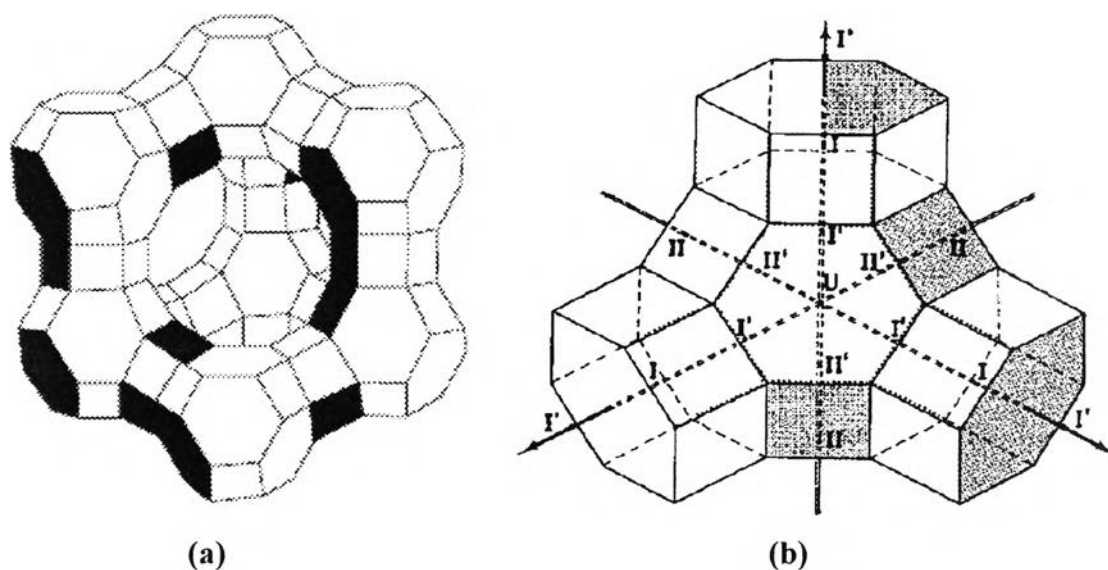
- ❖ The molecular-sieve effect described above is a limiting case of kinetic selectivity; that is selection according to differences in the rates of diffusion of molecules into the zeolite pores.

- ❖ The adsorption equilibrium is determined by electrostatic forces, including dipole and quadrupole interactions, and also by dispersion forces.

Zeolites are used in adsorption technology both in gas and liquid phases. Zeolite X, Y, and USY (Ultra-Stable-Y) are large-pore zeolites with the same framework structural type (FAU) but are markedly different in their framework composition and properties. Zeolite X has a  $\text{Si/Al} \approx 1.25$  ( $[\text{AlSiO}_4]$ ), zeolite Y a  $\text{Si/Al} \approx 2.3$ , and zeolite USY a  $\text{Si/Al} \approx 5.6$  or higher. Zeolite X is used primarily as an adsorbent. Zeolite Y and USY are the most widely used solid-acid catalysts in the world. The CBUs (composite building units) of the FAU framework type are depicted in Figure 2.6. The SBUs are double 6-rings, 6-2 (4- or 6-ring), the sodalite cage, and a very large cavity with four 12-ring windows. The FD (framework density) is  $12.7 \text{ T}/1000\text{A}^3$ , and the coordination sequence is: T (192) 4 9 16 25 37 53 73 96 120 145. The sodalite units are linked through 6-member prisms, as shown in the unit cell in Figure 2.7 (a). Each unit cell contains 192  $(\text{Si,Al})\text{O}_4$  tetrahedra. This cavity is of tetrahedral symmetry and it is known as the supercage. The connectivity of this cage allows molecules to diffuse in three dimensions in the crystal interior. The number of aluminum ions per unit cell varies from 96 to 77 for type X zeolite, from 76 to 48 for type Y zeolite. The framework of faujasite has the largest central cavity pore volume of any known zeolite, amounting to about 30% void fraction in the dehydrated form. The free diameter of the central cavity is  $13.7 \text{ \AA}$ . The major locations for the cation sites in the faujasite framework are indicated in Figure 2.7 (b). Site I is in the hexagonal prism ( $\text{D}_6\text{R}$ );  $\text{I}'$  is near the entrance to a hexagonal prism in the sodalite ( $\beta$ ) cage.  $\text{II}'$  is inside the sodalite cage near the single-6R entrances to the large ( $\alpha$ ) cage. II is in the large cage adjacent to  $\text{D}_6\text{R}$  and U is at the center of the sodalite cage. Other sites (IV, V) are in the large supercage cavities.



**Figure 2.6** CBUs and framework structure of the zeolite X, Y, or faujasite (FAU).



**Figure 2.7** (a) 'unit cell' of types X and Y, or faujasite. (b) The cation sites in the faujasite framework.

### 2.2.3.2 Application of adsorbent for sulfur removal process

Our research focuses on adsorption processes for the removal of sulfur compounds from transportation fuels because it can be operated at ambient temperature and pressure. Several recent studies have reported adsorptive removal using zeolites, activated carbon alumina porous solids, and silica-based sorbents. King *et al.* (2000) investigated the selective adsorption of thiophene and dimethylthiophene over toluene and p-xylene by using ZSM-5. They found that thiophene was more selectively adsorbed on the fixed bed packed with ZSM-5 using breakthrough experiments; but the capacities were low. Ma *et al.* (2001, 2002a) described a sorbent for the removal of thiophenic compounds from jet fuel. The sulfur capacity given as 0.015 g sulfur per ml of sorbent was not high. The sorbent was a transition metal compound supported on silica gel at 5 wt % loading. It can form a bond with the sulfur atom of the thiophenic compound. Chansa (2003) studied the adsorption of sulfur compounds comprising 3-MT and BT in simulated gasoline, and DBT in simulated diesel, by using Na-X and Na-Y zeolites. For simulated gasoline, the author found that Na-X zeolite was more effective in adsorbing both 3-MT and BT than NaY and showed nearly the same performance for adsorbing DBT



in simulated diesel. When increasing the temperature in the range of 25-80°C, sulfur compound adsorption for both zeolites will decrease. Kaewboran (2005) studied the adsorption of sulfur compounds such as 3-MT, BT, and DBT in simulated gasoline and diesel by using X zeolite. The breakthroughs of the three types of sulfur compounds were found to arrange in the order of BT > 3-MT > DBT. And shortly after that, Ng *et al.* compared the performance for removal of thiophenic sulfur compounds such as T, BT, DBT, and 4, 6-DMDBT in a hexadecane using Na-Y, USY, H-Y, and NaX zeolites. They found that Na-Y has the highest sorption capacity for the sulfur compounds. Kim *et al.* (2006) showed that the adsorptive capacities based on the adsorbent weight increase in the order of activated alumina < Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> < activated carbon for total sulfur.

A systematic approach has been taken in the search for a new selective sorbent which can lead to the forming of the  $\pi$ -complexation bonding with the sulfur compounds. Their bonds are stronger to adsorb sulfur compounds than the van der Waals interaction, but it is easier to regenerate by using only increasing temperature or decreasing pressure. Yang *et al.* (2001) indicated that the effective  $\pi$ -complexation sorbents for sulfur removal include Cu(I)-Y, Ag-Y, Cu-Cl/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, AgNO<sub>3</sub>/SiO<sub>2</sub>, and others. Takahashi *et al.* (2002) studied vapor-phase adsorption isotherms between benzene/thiophene and sorbents. It has shown that the sorbent capacities followed the order Cu-Y and Ag-Y >> Na-ZSM-5 > activated carbon > Na-Y > modified alumina and H-USY. Hernandez *et al.* (2003) studied the desulfurization by using Cu-Y, Ag-Y, H-Y, and Na-Y in fixed-bed breakthrough experiments using thiophene/benzene, and thiophene/n-octane as the model systems. They found that the adsorption capacity of the silver-based zeolite was almost twice that of the sodium-based zeolite. Cu-Y showed the highest selectivity and capacity among the adsorbents studied at both breakthrough and saturation points. Hernandez *et al.* (2004a) improved the adsorption capacity of the sulfur compound by using a layer bed consisting of activated carbon (AC) and/or activated alumina (Selexsorb CDX). In their experiment, the AC/CDX/Cu(I)-Y zeolite showed the highest capacity, followed by AC/Cu(I)-Y, CDX/Cu(I)-Y, and Cu(I)-Y zeolite. Xue *et al.* (2004) studied Na-Y zeolites exchanged with Ag<sup>+</sup>, Cu<sup>2+</sup>, and Ce<sup>3+</sup> ions and NH<sub>4</sub>Y zeolite exchanged with Ce<sup>3+</sup> ions for adsorption of the organic sulfur compounds. All

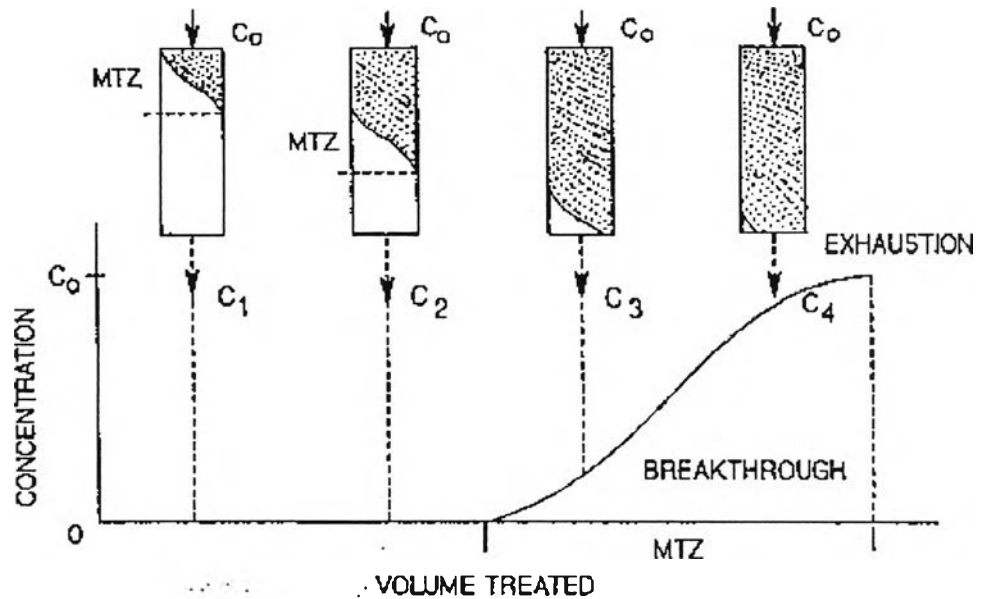
adsorbents showed markedly high adsorption capacities for thiophene and 1-benzothiophene in an organic model solution. The sorbent capacities followed the order  $\text{Cu-Y} < \text{Ag-Y} < \text{Ce-Y}$  for both organic sulfur compounds. Ma *et al.* (2005b) compared the adsorption capacity of Cu(I)-Y zeolite in a model gasoline and commercial gasoline. The much lower capacity of Cu(I)-Y zeolite for the desulfurization of the commercial gasoline indicated that aromatics and olefin mixed in the real gasoline might strongly compete with the adsorption of thiophenic sulfur compounds by  $\pi$ -complexation. Hernandez *et al.* (2005) produced the sorbents obtained by ion exchanging zeolites with  $\text{Cu}^+$ ,  $\text{Ni}^{2+}$  or  $\text{Zn}^{2+}$  cations by using various techniques such as vapor phase (VPIE), liquid phase (LPIE), and solid-state (STIE) ion exchange for the desulfurization of diesel, gasoline, and jet fuels. They found that the desulfurization performance decreases as follows:  $\text{Cu(I)-Y (VPIE)} > \text{Ni(II)-Y (STIE)} > \text{Ni(II)-X (LPIE)} > \text{Zn(II)-X (LPIE)} > \text{Zn(II)-Y (LPIE)}$ . Bhandari *et al.* (2006) investigated the adsorption capacity of ion-exchanged Y-zeolite with various metal ions such as Ni, Cu, Fe, and Zn in a model diesel containing DBT and 4, 6-DMDBT. It was shown that Ni-Y zeolite has the highest capacity for sulfur removal followed by Cu-Y, Fe-Y and Zn-Y zeolite. They also showed that the presence of aromatics and moisture have a detrimental effect on the desulfurization capacity.

There are some factors that can reduce the adsorptive capacity of sulfur compounds of zeolites. Velu *et al.* (2003) reported that the adsorption performance decreased by six times in the presence of 10 wt. % of 1-octene (olefin). Jayaraman *et al.* (2006) demonstrated the effect of organonitrogen and PAH compounds on the desulfurization by  $\pi$ -complexation with Cu(I)-Y zeolite. The relative inhibition effects were found to follow the order: carbazole > quinoline > phenanthrene > fluorine  $\approx$  naphthalene. Bhandari (2006) found that the aromatics content in the diesel, and moisture, had a detrimental effect on the desulfurization of transportation fuels.

#### 2.2.4 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, specific atoms...) and the adsorbent surface . Figure 2.8 illustrates the breakthrough curve used to represent the adsorption process.



**Figure 2.8** Idealized breakthrough curve of a fixed bed adsorber (<http://www.activated-carbon.com/solrec3.html>).

This Figure 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  $L_{MTZ}$ . When  $L_{MTZ} =$  bed depth, it becomes  $L_{CRIT}$ , 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. The MTZ is illustrated in Figure 2.8.

❖ Dynamic adsorption 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. This is illustrated in Figure 2.8.

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 wave front may change shape as it moves through the bed, and the mass transfer zone broaden or diminish. 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.