CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Sulfur Compounds in Petroleum Refining

Sulfur compounds are the most important heteroatomic components of petroleum and there are many varieties of sulfur compounds present in crude oils around the world (Table 2.1). In general, the higher density of crude oil for the lower API gravity of crude oil, the higher sulfur content (Figure 2.1). Total sulfur in crude oils can vary from 0.04%w/w for light crude oils to about 5.0%w/w for heavy crude oils. In addition, the total amount of sulfur contents of crude oils depends on the sources of crude oils which is different from one source to another (Wauquier, 1995).

Table 2.1 Some relevant characteristics of crude oils

Crude oil	Origin	Visc. mm^2/s	Asph. wt.%	O wt.%	N wt.%	S wt.%	Ni ppm	V ppm
Batiraman	Turkey	1180	22.1	0.53	0.49	7.04	99	153
Boscan	Venezuela	595	14.1	0.79	0.74	5.46	125	1220
Lacq.sup.	France	81.7	13.2	0.57	0.42	4.94	19	29
Chauvin Source	Canada	28	6.0	0.48	0.66	2.80	35	67
Bellshill Lake	Canada	7.9	2.2	0.34	< 0.3	1.97	11	18
Emeraude	Congo	113	1.7	1.10	0.65	0.57	64	9
Anguille	Gabon	14.1	1.2	0.92	0.26	0.82	115	14
Duri	Sumatra	51	0.7	0.65	0.47	< 0.1	39	1.5
Pematang	Sumatra	10.2	0.1	0.51	0.26	< 0.1	15	0.6
Edjeleh	Algeria	5.3	0.1	0.73	0.34	< 0.1	1.5	2.3
Hassi Messaoud	Algeria	2.32	0.1	1.93	0.38	< 0.1	< 0.2	< 0.2

There are also many types of sulfur compounds in crude oils including both inorganic and organic forms such as elemental sulfur, hydrogen sulfide H_2S, carbonyl sulfide COS as shown in Figure 2.2. However, the prevailing conditions during formation, maturation, and even in situ alternation may dictate only preferred types exist in any particular crude oils. Moreover, the types of sulfur in crude oils also depend on geological environment of sources, depth of the individual well, time and substrates to form crude oil.

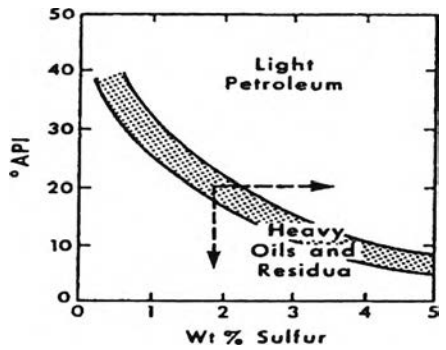


Figure 2.1 General relationship of sulfur content to API gravity.

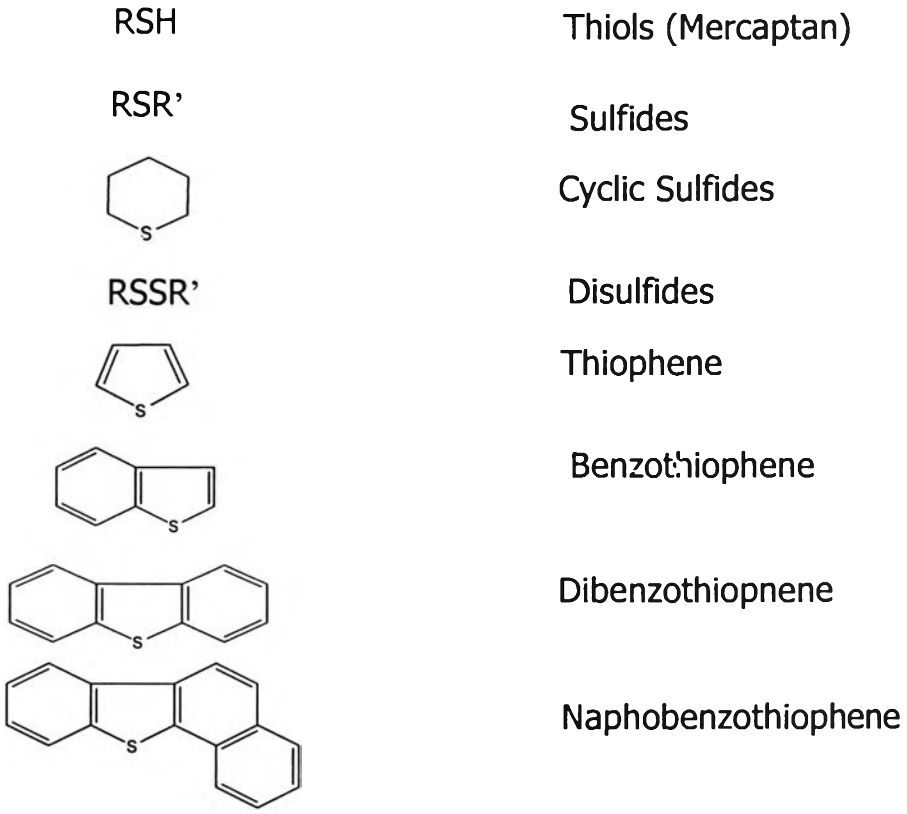


Figure 2.2 Nomenclature and types of organic sulfur.

Knowledge of the nature and quantity of sulfur compounds contained in crudes and petroleum cuts is of prime importance to the refiner, because in constitutes a constraint in the establishment of refinery flow sheets and the preparation of finished products. In fact a few of these products contain or entrain corrosive materials which, during refinery operations, reduce the service life of certain catalysts such as reforming catalysts, degrade the quality of finished products by changing their color and by giving them an unpleasant odor, reduce the service life of lubricating oils, without mentioning atmospheric pollution from formation of SO_2 and SO_3 during the combustion of petroleum fuels, and fires caused by contact between iron sulfide on the piping and air. The total sulfur contents in these fractions are quite different as shown in Table 2.2 (Wauquier, 1995).

Table 2.2 Distillation of total sulfur in the different cuts of crude Arabian Light

Cut	Light gasoline	Heavy gasoline	Kerosene	Gas oil	Residue
Temperature interval,C	20-70	70-180	180-260	260-370	370+
Specific gravity 15d4	0.648	0.741	0.801	0.856	0.957
Average molecular weight	75	117	175	255	400
Total sulfur, weight %	0.024	0.032	0.202	1.436	3.167
Number moles of sulfides/Total number of moles	1/1800	1/855	1/90	1/9	1/2.5

Nevertheless, the compositions of sulfur compounds in different fractions of petroleum are not same because each type of sulfur compounds has different boiling range. Ma *et al.* (2002) reported that the major sulfur compounds that exist in commercial gasoline are thiophene, 2-methylthiophene, 3-methylthiophene, 2,4-dimethylthiophene, and benzothiophene. Major sulfur compounds existing in JP-8 are 2,3-dimethylbenzothiophene, 2,3,7-trimetylbenzothiophen, 2,3,5-trimethyl benzothiophene, and/or 2,3,6-trimethylbenzothiophene. The sulfur compounds commonly found in commercial diesel fuel include both alkyl benzothiophenes and alkyl dibenzothiophenes (DBT), but the major compounds are dibenzothiophene derivatives with alkyl groups at 4 and/or 6-position, including 4-MDBT, 4,6-DMDBT, 3,6-DMDBT, and 2,4,6-TMDBT (Figure 2.3). In addition, Yin *et al.*

(2002) studied the distribution of sulfur compounds in FCC and RFCC naphthas of china fuels. They found that the contents of mercaptan and disulfide are comparative low. The sulfide accounts for 25% of total sulfur and the largest component of sulfur compound is thiophenic compounds.

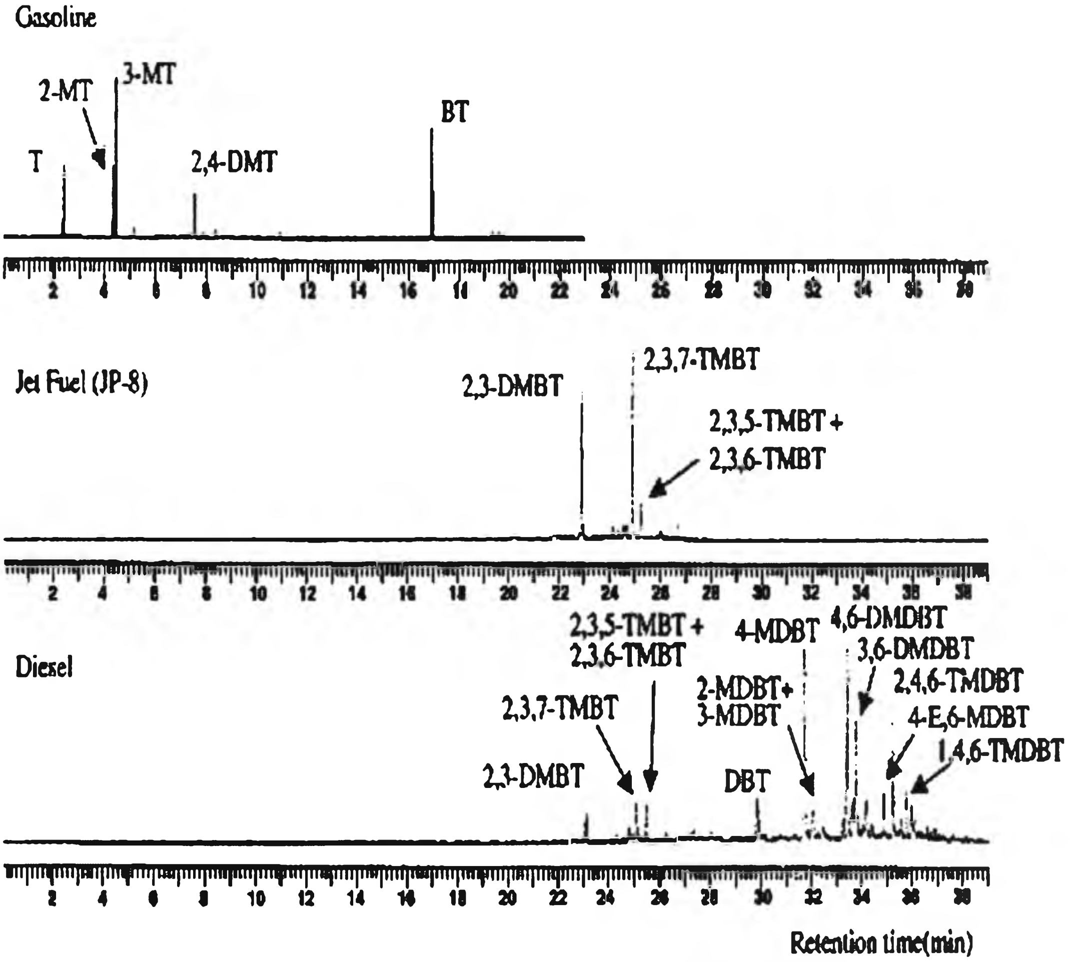


Figure 2.3 GC-FID chromatograms of gasoline, jet fuel and diesel fuel·for identification of sulfur compounds. (Ma *et al.*, 2002).

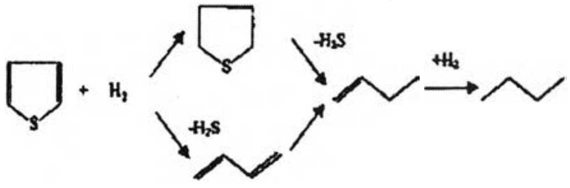
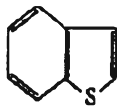
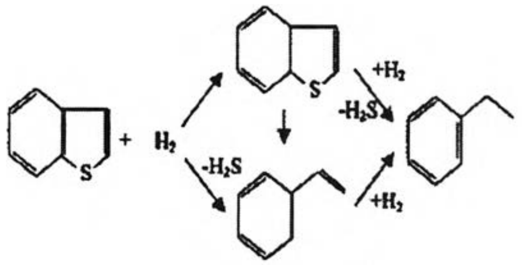
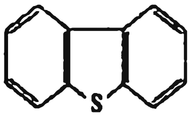
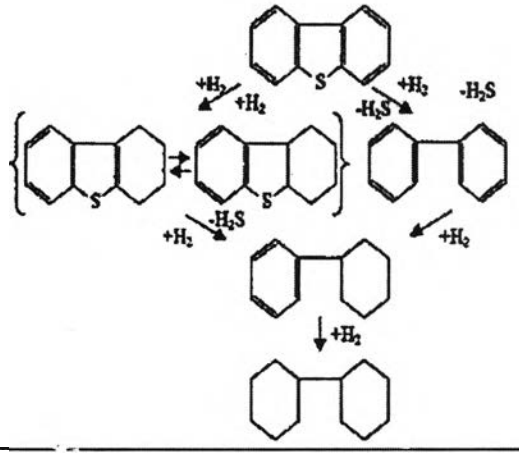
2.2 Hydrodesulfurization (HDS)

Hydrodesulfurization is the current method extensively used by the refining industry to remove sulfur compounds. In hydrodesulfurization process, a hydrocarbon feedstock is reacted with hydrogen to produce hydrogen sulfide and a desulfurized hydrocarbon product. This reaction requires a high hydrogen partial pressure in gas phase to maintain high desulfurization reaction rates and to suppress carbon deposition.

The conventional HDS process is usually conducted over sulfided CoMo/Al_2O_3 catalysts. 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 the sulfur compounds present in the feed stream (Figure 2.3), and reactor and process design. The operating conditions in hydrodesulfurization of distillates are dependent upon the stock to be charged as well as degree of desulfurization or quality of improvement. Kerosene and light gas oil are generally processed at mild condition and high throughput; whereas light catalytic cycle oils and thermal distillates are required slightly more severe conditions. Higher boiling point distillates, such as vacuum gas oils and lube oil extracts, require the most severe conditions. The principle variables affecting the required severity in distillate desulfurization are hydrogen partial pressure, space velocity, reaction temperature, and feed stock properties.

The reactivity of sulfur compounds varies widely depending on their structure and local sulfur atom environment. The low-boiling crude oil fraction contains mainly the aliphatic sulfur compounds: mercaptans, sulfides, and disulfides. They are very reactive in conventional hydrotreating processes and they can easily be completely removed from the fuel. The hydrotreating pathway of sulfur compounds is shown in Table 2.3. On the other hand, the thiophene darivatives are considerably more difficult to remove by HDS. 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. Deep desulfurization of the fuels implies that more and more of the least reactive sulfur compounds must be converted (Babich and Moulijn, 2003).

Table 2.3 Typical sulfur compounds and their hydrotreating pathway

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

Deep desulfurization of refinery streams becomes possible when the severity of the HDS process conditions is increased. Unfortunately, more severe conditions result not only in a higher level of desulfurization but also in undesired side reactions. When FCC gasoline is desulfurized at higher pressure, many olefins and aromatic are saturated and the octane number decreases. Higher temperature processing leads to increased coke formation and subsequent catalyst deactivation. Current trends toward stricter regulations on the sulfur compounds in the transportation fuels, is an impetus for a continued search for improved desulfurization processes.

2.3 Removal of Sulfur Compounds by Adsorption

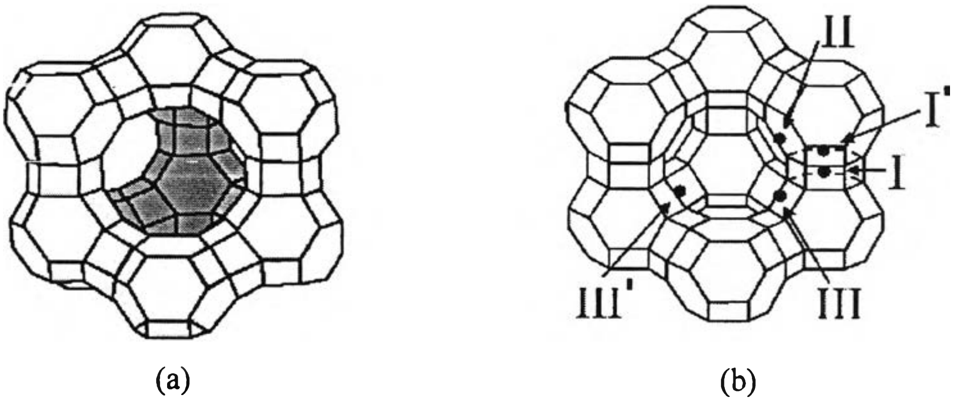
When solids are placed in contact with gasses or liquid, forces are exerted between the surface of the solid and compound causing bonds to be formed. This phenomenon is called adsorption. The bonds can vary in strength depending on the nature of compounds and of solid involved. They can cause selective adsorption of certain compounds in mixtures. From this theory, the adsorption processes have been used in petroleum industry in various applications. Recently, there is growing interest in studying and developing adsorption process for desulfurization of liquid fuels in order to meet current and future regulations since they can be operated at ambient condition. There are several adsorbents that can be used to adsorb sulfur species from transportation fuels and other petroleum products. In general, typical adsorbents are activated carbon, zeolites, silica gel, and activated alumina. Different types of adsorbent show different selectivity and capacity for sulfur compounds. From many research, they found that the faujasite zeolite was the most attractive adsorbent for desulfurization.

2.3.1 Zeolite

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium, and calcium, represented by the stoichiometry:

$$Mx/n\ [(AlO_2)x(SiO_2)y]zH_2O$$

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 cations are necessary to balance the electrical charge of the aluminum atoms, each having a net charge of –1. The water molecules can be removed with ease upon heat and evacuation, leaving an almost unaltered aluminosilicate skeleton with a void fraction between 0.2 and 0.5. The skeleton has a regular structure of cages, which are isially interconnected by six windows in each cage. The cages can imbide or occlude large amounts of guest molecules in place of water. The size of the window apertures, which can be controlled by fixing the type and number of cations, ranges from 3 Å to 10 Å. The sorption may occur with great selectivity because of the size of the aperture.



(a) (b)

Figure 2.4 (a) Unit cell of types X and Y,or faujasite; (b) cation sites in types X and Y (16 I, 32 I', 32 II, 32 II', 48 III, and 32 III' sites per unit cell).

For zeolite X and Y, the skeletal structure of Type X and Y zeolites are the same as that of the naturally occurring faujasite. The sodalite units are linked through six member prisms, as shown in the unit cell in Figure 2.4(a). Each unit cell contains 192 (Si, Al)O_4 tetahedra. The number of aluminum ions per unit cell varies from 96 to 77 for Type X zeolite, and from 76 to 48 for Type Y zeolite. This framework has the largest central cavity volume of any known zeolite, amounting to about 50% void fraction in the dehydrated form. A unit cell, when fully hydrated, contains approximately 235 water molecules, mostly in the central cavity. The aperture is formed by the twelve-member oxygen rings with a free diameter of approximately 7.4A. Three major locations for the cations are indicated in Figure 2.4(b). The locations are: center of the six-member prism(I) and opposite to I in the sodalite cage (I'); similar to I and I' but further from the central cavity (II and II'); and at the twelve-member aperture (III and III'). The commercial 10X zeolite contains Ca^{+2} as the major cation, and Na^+ is the major cation for 13X zeolite. The BET surface area measured with N_2 for zeolites falls in the range between 500 and 800 m^2/g (Yang, 1997).

2.3.2 Adsorbents and Selectivity for Sulfur Compounds

During the past decade, there have been many research studies on the use of adsorption for desulfurization of liquid fuels. Weitkamp *et al.* (1991) reported that thiophene adsorbed more selectively than benzene on ZSM-5 zeolite. Savage *et al.* (1995) studied various kinds of adsorbents by using dibenzothiophene (DBT) and methyl naphthalene (1-MN) in a paraffinic solvent as a model system. They found that zeolite, activated carbon, supported CoMo sorbents, and high alumina/silica-alumina preferentially adsorb dibenzothiophene in preference to 1-methyl naphthalene. The activated carbon has the most attractive combination of separation factor and capacity. Salem and Hamid (1997) showed that the capacity of 13X zeolite for sulfur compound was approximately an order of magnitude higher than ZSM-5. King *et al.* (2000) investigated the selective adsorption of thiophene and methyl-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.

Takahashi *et al.* (2002) studied various kinds of sorbents by using thiophene/benzene as a model system and vapor-phase experiments. Adsorption isotherms were generated to try to understand the interaction between the sorbate and sorbent. They found that the separation factors of thiophene over benzene (at low concentration of thiophene) exhibited the trend as follows: Ag-Y > Na-ZSM5 > Cu-Y ≈ activated carbon >> Na-Y >> H-USY ≈ modified activated alumina. The sorbent capacities for thiophene at low pressure followed the order Cu-Y and Ag-Y >> Na-ZSM-5 > activated carbon > Na-Y > modified alumina and H-USY. Chansa (2004) studied behavior of NaX and NaY zeolite for removal of organic sulfur compounds from transportation fuels by adsorption in batch reactor. In this study, the simulated transportation fuels were decane and isooctane as a model for diesel and gasoline, respectively. The sulfur compounds used were benzothiophene (BT) and 3-methylthiophene (3-MT) for simulated gasoline and dibenzothiophene (DBT) for simulated diesel. The adsorption isotherms were constructed to evaluate the adsorption capacity and selectivity of adsorbent. He found that NaX zeolite was more effective in adsorbing both 3-methylthiophene and benzothiophene than was NaY zeolite. For dibenzothiophene, both NaX and NaY zeolites showed nearly the same adsorption potential. For the effect of temperature on the adsorption of sulfur compounds, it is found that for all sulfur compounds on both zeolites the adsorption decreases with increasing temperature in the range of 25-80 degree cectigrade. The study on the effect of fuel to adsorbent weight ratio revealed a general trend that the adsorption of thiophene compounds used in the studies increases with increasing fuel to adsorbent ratio in the range of 20-85.

The modification and improvement of the adsorbents for high selectivity and high capacity of sulfur compounds have become more crucial since the effective commercial adsorbents are not currently available. Michlmayr (1980) studied silver-exchanged faujasite-type zeolite for removal of thiophenes from gasoline using the temperature in the range about 20 to 370 degree centigrade and the LHSV in the range about 0.1 to 20 V/V/Hr. He found that Ag-Y zeolite have a better capacity than the ordinary Y-zeolite and are effective adsorbent for the removal of residual thiophene in gasoline. Kulprathipanja *et al.* (1998) studied a process for removing sulfur containing compounds from a liquid hydrocarbon by using NiX, MoX and NiY zeolite in a batch reactor. In the batch there were placed 0.5g of the adsorbent and 3g of gasoline and the mixture maintained at ambient temperature for 16 hours. The starting gasoline was found to contain 345 ppm of sulfur. They found that the capacity of adsorbent followed the order of NiX>MoX>NiY. Zinnen (1999) studied removal of organic sulfur compounds from FCC gasoline using the UOP Y-zeolite which was ammonium ion exchanged at 1 atmosphere and calcined at 600 degree centigrade and anather one was second ammonium ion exchanged, then calcined to afford a second dealuminated zeolite Y. The fixed bed was used in the experimental at.65 degree centigrade. He found that the second dealuminated zeolite has the higher surface area but it is lower the sulfur compounds capacity.

Yang *et al.* (2001) studied Cu and Ag exchanged Y zeolite for desulfurization of liquid fuels using thiophene/benzene as a model system and vapor-phase adsorption isotherms were constructed. They found that both Cu-Y and Ag-Y zeolites adsorbed considerably large amount of thiophene and benzene at low pressure comparing to NaY. This is attributed to a result of pi-complexation with Cu^+ and Ag^+. On a per cation basis, more thiophene was adsorbed by Cu^+ than Ag^+. Takahashi *et al.* (2002) studied vapor phase adsorption using various kinds of sorbents and thiophene/benzene as a model in order to gain more understanding about the sorbate-sorbent interaction. They found that Ag^+ exchange was 100% complete but Cu^+ exchange was only 46% complete for Ag-Y and Cu-Y, respectively. Only half of Cu^{2+} was automatically reduced to Cu^+ after heat treatment at 450 °C. Song *et al.* (2003) studied various transition metal ion-exchanged zeolites for removing sulfur compounds by selective adsorption under static condition with a residence time of about 5 hours. They found that the Ce-exchanged Y zeolites show much higher selectivity for thiophene and tetrahydrothiophene as compared to the benzene and 1,5-hexadiene. These results indicate that sulfur compounds are adsorbed over Ce-exchanged zeolites by a direct S-adsorbent (S-M) interaction. Hernandez *et al.* (2003) studied the desulfurization by using Cu(I)-Y, Ag-Y, H-Y, and Na-Y in a fixed-bed adsorber using thiophene/benzene, thiophene/*n*-octane as the model systems. From the fixed-bed adsorption, silver-based zeolite was shown to adsorb almost twice as much as sodium-based one for benzene/thiophene mixture. Cu(I)-Y showed a little higher selectivity toward thiophene as compared to other adsorbents for benzene/thiophene mixture at the same conditions. However, for *n*-octane/thiophene mixture at the same feed conditions, Cu(I)-Y showed the highest selectivity and capacity among the adsorbents studied.

Recently, Yang *et al.* (2004) studied vapor-phase exchanged Cu(I)-Y zeolites for desulfurization of diesel fuels by using vertical reactor and a tin layer of activated alumina was placed on the top of a zeolite bed. They found that the Cu(I)-Y zeolites provide a desulfurization capacity of 0.29 mmol of sulfur per gram of zeolite. This corresponds to about 5 thiophenic molecules per unit cell. Moreover, the sulfur adsorption capacity was increased by 14% after a tin layer of activated alumina was placed on top of a zeolite bed because the activated aluminas are capable of adsorbing large thiophenic molecules.

2.3.3 Desorption of Sulfur Compound and Regeneration of Adsorbent

Regeneration is a very important part in the adsorption process which aims to bring the adsorbents for reuse. In general, there are four types of regeneration method: lowing total pressure, striping with an inert gas, increasing temperature, and displacing by desorbent. As a result, several research groups have studied various ways to regenerate used sorbents to their original properties. Yang (1993) studied the pressure swing adsorption techniques for removing sulfur oxides from gaseous mixtures and produce a desorption stream with SO_2 for conversion to elemental sulfur by the Claus process. A simulated pressure swing adsorption (PSA) apparatus was studied using computer simulation. The PSA sorbent bed was the polymeric sorbent bed and a void fraction of 0.4. The pressure in the adsorption chamber was 1.2 atmospheres, while the pressure in the desorption chamber was 0.03 atmospheres. The gas feed flow rate was about $1*10^6$ liters (STP) per hours and the total cycle time was approximately 9 minutes. In this work, the molar purge/feed ratio (P/F) was varied by changing the purge flow rate and the purge gas was inert gas such as helium gas, nitrogen or steam. They found that the preferable purge/feed ratio is 4 percent.

Zinnen (1999) studied the removal of organic sulfur compounds from FCC gasoline using regenerable adsorbent. The Pt-K-Y adsorbent was saturated with sulfur compounds and was desorbed by heating. The temperature was riased and the column was contacted with hydrogen at 288-300 degree centigrade for 113 minutes and flow rate of hydrogen was in the range of 623-755 GHSV. They found that the Pt-K-Y adsorbent is regenerable and unimpaired capacity of adsorption of sulfur compounds. Hernandez *et al.* (2003) studied the desulfurization of thiophene in benzene and *n*-octane by using Cu-Y, Ag-Y, H-Y, and Na-Y in fixed-bed adsorber and also investigated the regeneration of these adsorbents. They found that regeneration of copper-based adsorbent under air at 350 °C, followed by reactivation under helium at 450°C, recovered almost all of the original capacity of the adsorbent. Liu *et al.* (2003) studied regeneration of Fe/activated coke by using H_2 at different temperature to desorbed SO_2. They found that the regeneration at 350 degree centigrade is more effective than at 400 and 300 degree centigrade and recovers only 80% activity of the fresh Fe/activated coke. Wakita *et al.* (2003) studied the adsorption and desorption of dimethyl sulfide and tertiary butyl mercaptan by using various kind of zeolite. The adsorbent regeneration test was conducted at 500 degree centigrade for 5 hours and air was passed at 0.13 m/s through the sample tube in the reverse direction. They found that all of adsorbents can recover their adsorption characteristics. Thus, the adsorbents of this work can be regenerated by heating at 500 degree centigrade.

Feimer *et al.* (2003) reported that the adsorbent can be regenerated by desorbent. The desorbent used can be easily separated from the sulfur compounds by conventional techniques, such as distillation. If the selected separation technique is distillation, the boiling point of the desorbent should differ from the sulfur compounds by at least about 5 degree centigrade. The preferred desorbent include nitrogen and the mixture of hydrogen and hydrogen sulfide. Yang *et al.* (2004) studied the regeneration of the activated carbon/Cu(I)-Y by using layered bed. The air calcinations and solvent elution were chosen for regeneration teats. They found that the activated carbon/Cu(I)-Y bed can only recover 85% of the original adsorption capacity for regeneration with air at 350 degree centigrade for at least 6 hours followed by auto-reduction. For solvent elution technique, CCl_4 was capable of recovering a considerable part of the original adsorption capacity.