

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Fuel and Sulfur Composition

Crude oil formed during long-complex process is composed of many substances, from which various refined petroleum products (such as gasoline, kerosene, fuel oil and lubricating oil) are manufactured. These substances are mainly composed of carbon and hydrogen. Crude oils are complex mixtures of paraffinic, naphthenic, aromatic hydrocarbons and other components varying among geographic regions, and even within a single geological formation. The crude oils are classified as paraffinic or naphthenic crude oils on the basis of their components. Paraffinic crude oils are rich in the linear and branched paraffins, having a high API gravity, low density and viscosity, and containing a higher concentration of gasoline grade naphtha. Naphthenic crude oils mainly contain cycloparaffin and aromatic hydrocarbons, having low API gravity, higher density and viscosity. Other heteroatoms (e.g., sulfur-, nitrogen-, and oxygen-containing hydrocarbon analogs) may also be present in relatively smaller quantities, together with trace amount of heavy metals like nickel, iron, vanadium, and arsenic. Crude oils can further be divided into light, mid-range, and heavy crude oils possessing specific gravities in the range of less than 0.82, 0.82-0.97, and higher than 0.97, respectively. Crude oil containing small amount of sulfur is called sweet crude while the less desirable crude oil with higher sulfur content is called sour crude. However, the prevailing conditions during formation, maturation, and even in situ alternation may dictate only preferred types existing in any particular crude oils. Moreover, the types of sulfur in crude oils strongly depend on geological environment of sources, depth of individual well, time and substrates to form crude oil as summarized in Table 2.1.

Table 2.1 Some characteristics of crude oils

Crude Oil Source	Paraffins (% vol)	Napthenes (% vol)	Aromatics (% vol)	Sulfur (%wt)	API gravity (°API)
<u>Light Crude Oils</u>					
Saudi Light	63	18	19	2.0	34
South Louisiana	79	45	19	0.0	35
North Sea Brent	50	34	16	0.4	37
Nigerian Light	37	54	9	0.1	36
<u>Mid-Range crude oil</u>					
Venezuela Light	52	34	14	1.5	30
Kuwait	63	20	24	2.4	31
USA West Texas Sour	46	32	22	1.9	32
<u>Heavy Crude Oils</u>					
Prudhoe Bay	27	36	28	0.9	28
Saudi Heavy	60	20	15	2.1	28
Venezuela Heavy	35	53	12	2.3	24

Sulfur is present in crude oils as hydrogen sulfide (H_2S), elemental sulfur and various sulfur compounds including a diverse range of mercaptans, sulfides, disulfides, refractory sulfur compounds, thiophene and sterically hindered dibenzothiophene as shown in Table 2.2.

The compositions of the transportation fuels vary widely depending on the crude oils used in the refining process, the product demand and its specifications. Branched and n-alkanes are the main ingredients of these fuels, accounting more than 70% of the total compound. The major n-alkanes and the main branched alkanes are C5 to C8 compounds. The aromatic content constitutes about 30% of the fuel, and the main components are benzene, toluene, xylenes and alkybenzenes. Ma *et al.*

(2002) reported that the major hydrocarbon contents in commercial diesel fuel are dodecane and tetradecane as shown in Table 2.3.

Table 2.2 Type of organic sulfur and properties



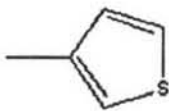
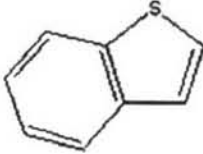
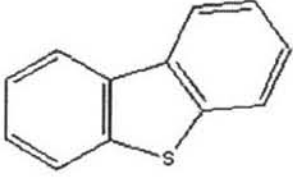
Type of organic sulfur	Nomenclature	Molecular weight	Boiling point (°C)
Ethane thiol (Mercaptan) C_2H_6S		62.1294	35
Thiophene C_4H_4S		84.1356	84.4
3-Methylthiophene C_5H_6S		98.1624	114 at 738 mm Hg
Benzothiophene C_8H_6S		134.1954	221
Dibenzothiophene $C_{12}H_8S$		184.2552	332-333

Table 2.3 Composition of commercial diesel fuel

Name	Content (wt%)
Sulfur compounds	
DBT (98%)	0.167
4,6-DMDBT (97%)	0.197
Total	0.362
Unsaturated Hydrocarbon	
Naphthalene	0.120
2-Methylnaphthalene	0.127
Buthylbenzene	11.6
1-Octene	4.7
Paraffin	
Dodecane	19.6
Tetradecane	62.5
Others	1.0
Total	100

Thiophene, benzothiophene, dibenzothiophene and their alkylated derivatives are the major sulfur compounds remaining in the fuel after HDS process corresponding to the boiling ranges of gasoline and diesel fuels as shown in the Figure 2.1. Therefore, the compositions of sulfur compounds in different fractions of petroleum are not the same depending on boiling point of each type of sulfur compounds.

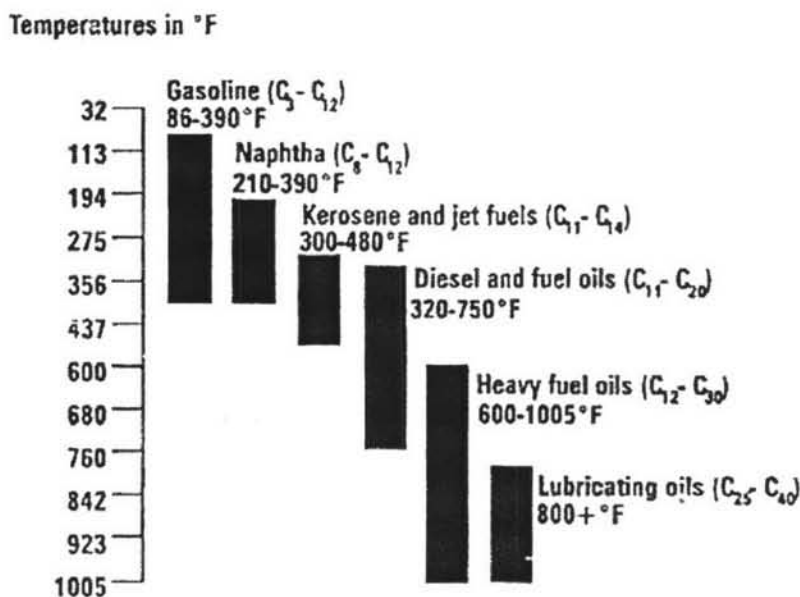


Figure 2.1 Hydrocarbon composition and boiling ranges for major refined products.

Ma *et al.* (2002) reported that the dominant sulfur compounds in the gasoline rearranging in decreasing order were 3-methylthiophene, benzothiophene, 2-methylthiophene and 2,4-dimethylthiophene, respectively. The sulfur compounds commonly found in diesel fuel include both alkyl benzothiophene and alkyl dibenzothiophene (DBT) but the major derivatives are dibenzothiophene with alkyl group at 4 and/or 6-position, including 4-MDBT, 4,6-DMBT, 2,4,6-TMBT, 3,6-DMDBT, DBT, 2,3,7-TMBT, 2,3,5-TNBT, 2,3-DMBT and others. In addition, Yin *et al.* (2002) showed that the contents of mercaptans and disulfides are comparatively low in Fluid Catalytic Cracking (FCC) and RFCC naphtha of china fuel. The sulfide accounts for 25% of total sulfur and the highest amount of sulfur compound is in the form of thiophenic compound.

2.2 Removal of Sulfur Compounds by Hydrodesulfurization (HDS)

Environmental concerns have driven the need to remove many impurities from fuel. Sulfur containing compounds are of particular interest because of their tendencies to produce precursors to airborne particulate material and acid rain since

it can diminish the efficiency of an automobile's catalytic converter, producing an increase in nitrogen oxide (NO_x) and other tailpipe emissions, such as sulfur oxide. Therefore, desulfurization of oil is extremely important in the petroleum processing industry. Several processes have been proposed in the past to deal with the problem of removing of these compounds in oil. The most prevalent and common industrial process is treating the fuel under high temperature and high pressure with hydrogen to maintain high desulfurization reaction rate and to suppress carbon deposition. This process is called hydrodesulfurization (Dishun, 2003). In this process, a hydrocarbon feedstock is reacted with hydrogen to produce hydrogen sulfide and desulfurized hydrocarbon product. It is achieved by using Co-Mo/ Al_2O_3 or Ni-Mo/ Al_2O_3 catalysts. The operating condition in hydrodesulfurization of fuels is dependent on the stock to be charged as well as the degree of desulfurization or quality of improvement. This process is highly efficient in removing thiols, sulfides, and disulfides but less effective for thiophenes and thiophene derivatives. Thus, the sulfur compounds remaining in the transportation fuels are mainly thiophene, benzothiophene, dibenzothiophene and their alkylated derivatives.

As a result, the production of transportation fuels with very low levels of sulfur containing compounds requires inevitably the application of severe conditions and use of special active catalysts. Unfortunately, more severe conditions result not only in a higher level of desulfurization but also in undesired side reaction affecting loss of octane number in gasoline fuel since many olefin and aromatic compounds are saturated at high hydrogen pressure while high temperature processing leads to increase coke formation and subsequent catalyst deactivation. Therefore, an alternative process that able to be operated under ambient conditions and without urgent requirements for hydrogen is imminently required for improved desulfurization processes.

2.3 Removal of Sulfur Compounds by Adsorption

2.3.1 Fundamental of Adsorption

The adsorption process is used for treating feedstock in petroleum industry for long time ago because of the selective adsorption of certain compounds

in mixture. Recently, there is growing interest in studying and developing adsorption for desulfurizing of liquid fuels in order to meet current and the future regulations since they can be operated at ambient condition. Adsorption is a separation process in which the molecules of a fluid phase, *i.e.*, gas or liquid are transferred to a solid surface. Therefore, the composition of the system is heterogeneous consisting of two or more fluid phases including the solid adsorbent. Molecules that have been adsorbed onto solid surfaces are referred to as adsorbates, and the surface to which they are adsorbed are referred to as the substrate or adsorbent. Adsorption takes place in the boundary between the phases called the interface. Most adsorbent are highly porous material and adsorption occurs on the walls of the pores. In many cases, the components are held strongly enough to permit complete removal of a component with very little adsorption of other components. The chemical bond due to the adsorption can vary in strength depending on the nature of compounds and of solid involved.

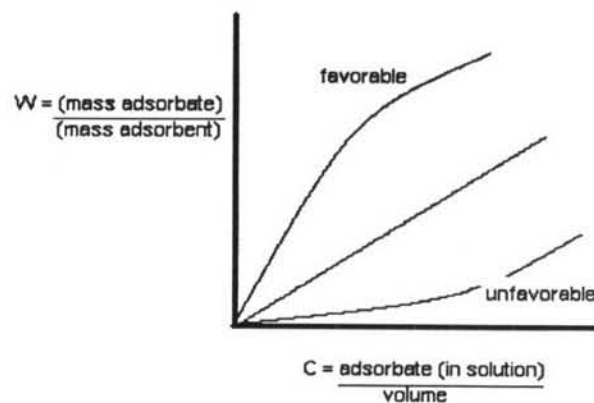


Figure 2.2 Adsorption isotherms. (<http://www.cbu.edu/~rprice/lecture/adsorb.html>, 10/12/05)

Adsorption equilibrium data is typically plotted in the form of an adsorption isotherm at constant temperature with the mass adsorbed on the y-axis and the mass in the fluid on the x-axis as depicted in Figure 2.2. The shape of the curve is significant and factors heavily into design. For "Favorable" isotherms, the

slope of this curve is very high at low adsorbate content and then reduced at high adsorbate content. Isotherms which start out flat are "unfavorable", since they only work well at high concentrations of solute.

In general, as temperature increases, the amount adsorbed decreases permitting thermal regeneration. Various correlations have been proposed to describe the adsorption isotherms as summarized in Table 2.4. However, the most general correlation is the Langmuir isotherm as given by Eq. (2.1).

Table 2.4 Correlations proposed to describe the adsorption isotherm

Name of isotherm	Equation
Langmuir	$q = \frac{q_{max}kc_b}{1 + kc_b} \quad (2.1)$
Freundlich	$q = kc_b^n \quad (2.2)$

where, q is the amount of adsorbed (mole g^{-1} adsorbent), q_{max} the maximum amount of adsorbed (mole g^{-1} adsorbent), c_b the adsorbate amount in mobile phase (mole m^{-3}), k the adsorption equilibrium constant ($m^3 \text{ mole}^{-1}$) and n Freundlich exponent. If n equal 1, the Freundlich isotherm reduces to the linear isotherm.

2.3.2 Adsorbents and Selectivity for Sulfur Compounds

During the past decade, several adsorbent have been studied to adsorb sulfur compounds from transportation fuels and petroleum products such as, ZSM5, zeolite and activated carbon (Hernandez *et al.*, 2003). Each type of adsorbent has different selectivity and capacity to adsorb sulfur compounds. Commercially available adsorbents (e.g. zeolite, activated carbon, and activated alumina) were used in all of these studies but it was found that the faujasite zeolite was the most attractive adsorbent for desulfurization. Weitkamp *et al.* (1991) studied ZSM-5 for removing thiophene from benzene using fixed bed experiments. They found that thiophene adsorbed more selectively than benzene on ZSM-5 zeolite. Salem and Hamid (1997) showed that the capacities of 13X zeolite for adsorbing sulfur

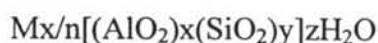
compounds was approximately an order of magnitude higher than that of ZSM-5. They also indicated that both 13X zeolite and activated carbon had much higher sorption capacities for sulfur compounds. Based on the results of Weitkamp *et al.* (1991) experiment, King *et al.* (2000) also performed vapor phase fixed bed breakthrough experiments to remove thiophene and dimethyl thiophenes from toluene and *p*-xylene instead of benzene. They also showed that thiophene was more selectively adsorbed on ZSM-5. Although both experiments showed that selectivity toward thiophene was accomplished, saturation adsorption capacities were low. Takahashi *et al.* (2002) performed experiments to understand the interaction between benzene/thiophene and various kinds of adsorbents in vapor phase isotherm adsorption. They observed that the separation factors of thiophene over benzene (at low concentrations of thiophene) exhibited the trend of Ag-Y > Na-ZSM-5 > Cu-Y \approx activated carbon \gg Na-Y \gg H-USY \approx modified activated alumina. The adsorbent capacities for thiophene at the low pressure followed the order of Cu-Y and Ag-Y \gg Na-ZSM-5 > activated carbon > Na-Y > modified alumina and H-USY.

Chansa (2004) studied behavior of NaX and NaY zeolites for removal of thiophenic sulfur compounds from transportation fuels by adsorption in batch reactor. In this study, the simulated transportation fuels were decane and *i*-octane as a model for diesel and gasoline, respectively. The sulfur compounds used were 3-methylthiophene (3-MT) and benzothiophene (BT) for simulated gasoline and dibenzothiophene (DBT) for simulated diesel. The adsorption isotherms were developed to evaluate the adsorption capacity and selectivity of adsorbent. It was found that NaX zeolite was more effective in adsorbing both 3-methylthiophene and benzothiophene than NaY zeolite was. 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 was found that for all sulfur compounds on both zeolites the adsorption decreases with increasing temperature in the range of 25-80°C. The investigation 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°C. Rahman *et al.* (2005) studied competitive adsorption on commercial zeolites (NaY, USY, HY,

and 13X) using a mixture of anthracene, dibenzothiophene, and quinoline in a hexadecane solution. They found that NaY selectively adsorbs quinoline while anthracene have similar affinity to NaY and also showed NaY has the highest saturation sorption capacities for the sulfur compounds when compared to other adsorbents. Siriyut (2005) further studied the adsorptive desulfurization on the effect of aromatic content and water content in zeolite. Fuel to adsorbent weight ratio used in this study was fixed at 85. He found that benzothiophene and dibenzothiophene were preferentially adsorbed by NaX and NaY zeolites than 3-methylthiophene, especially at low concentration. The adsorbed amount of thiophenic sulfur compound decreased with increasing aromatic content or water content in zeolite.

2.3.3 Zeolite

Zeolites are porous crystalline aluminosilicates. The zeolite framework consist of an assemblage of AlO_4 and SiO_4 tetrahedra, joined together in various regular arrangements through shares oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Zeolites are subset of the larger class of molecular sieves. A pure silica framework is neutral. The presence of aluminum in the framework results in the negative frame work charge, which is balanced by cations. These cations are relatively mobile, and can be replace using standard method of ion exchange techniques. The exchangeable cations are located at preferred sites within the framework and play an important role in determining the adsorptive properties. Zeolite can be represented by the stoichiometry as,



where x and y are integers with y/x equal to or greater than unity, 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 faction between 0.2 and 0.5. The Si/Al ratio in zeolite is never less than unity but there is no upper limit and pure silica analogs of some of the zeolite structures have been prepared. The adsorptive properties show a

systematic transition from aluminum rich sieve, which has very high affinities for water and other polar molecules, to the microporous silicas such as silicalite which are essentially hydrophobic and adsorb n-paraffins in preference to water.

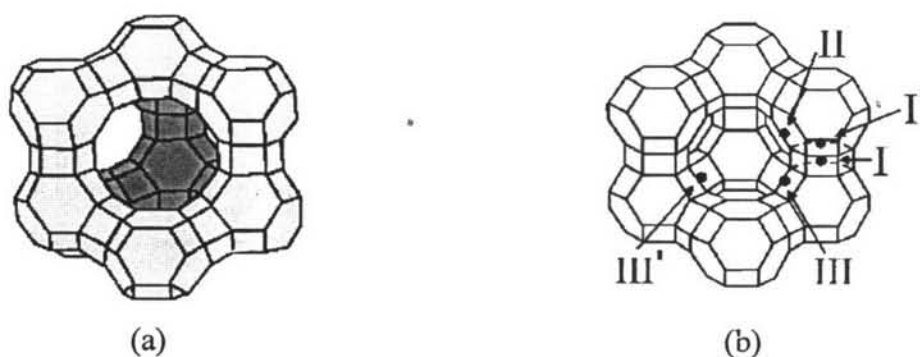


Figure 2.3 Schematic representation of (a) framework structure of zeolite X and Y, (b) cation sites in type X and Y. (To translate these schematic diagrams into the actual structure, a Si or Al is placed at each vertex and an O at or near the center of each line.)

The synthetic zeolites X and Y and the natural zeolite faujasite all have the same framework structure as shown in Figure 2.3. The crystallographic unit cell consists of an array of eight cages containing a total of 192 AlO_2 and SiO_2 tetrahedral units. The framework may be thought of as a tetrahedral lattice of sodalite units connected through six-membered oxygen bridges, or equivalent to a tetrahedral arrangement of double six-ring units. The resulting channel structure is very open with each cage connected to four other cages through twelve-membered oxygen ring of free diameter $\sim 7.4 \text{ \AA}$. The difference between the X and Y zeolites lies in the Si/Al ratio which is within range 1-1.5 for X and 1.5-3.0 for Y. There is corresponding difference in the number of exchangeable univalent cations, which varies from about 10-12 per cage for X to as low as 6 for high silica Y. The distribution of the cations between the various sites depends on both the nature and the number of the cations and is affected by the presence of traces of moisture. There is even some tentative evidence that the equilibrium distribution may change

when the sieve is loaded with adsorbent. Therefore, the adsorptive properties of X and Y zeolites may be greatly modified by ion exchange that improves the selectivity

For commercial X and Y zeolite from IFP, The specific surface area of NaX and NaY zeolite are $580 \text{ m}^2/\text{g}$ and $549 \text{ m}^2/\text{g}$, respectively. The thermo gravimetric analysis (TGA) results of both NaX and NaY zeolites are shown that the water content in original NaX and NaY zeolites before treating are 20.43%wt and 19.17%wt, respectively. The both adsorbents should be treated at 300°C for 3 hours before use (Chansa, 2004).

According to the effective commercial adsorbents are not currently available, the modification and improvement of the adsorbents for high selectivity and high capacity of sulfur compounds have become more crucial. For many years ago, many experiments have been studied the improvement of adsorbent performance by metal loading on adsorbent. Michlmayr (1980) studied the removal of thiophene from gasoline by adsorption on silver exchanged faujasite-type zeolite. He found that Ag-Y zeolite has a better capacity than the ordinary Y-zeolite and is effective adsorbent for the removal of residual thiophene in gasoline. Mingels *et al.* (1988) used Cu(II)-Y zeolite to remove thiophene from benzene in both batch and fixed bed adsorption. Their adsorbent was activated in air which did not reduce Cu^{2+} . They found that their adsorbent capacities showed approximately 0.6 % wt which is quite low (for an influent concentration of 4320 ppm thiophene). Kulprathipanja *et al.* (1998) studied a process for removing sulfur containing compounds from various hydrocarbon streams using NiX, MoX and NiY zeolites in a batch reactor at ambient temperature placed 0.5 g of the adsorbent and 3 g of gasoline and maintained this mixture for 16 hours. They found that the capacity of adsorbent followed the order $\text{NiX} > \text{MoX} > \text{NiY}$. Zinnen (1999) studied removal of aromatic sulfur compounds from an FCC gasoline using the UOP Y-zeolite which was ammonia ion exchanged at 1 atmospheric pressure and calcined at 600°C and one second ammonium ion exchanged, then calcined to afford a second dealuminated zeolite Y. The temperature of fixed bed used in the experiment was 65°C . He found that the second dealuminated zeolite has the higher surface area but the adsorption capacity of sulfur compounds is lower.

Yang *et al.* (2001) studied CuY and AgY zeolite as selective adsorbents for the desulfurization of thiophene from benzene and vapor phase adsorption isotherm were developed. When compared to NaY, CuY and AgY adsorbed significantly higher amount of both benzene and thiophene at low pressure as a result of π -complexation with Cu^+ and Ag^+ . On cation basis, more thiophene was adsorbed by Cu^+ than by Ag^+ . Molecular orbital calculations confirmed that the relative strengths of π -complexation as thiophene is greater than those of benzene and the relative strengths of π -complexation Cu^+ is greater than those of Ag^+ . Takahashi *et al.* (2002) studied vapor phase adsorption using various kinds of adsorbents and thiophene/benzene as a model in order to gain more understanding about the adsorbate-adsorbent interaction. They found that Ag^+ exchange was totally complete in Ag-Y whereas Cu^+ exchange was only 46% complete in Cu-Y. Only half of Cu^{2+} was automatically reduced to Cu^+ after heat treatment at 450°C . Hernandez *et al.* (2003) studied the separation of low concentration thiophene from mixtures including benzene and/or n-octane by using Cu(I)-Y, Ag-Y, H-Y and Na-Y zeolites in fixed bed breakthrough experiments. From experiments, they showed the adsorption capacity of the silver-based zeolite is almost twice that of the sodium-based zeolite. Cu(I)-Y provided the best adsorption capacity at both breakthrough and saturation points, surpassing all other adsorbents by more than 50%.

Xue *et al.* (2004) studied Na-Y zeolites exchanged with Ag^+ , Cu^{2+} , and Ce^{3+} ions and NH_4Y zeolites exchanged with Ce^{3+} ions for adsorption of the organic sulfur compounds. All adsorbents showed markedly high adsorption capacities for thiophene (TP) and 1-benzothiophene (1-BTP) in an organic model solution (heptane with 1 %wt toluene and 5 ppmw as TP or 1-BTP). The sulfur uptake increased in the order $\text{CuY-zeolite(Na)} < \text{AgY-zeolite(Na)} < \text{CeY-zeolite(Na)}$ for both organic sulfur compounds. Hernandez *et al.* (2005) studied faujasite zeolite ion exchanged with Cu^+ , Ni^{2+} and Zn^+ for desulfurization of diesel, gasoline, jet fuels. Cation hydrolysis limitation could be avoided, in order to enhance the ion exchange level, when vapor phase (VPIE) and solid-state (SSIE) ion exchange techniques were used instead liquid phase ion exchange (LPIE). From the fixed bed experiments, they showed that the π -complexation sorbents desulfurization

performance decrease as follows: Cu(I)-Y(VPIE) > Ni(II)-Y(SSIE) > Ni(II)-X(LPIE) > Zn(II)-X(LPIE) > Zn(II)-Y(LPIE) corresponding to molecular orbital calculations. Ma *et al.* (2005) comparatively studied the performance of a Ni-based adsorbent and a Cu(I)-Y zeolite for desulfurization of a commercial gasoline by fixed bed adsorption. The Ni-based adsorbent showed higher breakthrough capacity of adsorbent than Cu(I)-Y zeolite and the breakthrough capacity of the Ni-based adsorbent was increased by 38% at 200°C.

2.3.4 Fixed Bed Adsorption

Adsorption is a transient process because the adsorbate concentration exhausted from the adsorber depends on processing time. Most commercial applications use small particles of adsorbent in fixed bed. Fluid passes through the bed and adsorbate component is adsorbed onto the solid surface of the adsorbent. The amount of compound adsorbed within a bed depends on position in the fixed bed and time. Figure 2.4 illustrates the breakthrough curve used to represent the adsorption process. This figure plots the relationship between outlet concentration of the adsorbate from the fixed bed adsorber and volume treated which is a function of time. Volume treated is calculated by multiplying volume flow rate of fluid through the adsorber which is constant and processing time. From this figure, when the fluid is initially fed to the adsorber, the adsorbate is mostly adsorbed onto the adsorbent surface near the entrance of the adsorber because the fresh adsorbent has high capacity of adsorption. Therefore, the fluid exhausted from the adsorber initially contains a trace amount of adsorbate. However, as processing time increases, the adsorbent near the entrance of the adsorber is saturated. Accordingly, the active region for adsorption moves down from the entrance to the middle of the adsorber and the overall adsorption capacity decreases. However, as shown in Figure 2.4, the outlet concentration of the adsorbate is still negligible as processing time increases until it reaches the breakthrough point. Afterwards, an increase in outlet concentration of the adsorbate is observed as processing time goes on. Finally, once the active region of the adsorbent is totally occupied by the adsorbate throughout the adsorber, the outlet concentration of the adsorbate is equal to its inlet concentration. Then, the adsorbent is needed to regenerate before it is reused again. Usually, a

breakthrough point concentration is set to be the maximum amount of solute that can be acceptably released, typically something between 1 and 5 percent (McCape *et al.*, 2001).

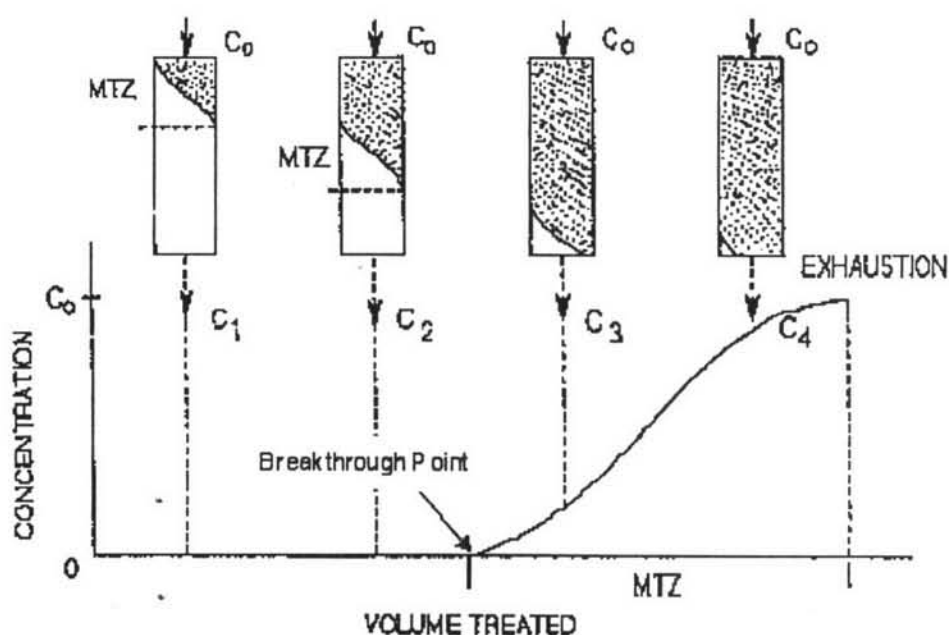


Figure 2.4 Idealized breakthrough curve of a fixed bed adsorber.

(<http://www.activated-carbon.com/solrec3.html>., 10/12/05)

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 may broaden or diminish. Unfavorable and linear isotherms tend to broaden. Favorable Langmuir and Freundlich isotherms 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.

2.3.5 Desorption of Sulfur Compounds and Regeneration of Adsorbent

According to economical consideration, the used adsorbent should be regenerated in order to remove adsorbate as much as possible so that it can be reused again. In general, the regeneration of the adsorbent can be performed by decreasing total pressure, stripping with an inert gas, increasing temperature and displacing by desorbent. Nevertheless, the most general way is to enhance temperature. Zinnen *et al.* (1999) studied the removal of organic sulfur compounds from FCC gasoline using regenerable adsorbent. They found that if KY adsorbent is impregnated with platinum, the sorbent saturated with sulfur compound can be regenerated by contacting with hydrogen at 288-300°C for 113 minutes and the flow rate of hydrogen was in the range of 623-755 GHSV. They also found that the regenerable Pt-K-Y adsorbent was unimpair capacity even after many cycles of operation. Hernandez *et al.* (2003) investigated the regeneration of Cu-Y that is a part of the experiments which studied the separation of low concentration thiophene from benzene and n-octane by using Cu-Y, Ag-Y, H-Y and Na-Y in fixed bed adsorber. They found that the regeneration of Cu-Y was accomplished by using air at 350°C followed by reactivation in helium at 450°C which recovered almost all the origin adsorption capacity. Xue *et al.* (2004) studied the removal of thiophene and 1-benzothiophene in simulated gasoline (heptane with 1 %wt toluene) by using Na-Y zeolites exchanged with Ag⁺, Cu²⁺, and Ce³⁺ ions and NH₄Y zeolites exchanged with Ce³⁺ ions for adsorption and also studied the regeneration of CeY-zeolite(Na). After desorption saturated CeY-zeolite(Na) at 450°C in air for 2 hours, they found that thiophene uptaked more than 90% of the first adsorption.

Yang *et al.* (2004) studied the regeneration of the activated carbon/Cu(I)-Y saturated with sulfur during desulfurization with a diesel fuel by using layered bed. The air calcinations and the solvent elution were chosen for regeneration tests. They observed that the activated carbon/Cu(I)-Y bed can only recover 85% of the original adsorption capacity for regeneration with air at 350°C for at least 6 hours followed by auto-reduction. For the solvent elution technique, CCl₄ was capable of recovering a considerably part of the original adsorption capacity. Rahman *et al.* (2005) studied the desorption/combustion of the sulfur compounds adsorbed on the NaY zeolite. This regeneration was carried out in the flow of helium

containing 5% oxygen analyzed by using thermal gravity analysis (TGA) technique. From TGA results, they indicated that high temperature is required to desorb the refractory sulfur compound. Siriyut (2005) studied the effect of temperature on sulfur desorption on NaX and NaY zeolite in the range of 45-75°C. It was found that the desorption amount of thiophenic sulfur compounds increase with increasing temperature. Moreover, 3-methylthiophene showed the highest amount of 3-methylthiophene desorbed as a result from size of sulfur compounds.

2.4 Mathematical Modeling of a Fixed Bed Adsorber

Use of fixed bed column which contain the porous adsorbent particles for sulfur removal process has been studied and become more prevalent during recent years. To improve the bed design and to find the optimum operating condition, the mathematical model of a fixed bed adsorber need to be developed. Both design and operation of adsorption column are related to the characteristic of breakthrough curve in which readily measured effluent concentration is plotted as a function of elapsed time. Mass balance and the equilibrium isotherm should be accounted for the adsorption model (Babu and Gupta, 2004)

The mathematical models have been published in recent years to describe the phenomena of fixed bed adsorption. All of these model are based on the following fundamental relation; transport phenomena equation (mass and heat balances), equilibrium isotherm equations, boundary and initial condition. Consequently, this section presents some research works related to adsorber modeling. Brosillon *et al.* (2001) studied mass transfer in volatile organic compound (VOC) adsorption on hydrophobic commercial zeolite. They proposed simulations of breakthrough curves based on the Linear Driving Force model (LDF). To improve the model and to study the parametrical effects on the breakthrough curves, a parameter sensitivity analysis was performed. It was found that the sensitivity of the intrapellet mass transfer coefficient (k_p) to the slope of breakthrough curve is much higher than interphase mass transfer coefficient (k_p). Therefore, it can be deduced that the overall mass transfer is controlled by internal mass transfer coefficient. A good agreement between experimental and numerical results was found when

adjustable value of the internal mass-transfer was used. An effective diffusivity was found independently to the nature of fluid and the amount of VOCs adsorbed. A relation linking intrapellet mass transfer coefficient and equilibrium constant and average effective diffusivity was proposed to make predictions of breakthrough curve for any kinds of volatile organic pollution in gaseous effluents. Malerius and Werther (2003) developed a model for studying the mercury removal in the flue gas of sewage sludge incineration. The model was established based on the unsteady-state mass transfer, Freundlich and Langmuir equilibrium equations. All of these equations were solved using Mathcad Professional 7 (Mathsoft) with Runge-Kutta method. This model was also assumed that the adsorption process was not limited by mass transfer. For the determination of the kinetic parameter k_{ads} (adsorption constant), the breakthrough curve was fitted basically with the mathematical model by adjusting the kinetic parameter. The agreement between simulation results and the available measurement was quite satisfactory. Uttamaroop (2004) developed the mathematical model to study the adsorption of water vapor onto a multi-layer adsorber (silica gel and 4A zeolite). Simulations of the breakthrough curves of water vapor, based on axial plug flow and Linear Driving Force (LDF) model, was obtained by solving the set of governing equations. The method of lines (MOL) combined with the finite difference method and computer programming was utilized to obtain the theoretical breakthrough curve. From sensitivity analysis of parametrical effects on breakthrough curve, it was found the interstitial velocity and effective bed voidage were more sensitive than the effective axial dispersion coefficient. The parameters and the equilibrium adsorption isotherm developed for each adsorbent were employed specifically in the model. The results showed that the mathematical breakthrough curve provided an excellent correspondence with the experimental breakthrough curve.

Babu and Gupta (2004) developed the mathematical model to study the adsorption of α -amylase from *Aspergillus oryzae* in a fixed bed adsorber. The mathematical model was employed to describe the kinetic behavior of adsorption phenomena incorporating the fluid velocity variation along the column length also. Internal mass-transfer resistances due to pore diffusion mechanism were considered in the model. The proposed mathematical model for fixed-bed adsorber was solved

numerically and compared with earlier model (Bautista *et al.*, 2003) which did not consider the fluid velocity variation along the bed that the results shown that the breakpoint was obtained earlier which represents the realistic behavior in adsorption phenomena. Initially the sharp front of the breakthrough curve was seen followed by broadening of tail of the breakthrough curve. Delgado *et al.* (2005) studied the fixed-bed adsorption of carbon dioxide and nitrogen on silicalite pellets. Adsorption equilibrium and kinetic measurements of carbon dioxide and nitrogen on this adsorbent at several temperatures were performed, and the single adsorption equilibrium isotherms were obtained for both adsorbates. A model based on the LDF approximation for the mass transfer, taking into account the energy and momentum balances, was used to describe the adsorption kinetics of carbon dioxide and nitrogen as single components. The model reproduced satisfactorily the breakthrough curves obtained with carbon dioxide–nitrogen mixtures.