CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Crude Oil Composition

Crude oil mainly comprises a variety of hydrocarbon and non-hydrocarbon components. The hydrocarbon components of petroleum are composed of paraffinic, naphthenic, aromatic groups. Olefinic groups are not usually found in crude oils. The hydrocarbon components can be divided into the following three classes.

1. Paraffins, which are saturated hydrocarbons with straight or branched chains, but without any ring structure.
2. Naphthenes, which are saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as alicyclic hydrocarbons).
3. Aromatics, which are hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, which may be linked up with (substituted) naphthene rings and/or paraffinicside chains.

For non-hydrocarbon components, they are composed of principally organic compounds of sulfur, nitrogen, oxygen and organometallic compounds containing nickel and vanadium and occasionally iron and arsenic. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the nonvolatile residues. Even if their concentration in certain fractions may be quite small, their influence is important. The presence of these compounds can impact objectionable characteristics to finished products, leading to discoloration and/or lack of stability during storage. Catalyst poisoning corrosion is also the most noticeable effects during refining sequences when these compounds are present. Thus, in recent years, many refining industries pay attention to the non-hydrocarbon constituents of petroleum.

2.2 Sulfurs in Crude Oil

The sulfur contents of crude oils can vary from virtually zero to as high as 7 or 8 wt% in extreme cases, depending on the source of the crude. Table 2.1 shows some examples of sulfur content and density in various sources of crude.

Table 2.1 Sulfur content and density of various crudes

Zone	Name	Origin	%S	Density (d^{15})
Middle East	Safaniya	Saudi arabia	2.80	0.88
	Arabian light	Saudi arabia	1.80	0.858
	Kirkuk	Iraq	2.00	0.849
North Sea	Brent	United kingdom	0.26	0.834
	Ekofisk	Norway	0.14	0.809
North Africa	Zarzaitine	Algeria	0.07	0.811
	Gregta	Lybia	0.21	0.841
West Africa	Bonny light	Nigeria	0.12	0.841
	Djeno	Congo	0.33	0.893
	Gamba	Gabon	0.11	0.866
Latin America	Bachaquero	Venezuela	2.40	0.954
	Isthmus	Mexico	1.50	0.861
	Maya	Mexico	3.30	0.922
North America	Rainbow	Alberta-Canada	0.50	0.822
	North slope	Alaska-USA	1.10	0.896

For high boiling fractions, they may contain two or more sulfur atoms per molecule. Not only the sulfur contents of crude oil vary, but the types of sulfur compounds also vary from very simple compounds in the lightest fractions to much more complicated ones, which are difficult to identify in heavier fractions as summarized in Figure 2.1.

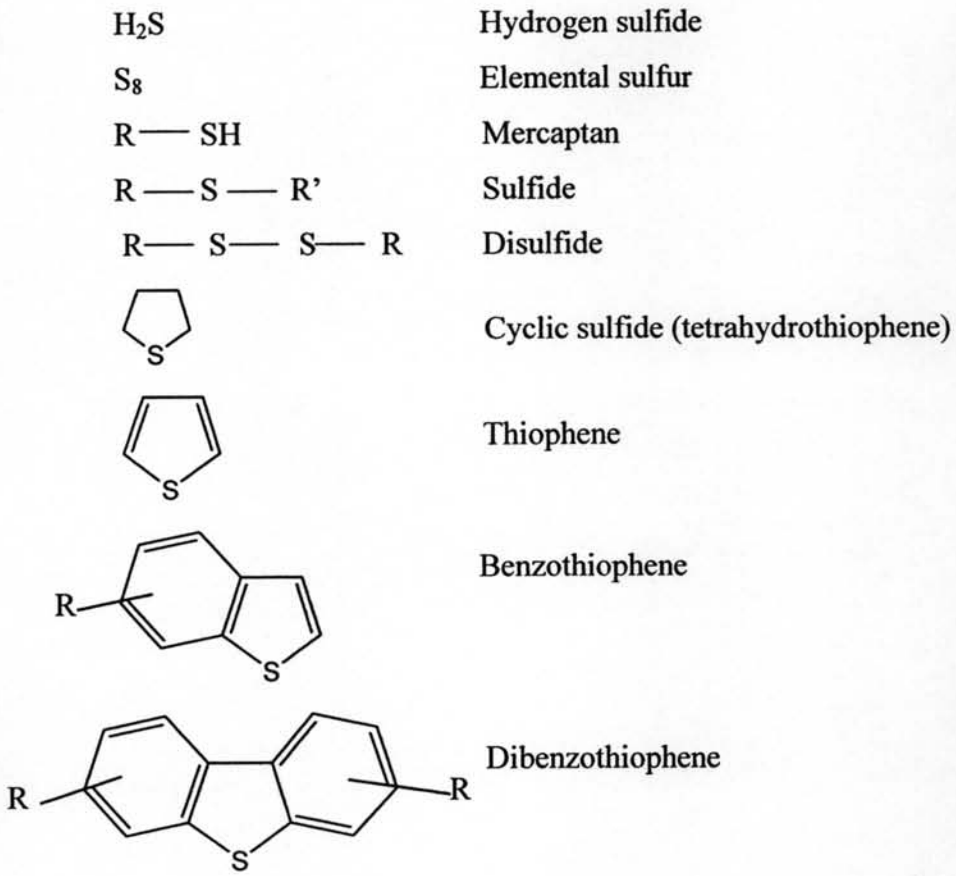


Figure 2.1 Examples of sulfur compounds in petroleum

As seen in Figure 2.2, sulfur is typically present as aliphatic compounds in light fractions. When the boiling range increases, the sulfur tends to be more cyclic, and the sulfur is almost present in the form of complex ring structures in heavier fractions.

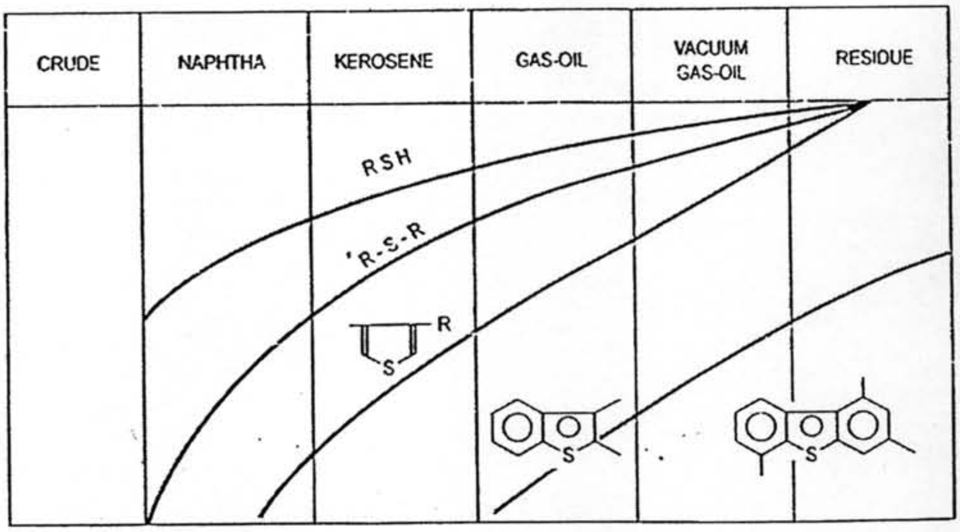


Figure 2.2 Typical sulfur compounds distribution in the various distillation cuts

The sulfur compounds found in gasoline mainly comprise mercaptans, aliphatic sulfides, aliphatic disulfides, and five- and six- membered ring cyclic sulfides. In addition, thiophene and thiophene derivatives are usually found in gasoline produced from cracking heavier fractions, but rarely present in straight-run gasoline. Few mercaptans occur above the gasoline boiling range. The majority of sulfur structures in kerosene and gas oil are sulfides, cyclic sulfides, benzothiophenes, and dibenzothiophenes.

Hernandez-Maldonado *et al.* (2004d) reported that the dominant sulfur compounds in the gasoline were 3-methylthiophene (3-MT), benzothiophene (BT), Thiophene (T), 2-methylthiophene (2-MT), and 2, 4-dimethylthiophene. Diesel were 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-Dimethylbenzo-thiophene (2, 3-DMBT) and others. The sulfur compounds commonly found in the jet fuel were 2, 3, 7-trimethylbenzothiophene (2, 3, 7-TMBT), 2, 3-dimethylbenzo- thiophene and the minor species 2, 3, 5-trimethylbenzothiophene (2, 3, 5-TMBT) and 2, 3, 6-trimethylbenzothiophene (2, 3, 6-TMBT).

2.3 Treatment Process for Sulfur Removal

In recent years, the considerations of environmental impact have driven the need to reduce the sulfur content in transportation fuels. Many restrictions of sulfur concentration in fuels have been mandated in many countries. Hence, there are several processes that used for decreasing the sulfur compounds to reach these specifications. Typically, the processes are hydrotreating process, caustic process, acid process and adsorption process.

2.3.1 Hydrotreating Process

Hydrotreating process, in particular the hydrodesulfurization of petroleum residue, is catalytic processes. Hydrocarbon feedstock and hydrogen are passed through a catalyst bed typically containing Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 at elevated temperatures and pressures (300°C and 20-100 atm H_2) in transportation fuels (Hernandez-Maldonado, 2004d). This reaction requires a high hydrogen partial pressure in gas phase to maintain high desulfurization reaction rates and to suppress carbon deposition. Some of sulfur atoms attached to hydrocarbon molecules react with hydrogen on the surface of catalyst to form hydrogen sulfide. This gas is scrubbed out of the reactor effluent gas stream. 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 suffer. The hydrodesulfurization process is highly effective in removing thiols, sulfides, and disulfides but less effective for thiophenes and thiophene derivatives. There are some catalysts that can also be used in hydrodesulfurization. Barrio *et al.* (2003) prepared silica-alumina supported Pd catalysts with a second metal such as Cu, Ru or Pt for dibenzothiophene hydrodesulfurization (HDS) model reaction. They found that the PtPd system showed the highest DBT conversion. Kemsley (2003) reported that Akzo Nobel Catalysts produced a new HDS catalyst, known as Nebula, based on NiMo that has a performance higher than current HDS catalysts about 15-20%.

2.3.2 Caustic Process

Treating of petroleum products b washing with alkali solutions is almost as old as the petroleum industry itself. The process consists of mixing a water solution of lye with petroleum fraction. The treatment is carried out as soon as the petroleum fraction is distillated, since contact with air forms free sulfur, which is very corrosive and difficult to remove. The lye reacts with any hydrogen sulfide present to form sodium sulfide, which is soluble in water.

2.3.2.1 Lye Treatment

The lye treatment is carried out in continuous treaters, which consist of the pipe containing baffles or other mixing devices into which the oil solution are both pumped. Caustic solutions ranging from 5 to 20 % w/w are used at 20-45°C and 40 psi. High temperatures and strong caustic are usually avoided because of the risk of color formation and stability loss.

2.3.2.2 Steam-Regenerative Caustic Treatment

This treatment is essentially directed towards removal of mercaptans from such products as light, straight-run gasoline. The caustic is regenerated by steam blowing in striping tower. The nature and concentration of mercaptans to be removed dictate the quantity and temperature of process.

2.3.2.3 Sosal Process

A lye solution removes only the lighter or lower boiling point mercaptans, but various chemicals can be added to the lye solution to increase its ability to dissolve heavy mercaptans. In this process, the lye solution, with solutizers incorporated, is then ready to treat product stream, such as straight-run naphtha and gasoline.

2.3.2.4 Polysulfide Treatment

Polysulfide treatment is a nonregenerative chemical treatment process used to remove elemental sulfur from refinery liquids. Dissolving 1 pound of sodium sulfide and 0.1 pound of elemental sulfur in a gallon of caustic solution prepare the polysulfide solution. The sodium sulfide can actually be prepared in refinery by passing hydrogen sulfide, an obnoxious refinery by product gas, through caustic solution.

2.3.2.5 Dualayer Distillate Process

This process is similar in character to Duosol process in that it uses caustic solution and crysylic acid. The process extracts organic acid including mercaptans from cracking or virgin distillate fuels.

2.3.2.6 Dualayer Gasoline Process

This process is a modification of the Dualayer distillate process in that it is used to extract mercaptans from liquid petroleum gas, and naphtha using the Dualayer reagents. The gasoline, free hydrogen sulfide, is contacted with Dualayer solution at 50°C in at least two stages, after which the gasoline is washed and stored.

2.3.3 Acid Process

Treating petroleum with acid is, like caustic treatment, a procedure that has been in use for considerable time in petroleum industry. Various acids, such as hydrofluoric acid, hydrochloric acid, and phosphoric acid, have been used in addition to more commonly used sulfuric acid, but in most instances, there is little advantage in using any acid other than sulfuric. Sulfuric acid treatment is a continuous or batch method that is used to remove sulfur compounds. The use of strong acid dictates the use of a fairly low temperature, but higher temperatures are possible if the product is to be redistilled.

2.4 Removal of sulfur compounds by adsorption

2.4.1 Fundamental of Adsorption

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

There are various correlations which are used to represent the adsorption isotherms as shown in Table 2.2. However, the Langmuir isotherm is the most important model.

Table 2.2 Correlations used to represent the adsorption isotherm

Name of isotherm	Equation
Langmuir	$q = \dfrac{q_{max} k c_b}{1 + k c_b}$ (2.1)
Freundlich	$q = k c_b{}^n$ (2.2)

where, q = 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 $mole^{-1}$)

n = Freundlich exponent. If n equal 1, the Freundlich isotherm reduces to the linear isotherm.

2.4.2 Adsorbents

Adsorbents have been developed for a wide range of separations. Commercial materials are provided usually as pellets, granules, or beads, although powders are used occasionally. 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. Adsorbates are generally used in cylindrical vessels.

Commercial adsorbents are divided into four major classes: activated alumina, silica gel, activated carbon and molecular-sieve zeolites. Since adsorption is a surface-related phenomenon, the useful adsorbents are all characterized by a large surface area per unit of weight (or volume). The applications for these adsorbents depend on their particular adsorptive properties.

The specific information on various aspects of adsorption technology is shown in Table 2.3.

Table 2.3 Adsorbents in commercial adsorption separations

Separation[a]	Adsorbent
Gas Bulk Separations	
Normal paraffins, isoparaffins, aromatics	Zeolite
N_2/O_2	Zeolite
O_2/N_2	Carbon molecular sieve
$CO, CH_4, CO_2, N_2, A, NH_3/H_2$	Zeolite, activated carbon
Acetone/vent streams	Activated carbon
C_2H_4/vent streams	Activated carbon
H_2O/ethanol	Zeolite
Gas Purifications[c]	
H_2O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite
CO_2/C_2H_4, natural gas, etc.	Zeolite
Organics/vent streams	Activated carbon, others
Sulfur compounds/natural gas, hydrogen, liquified petroleum gas (LPG), etc.	Zeolite
Solvents/air	Activated carbon
Odors/air	Activated carbon
NO_x/N_2	Zeolite
SO_2/vent streams	Zeolite
Hg/chlor-alkali cell gas effluent	Zeolite
Liquid Bulk Separations[b]	
Normal paraffins, isoparaffins, aromatics	Zeolite
p-Xylene/*o*-xylene, *m*-xylene	Zeolite
Detergent-range olefins/paraffins	Zeolite
p-Diethyl benzene/isomer mixture	Zeolite
Fructose/glucose	Zeolite
Liquid Purifications[c]	
H_2O/organics, oxygenated organics, chlorinated organics, etc.	Silica, alumina, zeolite
Organics, oxygenated organics chlorinated organics, etc./H_2O	Activated carbon
Odor, taste bodies/drinking H_2O	Activated carbon
Sulfur compounds/organics	Zeolite, others
Various fermentation products/fermentor effluent	Activated carbon
Decolorizing petroleum fractions, sugar syrups, vegetable oils, etc.	Activated carbon

[a] Adsorbates listed first.

[b] Adsorbate concentrations of about 10 wt.% or higher in the feed.

[c] Adsorbate concentrations generally less than about 3 wt.% in the feed.

2.4.2.1 Activated Alumina

Activated alumina adsorbents are amorphous or transition aluminas whose chemical composition is Al_2O_3. Their surface area is generated by the removal of water of constitution from hydrated aluminas. They are a porous high-area form aluminum oxide. Their fine pore structure and surface chemistry provide the observed adsorption selectivities. The product is commonly provided as granules.

The most important industrial application for activated aluminas is in drying processes for both liquids and gases. Activated alumina has 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 the gases commonly dried by activated alumina are air, argon, helium, hydrogen, methane, chlorine, hydrogen chloride, sulfur dioxide, and the refrigerant fluorocarbons. Liquid are also dried, and the list includes kerosene, aromatics, gasoline fractions, and chlorinated hydrocarbons.

2.4.2.2 Silica Gel

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

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

2.4.2.3 Activated Carbon

The structure of activated carbon consists of elementary microcrystallites of graphite, but these microcrystallites are stacked together in random orientation and it is the spaces between the crystals 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. The surface of carbon is essentially nonpolar although a slight polarity may arise from surface oxidation. As a result, carbon adsorbents tend to be hydrophobic and organophilic. Two distinct types of activated carbon are recognized commercially. Liquid-phase, or decolorizing, carbon are generally light, fluffy powders that exhibit surface areas of about 300 m^2/g. Gas- or vapor-phase carbons are hard granules or formed pellets that exhibit surface areas from 800 to 1200 m^2/g.

Liquid-phase activated carbons are used primarily for decolorizing and deodorizing aqueous solutions. This is due to their affinity for organic compounds in the presence of water. The largest application for vapor-phase activated carbons is solvent recovery and deodorizing air in ventilation systems.

2.4.2.4 Molecular Sieve Zeolites

Molecular-sieve zeolites are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium, and calcium. Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions. This flamework structure contains channels or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange. The water may be removed reversibly, generally by the application of heat, which leaves the same a crystalline host structure permeated by micropores. The structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure, represented by

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \, . \, wH_2O$$

Where n is the valence of cation M, w is the number of water molecules per unit cell, x and y are the total number of tetrahedral per unit cell. Many new crystalline zeolites have been synthesized, and several fulfill important functions in the chemical and petroleum industries. The most important molecular sieve zeolite adsorbents are the synthetic Type A, Type X, Type Y, synthetic mordenite, and their ion-exchanged variations, and the mineral zeolites, chabazite, and mordenite. The molecular sieve zeolite are distinct from other three major adsorbents in that they are crystalline and that adsorption takes place inside the crystals, the access to which is limited by the pore size.

Separation may be based on the molecular-sieve effect or may involve the preferential or selective adsorption of one molecular species over another. These separations are governed by several factors.

1. The basic framework structure, or topology, of the zeolite determines the pore size and the void volume.

2. The exchange cations, in terms of their specific location in the structure, their population or density, their charge, and size, affect the molecular-sieve behavior and adsorption selectivity of the zeolite. By changing the cation types and number, one can tailor or modify with in certain limits the selectivity of the zeolite in a given separation.

3. The cations, depending on their locations, contribute electric field effects that interact with the adsorbate molecules.

4. The effect of the temperature of the adsorbent is pronounced in cases involving activated diffusion.

Some typical molecular dimensions are shown in Figure 2.3 based on the Lennard-Jones potential function.

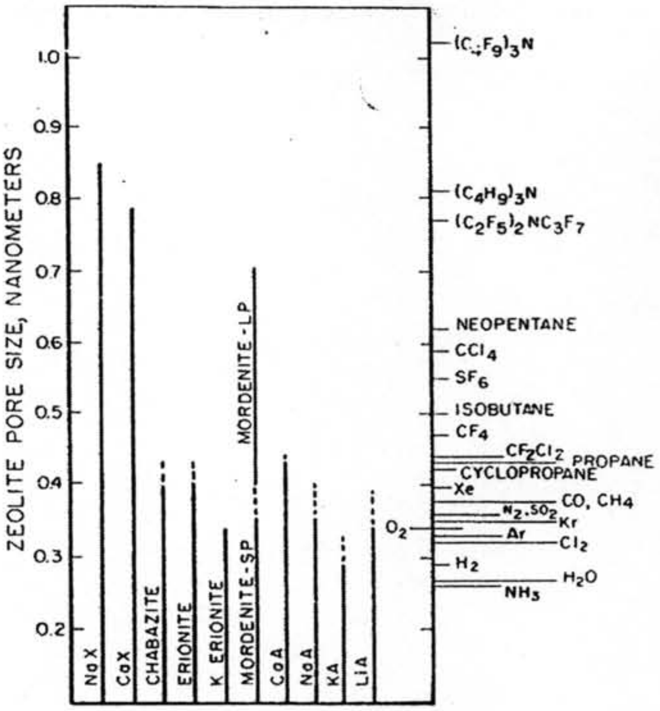


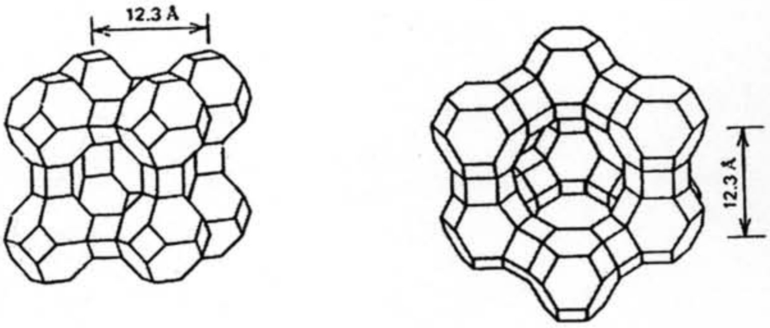
Figure 2.3 Effective pore sizes of various zeolites over temperature of 77-420 K

- Zeolite A

The pseudo cell consists of eight β cages (or sodalite cages) located at the corners of a cube and joined through four-membered oxygen rings (S4R). This arrangement forms a large polyhedral α cage of the free diameter about 11.4 A° accessible through eight-membered oxygen windows. Stacking these units in a cubic lattice gives a three-dimensional isotropic channel structure, constricted by eight-membered oxygen rings. The framework structure is shown in Figure 4(a).

Each pseudo cell contains 24 tetrahedral (AlO_2 or SiO_2) units and as the Si/Al ratio in zeolite A is always close to 1.0 and there are 12 univalent exchangeable cations per cell. Three distinct cation sites have been identified; neat the centers of the six-rings in the eight corners of the central cavity (type I), in the eight-rings (type II), and on the cage wall in close proximity to a four-ring (type III). With most cations the type I sites are preferentially occupied, followed by the type II sites, and the type III sites are filled only after all sites of type I and II have been occupied. In the sodium form (4A), there are 12 cations per cage. These are accommodated in the eight type I sites and the three type II sites (the six eight-rings are each shared between two cages) with one cation in a type III site. All windows are therefore partially obstructed by a sodium cation and the effective aperture of the sieve is therefore reduced from about 4.4 to 3.8 A°. If the Na^+ cations are exchanged for Ca^{2+} or Mg^{2+}, the number of cations per cell decreases. At 67 % exchange, there are only eight cations per cell and all these can be accommodated in the type I sites. Thus in Ca^{2+} or Mg^{2+} form (5A) the effective aperture is increased and somewhat larger molecules can penetrate.

Since the diameter of the potassium ion is greater than that of sodium, a sieve with a smaller effective aperture (3A sieve) is obtained by potassium exchange. The 3A sieve is widely used for drying reactive hydrocarbons such as olefins since the small pore size prevents penetration of the lattice and thus the possibility of reaction.



(a) (b)

Figure 2.4 Framework structure of (a) zeolite A, (b) zeolite X and Y

- Zeolites X and Y

The synthetic zeolites X and Y and the natural zeolite faujasite all have the same framework structure which is sketched in Figure 4(b). 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 equivalently as 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 rings of free diameter 7.4 Å. The difference between the X and Y sieves lies in the Si/Al ratio which is with in the range 1-1.5 for X and

1.5-3.0 for Y. There is a 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 both on the nature and number of the cations and is affected by the presence of traces of moisture. The adsorptive properties of X and Y sieves may therefore be greatly modified by ion exchange.

- Modenite

The framework structure of modenite, which can be considered as built up from stacked T_8O_{16} units, as shown in Figure 5. The Si/Al ratio in both natural and synthetic forms is generally close to 5.0 but the aluminium content of the framework may be decreased substantially by acid leaching without significant loss of crystallinity. The channel structure of mordenite is unidimensional with blind side pockets. The main channel, which is formed from twelve-membered oxygen rings, has a nominal free diameter of 6.7-7.0 Å. However, natural modenite behaves as a small-port zeolite. This appears to be due to blocking of the main channels by extraneous materials. The sieve may be opened by controlled acid leaching which evidently removes some of the detrital material from the channels.

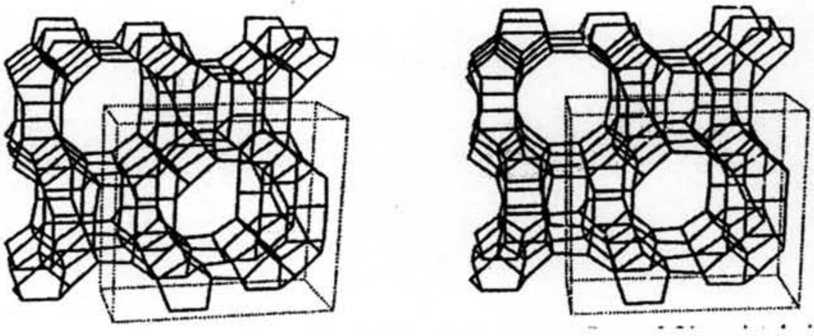


Figure 2.5 Modernite structure

- Pentasil Zeolites

The pentasil zeolite comprises a family of silica-rich zeolite with structures based on the double five-ring unit. The structure of a characteristic layer of a pentasil zeolite is shown in Figure 6. The channels are characterized by a ten-membered oxygen ring of free diameter about 6 Å, which is intermediate between the small-port sieves with 8-ring channels and the large-port sieves with 12-ring channels. The Si/Al ratio is typically about 30 but wide variation is possible and the structures may be prepared in essentially aluminum-free form. The aluminum-free form of ZSM-5 is often referred to as silicalite.

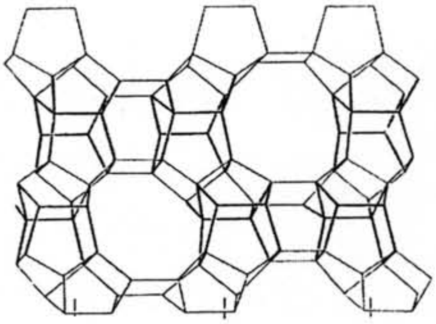


Figure 2.6 One layer of a pentasil zeolite structure

2.4.3 Adsorbents and Selectivity for Sulfur Compounds

In a past few years, there were a lot of researches which concentrated on the removal of sulfur compounds from transportation fuels. The interesting process is adsorption due to it can be operated at ambient temperature and pressure. However, success would depend on the development of a highly selective sorbent with a high sulfur capacity. Many materials have been reported as sorbents such as activated carbon, activated alumina, silica-based sorbents, zeolites and metal exchanged impregnated activated carbon/zeolites/mesoporous materials. McKinly *et al.* (2003) studied the removal of sulfur compound in model diesel comprising DBT and 4, 6-DMDBT by using silver-loaded mesoporous materials as sorbents. They found that the sorption capacity was substantially low. Kim *et al.* (2006) showed that the adsorptive capacities based on the adsorbent weight increase in the order of activated alumina < Ni/SiO_2-Al_2O_3 < activated carbon for total sulfur. Ma *et al.* (2005a) studied adsorptive desulfurization of model gasoline and a real gasoline over a nickel-based adsorbent Ni-Al. They found that nickel-based adsorbents show high selectivity and considerable capacity for sulfur removal and the performance can be improved by increasing the temperature to 200°C. The performance can be decreased by the presence of olefins. From their experiments, the sulfur adsorption capacity of these sorbents is relatively low. Thus, there are some researches pay attentions to zeolites that can give better properties for desulfurization. Ng *et al.* (2005) compared the performance for removal of thiophenic sulfur compounds such as T, BT, DBT and 4, 6-DMDBT in a hexadecane using NaY, USY, HY and 13X zeolites. It has been investigated by flow calorimetry technique. They found that NaY has the highest sorption capacity for the sulfur compounds. King *et al.* (2000) found that ZSM-5 selectively adsorbed thiophene over toluene and p-xylene but the capacities were low. Chansa (2003) studied the adsorption of sulfur compounds by using NaX and NaY zeolites. The sulfur compounds comprise 3-MT and BT in simulated gasoline and DBT in simulated diesel. In simulated gasoline, NaX zeolite showed 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) studies the continuous liquid adsorption of sulfur compound 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.

Recently, many researchers attempt to develop a new adsorbent which adsorb sulfur compounds via π-complextion bonding because their bonds are stronger to adsorb sulfur compounds than van der Waals interaction, but it is ease to regenerate by using only increasing temperature or decreasing pressure. 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 dentrimental effect on the desulfurization capacity. Xue *et al.* (2005) studied the adsorption of the TP and 1-BTP in a model gasoline by a batch method using ion-exchanged metal like Ag^+, Cu^{2+}, and Ce^{3+} with NaY-zeolites. The sulfur loading increased in the order CuY-zeolite (Na) < AgY-zeolite (Na) < CeY-zeolite (Na) for both the organic sulfur compounds. Takahashi *et al.* (2002) studied vapor-phase adsorption isotherms between benzene/thiophene and sorbents. It is 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-Maldonado *et al.* (2005) produced the sorbents obtained by ion exchanging zeolites with Cu^+, Ni^{2+} or Zn^{2+} cations by using various techniques such as vapor phase (VPIE), liquid phase (LPIE) and solid-state (SSIE) ion exchange for desulfurization of diesel, gasoline and jet fuels. They found that the desulfurization performance decreases as follows: Cu(I)-Y (VPIE) > Ni(II)-Y (SSIE) > Ni(II)-X (LPIE) > Zn(II)-X (LPIE) > Zn(II)-Y (LPIE). Yang *et al.* (2001) found that the relative strengths of the π-complexation bonds follow the orders thiophene > benzene and $Cu^+ > Ag^+$. Ma *et al.* (2005b) compared the adsortion 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 indicates that aromatics and olefin mixed in the real gasoline might strongly compete with the adsorption of thiophenic sulfur compounds by π-complexation.

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 desulfurization by π-complexation with Cu(I)-Y zeolite. The relative inhibition effects were found to follow the order: carbazole > quinoline > phenanthrene > fluorine ≈ naphthalene.

To improve the desulfurization capacity of zeolites, layered bed was applied by using various materials. The layered bed will adsorb some components that compete with sulfur compounds to form π-complexation bonding. Hernandez-Maldonado *et al.* (2004c) observed the desulfurization of a commercial diesel fuel by different nickel(II)-exchanged zeolites and different preparation (solid-state (SS) ion-exchange and liquid-phase (LP) ion-exchange). The total sulfur adsorption capacity followed the order: Selexsorb CDX (alumina)/Ni(II)-Y(SSIE-500) > Selexsorb CDX (alumina)/Ni(II)-X (LPIE-RT) > Ni(II)-Y (SSIE-500) > Ni(II)-X (LPIE-RT) > Ni(II)-Y (LPIE-135). Hernandez-Maldonado *et al.* (2004b) studied the desulfurization of a commercial jet fuel by vapor phase ion exchange (VPIE) Cu(I)-Y adsorbents. The total sulfur adsorption capacity followed the order:

Selexsorb CDX < Cu(I)-Y (VPIE) < Selexsorb CDX/Cu(I)-Y (VPIE). Hernandez-Maldonado *et al.* (2004a) improved the adsorption capacity of sulfur compound by using a layer bed consisting of activated carbon (AC) and/or activated alumina (Selexsorb CDX). From their experiment, AC/CDX/Cu(I)-Y zeolite shows the highest capacity followed by AC/Cu(I)-Y, CDX/Cu(I)-Y, which are nearly the same amounts, and Cu(I)-Y zeolite.

2.4.4 Regeneration of Adsorbents

Desorption or regeneration step is quite important in the overall process. First, desorption allows recovery of adsorbates in those separations where they are valuable; and second, it permit reuse of the adsorbent for further cycles. In a few cases, desorption is not practical, and the adsorbate must be removed by thermal destruction or another chemical reaction, or the adsorbent is simply discarded. Kaewboran (2005) investigated the desorption of NaX after desulferized the sulfur compounds such as 3-MT and BT in simulated gasoline and DBT in simulated diesel by heating technique at 400°C. She found that this method is not proper for DBT but 3-MT and BT. In addition, the recovered adsorption capacity of NaX that adsorbed with BT was a slightly lower than 3-MT. Xue *et al.* (2005) found that the regeneration of CeY-zeolite (Na) was accomplished by calcining at 450°C in air for 2 hours. More than 90% of that of the first adsorption was recovered. Hernandez-Maldonado *et al.* (2004) regenerated the layered adsorbents by using two techniques. In regeneration of AC/Cu(I)-Y zeolite by using solvents, the CCl_4 showed the highest capacity recovery when compared with DMF, methanol and toluene. When regenerated by flowing air at 350°C for 6 hours followed by autoreduction, the CDX/Cu(I)-Y can be fully regenerated while the AC/Cu(I)-Y can recover only 85%. Hernandez-Maldonado *et al.* (2004) reported that the regeneration of Ni(II)-Y (SSIE-500) was achieved by calcination in dry air at 350°C for 6 hours. Hernandez-Maldonado *et al.* (2004) demonstrated that Selexsorb CDX Cu(I)-Y (VPIE) was regenerated by using air at 350°C followed by reduction of the copper species in helium.

2.5 Adsorption in the presence of supercritical fluid in separation technology

In the past decade, supercritical fluids have widely developed in many areas due to their properties which are gas-like transportation properties and also enhancing solvating power when compressed to conditions above critical point. The critical region for a pure component is illustrated in Figure 2.7 as P-T diagram and some properties of supercritical fluid compared with gas and liquid at ambient conditions are shown in Table 2.4.

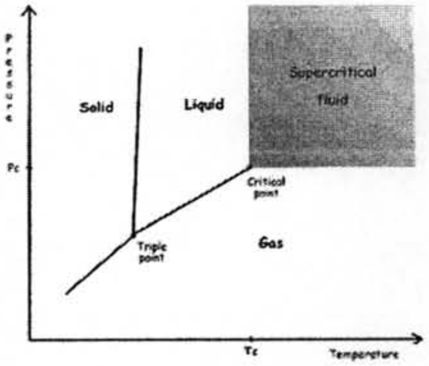
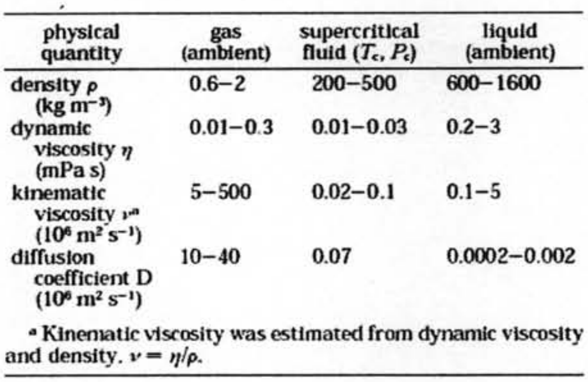


Figure 2.7 P-T diagram for the pure component

Table 2.4 Comparison of physical properties of liquids, gases and supercritical fluids in the near critical region (Baiker, 1999)



physical quantity	gas (ambient)	supercritical fluid (T_c, P_c)	liquid (ambient)
density ρ (kg m^{-3})	0.6−2	200−500	600−1600
dynamic viscosity η (mPa s)	0.01−0.3	0.01−0.03	0.2−3
kinematic viscosity ν^a (10^6 m^2 s^{-1})	5−500	0.02−0.1	0.1−5
diffusion coefficient D (10^6 m^2 s^{-1})	10−40	0.07	0.0002−0.002

[a] Kinematic viscosity was estimated from dynamic viscosity and density. $\nu = \eta/\rho$.

As seen in Table 2.4, the physical properties of supercritical fluid are intermediate between gases and liquids phase. The combination of enhancing solvating power in liquid-like properties and mass transfer in gas-like properties makes supercritical fluids to be attractive in many applications as solvent. Information of critical temperature, pressure and density of supercritical fluids used frequently is listed in Table 2.5.

Table 2.5 Critical Data of various solvent frequently used (Baiker, 1999)

solvent	T_c, °C^a	P_c, MPa^a	ρ_c, kg m$^{-3\,b}$
sulfur hexafluoride (SF_6)	45.5	3.77	735
nitrous oxide (N_2O)	36.4	7.255	452
water (H_2O)	373.9	22.06	322
ammonia (NH_3)	132.3	11.35	235
carbon dioxide (CO_2)	30.9	7.375	468
methanol (CH_3OH)	239.4	8.092	272
ethane (C_2H_6)	32.2	4.884	203
ethene (C_2H_4)	9.1	5.041	214
ethanol (CH_3CH_2OH)	240.7	6.137	276
propane (C_3H_8)	96.6	4.250	217
propene (C_3H_6)	91.6	4.601	233
1-propanol ($CH_3CH_2CH_2OH$)	263.6	5.170	275
2-propanol ($CH_3CH_2(OH)CH_3$)	235.1	4.762	273
xenon (Xe)	16.5	5.84	1110

[a] The number of digits given indicates the estimated accuracy of this quantity. [b] Although values for the critical density are given to three decimal places, they cannot be assumed accurate to better than a few percent

Among solvents, CO_2 is the most widely used due to its convenient critical temperature, cheapness, chemical stability, non-flammability, stability in radioactive applications, and non-toxicity (Clifford, 2002).

2.5.1 Adsorption Process in the Presence of Supercritical Fluid

In the past decade, there are many attempts by numerous industrial and academic researches to study the adsorption in the presence of supercritical fluid. Because of their ease of controlling the physical properties by minor adjustment in pressure and temperature, the supercritical fluid was widely applied in various adsorption processes. Thus, the great understanding of adsorption behavior in the presence of supercritical fluid was leading to the accuracy in determining the amount of adsorption loading.

2.5.1.1 Solubility

Solubility data is an important factor in study the adsorption in the presence of supercritical fluid. Accurate solubility information was leading to high precision in determining the adsorption capacities of solute in supercritical fluid. Pressure and temperature were the main parameters in controlling the solubility. An example that illustrated the correlation between pressure, temperature and solubility was the consideration of solubility behavior of solid naphthalene in supercritical CO_2 (Iwai *et al.*, 1993). Figures 2.8 and 2.9 showed the variation of the density of pure component CO_2 and solubility behavior of solid naphthalene in supercritical CO_2.

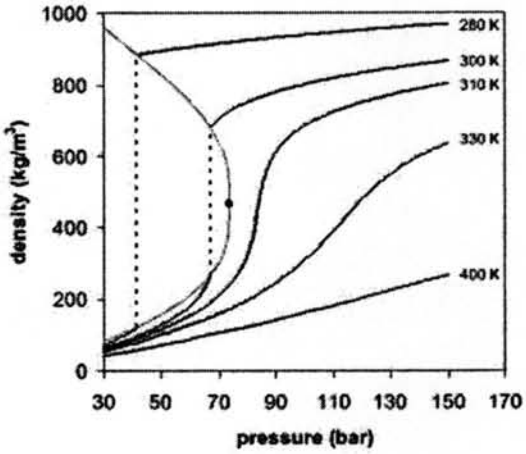


Figure 2.8 Variation of the density of a pure component CO_2 [http://en.wikipedia.org]

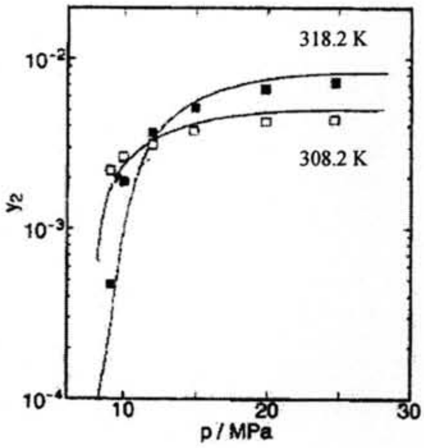


Figure 2.9 Solubility behavior of naphthalene in supercritical CO_2 (Iwai *et al.*, 1993)

As the same reason of solubility behavior of solid naphthalene in supercritical ethylene described by McHUGH and Krukonis (1986), at T=308.2 K, the solubility of naphthalene dramatically increases when pressure was about 8 MPa (79 bar) and levels off to constant value at higher pressure. This behavior is matched with the change of density in this range of pressure which exhibited liquid-like density. Thus, it can be pointed out that the solvent behavior of CO_2 is related to the density in the transition region. At T=318.2 K, the gross increase in solubility occur at pressure above 8 MPa and it can be interpreted by the rapid change of densities occurred at higher pressure when temperature increased. Also, the higher solubility of naphthalene in supercritical CO_2 at T=308.2 K at higher pressure is due to the competing effect of densities and increasing in solid sublimation pressure.

As can be seen that pressure and temperature affected to the solubility, the investigation of these behavior has been studied by many researchers in various systems. Elizalde-Solis and Galicia-Luna (2005) investigated the solubility of thiophene in carbon dioxide and they found that increasing pressure did not benefit the solubility of thiophene at subcritical conditions and constant temperature but it was marked change when the pressure was increased over the critical temperature. The solubility of DDT and 2,4-D was observed by Macnaughton and Foster (1994). They reported the crossover of temperature in supercritical region. Below crossover region, the solubility was directly proportional to the increasing of temperature due to the density dependence and they were in the reverse direction above crossover region because of the effect of vapor pressure of solute. This phenomenon was also reported by Clofford (2002). To adjust the solvate character of supercritical fluid, some substances were added to improve it.

- *Modifier* (Clofford (2002))

Modifiers or entrainers are the substances which added to a fluid substance to change its solvate character such as the decrease or increase in polarlity, aromaticity, chirality and the ability to further complex metal-organic compounds. For CO_2, which is the most popular supercritical fluid widely used in many application, it is also the substance to which modifiers are most frequently added. They are often added in 5 or 10 %vol, but sometimes may be up to 50%. They can have significant effects when added in small quantities and in these cases it may be the effect on surface processes rather than solvent character which is important. For example, the modifier may be effective in extraction by adsorbing onto surface sites, preventing the readsorption of the compound being extracted. The substances which are widely used as modifiers were listed in Table 2.6.

Table 2.6 Substances which are useful modifiers in carbon dioxide

Substance	T_c (K)	P_c (bar)
Methanol	513	81
Ethanol	514	61
1-Propanol	537	51
2-Propanol	508	48
2-Butanol	536	42
Acetone	508	47
Acetonitrile	546	48
Acetic acid	593	58
Diethyl ether	467	36
Dichloromethane	510	63
Chloroform	536	54
Hexane	508	30
Benzene	562	49
Toluene	592	41
Trimethyl phosphate	742	24

There are some literatures that reported the effect of modifiers to solubility. Elizalde-Solis and Galicia-Luna (2005) observed that addition of 1-propanol in small amounts to thiophene and supercritical CO_2 did not enhance the solubility of thiophene against supercritical CO_2 but solubility was improved when adding more 1-propanol up to 6.5 mol%. The effect of adding water to supercritical CO_2 was noted by Macnaughton and Foster (1994). They found that addition of water into supercritical CO_2 had an adverse effect to solubility of DDT due to slightly increasing in density. Contrastingly, the solubility of polar 2,4-D was dramatically increased from the strong interaction with water.

2.5.1.2 Effect of pressure and temperature to adsorption loading

As seen in section 2.4.1.1, there are many factors affected to solubility which mainly depend on temperature and pressure. Thus, the effect of these parameters to the adsorption capacities was discussed in various adsorption processes by many researchers. Shojibara *et al.* (1995) showed that the equilibrium adsorption loading of benzene on activated carbon in the presence of supercritical CO_2 decrease with increasing in pressure in supercritical region. It is contributed to the increasing in density of supercritical CO_2 which related to higher solubility between benzene and supercritical CO_2. Chou *et al.* (1997) agreed with these results and they also compared the benzene loading of their results with Lai and Tan (1993) who studied the adsorption of toluene on activated carbon. They found that the amount of adsorption of benzene was less than toluene about 40% and they claimed that it was due to a higher extraction capacity of benzene in CO_2. Lee *et al.* (1996) studied the effect of pressure and temperature to adsorption equilibrium constant of toluene and naphthalene on silica gel. The adsorption equilibrium constant decreases with increase in pressure or decrease in temperature of adsorption. It is due to the rapid change in physical properties in transition region. Harikrishnan *et al.* (1998) studied the adsorption of ethyl benzene on activated carbon in the presence of supercritical fluid CO_2 and a frontal analysis technique was used in adsorption process. They found that the amount of adsorption loading can be controlled by temperature and pressure in the adsorption process. The crossover effect was also observed in this experiment. At low pressure, the adsorption loading of ethyl benzene decreased with increasing temperature but the influence of adsorption loading became reversed at high pressure (in supercritical fluid region). It was indicated that the rapidly change of density in supercritical fluid region, which is caused by the effect of temperature, was the factor in determining the adsorption loading. This phenomenon agrees with the results from adsorption of benzene (Yan and Yang, 2004), toluene (Tan and Liou, 1990) in supercritical CO_2 on activated carbon as well as adsorption of supercritical CO_2 on activated carbon (Hamayun *et al.*, 2000). Macnaughton and Foster (1995) investigated the supercritical adsorption behavior of DDT on activated carbon by using CO_2. They observed that increasing in isochoric temperature (densities were fixed) result in lowering in amount of loading on activated carbon. It was confirmed by Lucus et al. (2004) and Tan and Liou (1990)'s experimental results in adsorbing ethylacetate as well as furfural and toluene, respectively, from supercritical CO_2 on activated carbon.

In the experiment of Iwai *et al.* (1994), the observed the effect of pressure in separating isomeric dimethylnaphthalene like 2,6- and 2,7-Dimethylnaphthalene in supercritical CO_2 and in liquid octane. The temperature was fixed and various types of zeolite were used as adsorbent. From their results, high separation efficiency and low amount of adsorption were obtained above supercritical pressure compared with at lower pressure and in liquid octane. Next, Uchida et al. (1997) extended their work by increasing the temperature in adsorption and they found that the higher separation efficiency and lower adsorption loading of these two isomeric dimethylnaphthalene can be obtained at lower temperature. As observed by Iwai *et al.* (2003), the reduction of amount of loading of two isomeric isomers on NaY zeolite with increasing total pressure was greater than the change of solubility in supercritical fluid CO_2. From the adsorption isotherms of CO_2 in their experiment, the surface excess amount of CO_2 display a plateau near the critical pressure which caused by the rapid change in density at transition region. Afterward, it becomes decrease and levels off to constant value. Thus, it can be implied that at high pressure, the density of CO_2 in the pore increases with increasing in the bulk density of CO_2. The result of adsorption of CO_2 also supported by Gao *et al.* (2004) and Chen *et al.* (1997) who study the adsorption of CO_2 on NaY zeolite and on activated carbon, respectively. According to the adsorption behavior of CO_2, a competitive adsorption of CO_2 with isomeric DMN may occur when increasing total pressure.

2.5.2 Desorption Process in the Presence of Supercritical Fluid

Due to their powerful properties of supercritical fluid as desorbent, the applications of supercritical fluid in regeneration of adsorbents were widely developed by many researchers. Also, their physical properties can be controlled by adjusting only temperature or pressure. Therefore, the effect of process variables such as pressure, temperature and flow rate of supercritical fluid was investigated by various researchs.

2.5.2.1 Effect of pressure and temperature

There are many researchers who investigated the effect of pressure and temperature in tuning the physical properties of supercritical fluid affected to the desorption amount. Tan and Liou (1989) observed that lower temperature and higher pressure were favorable in desorption of benzene and toluene from activated carbon due to higher density and another literature in desorbing DDT from activated carbon (Macnaughton and Foster, 1995) also supported this experiment They also found that increasing in isochoric temperature result in increasing in amount of desorption. Srinivasan *et al.* (1990) demonstrated that the regeneration of activated carbon was depended on many factors. In the temperature effect, desorption capacities highly depend on the temperature at lower pressure above critical pressure but it becomes less temperature dependence at higher pressure. This phenomenon was described by the density changes which were significantly different with temperature at low pressure and less apparent at higher temperature.

Tan and Liou (1989) reported that adsorptive capacities in adsorbing benzene and toluene were dropped about 15% from virgin activated carbon after the first cycle of regeneration and it becomes stable after followed cycles. It was also observed by Tan and Liou (1988) in desorbing ethyl benzene from activated carbon. It is due to there are some sites which strongly interact with solute and they cannot be regenerated by using supercritical CO_2 as claimed by McHUGH and Krukonis (1986). From their experiment, they noted that the density effect becomes important at low pressure which enhances solubility of solute in supercritical fluid but the viscosity affected to mass transfer was also an additional factor at higher pressure. Madras *et al.* (1993) investigated that the amount of supercritical CO_2 requirement in regenerating the activated carbon is significantly higher than that predicted by solubility of solute in supercritical CO_2. They concluded that solubility does not represent the desorption profile and the limitation of desorption was limited by adsorption equilibrium.

2.5.2.2 Effect of flow rate of supercritical fluid

Effect of flow rate of supercritical fluid in desorbing solute from supercritical fluid was studied to investigate effect of the mass transfer in desorption. Tan and Liou (1989) investigated the effect of flow rate of supercritical CO_2 in desorption of benzene and toluene from activated carbon by fixing time. They indicated that interphase mass-transfer resistant plays an crucial role in regeneration. From their results, they showed that increasing in flow rate of supercritical CO_2 results in increase in rate of desorption as well as desorption amount. These results agreed with the experiment of Srinivasan *et al.* (1990), Tan and Liou (1988, 1995).

2.5.3 Potential of Supercritical Fluid in Separating Sulfur Compounds from Transportation Fuels

From the literature review of many researchers in adsorption and desorption in the presence of supercritical fluid, the potential of supercritical fluid in separating sulfur compounds from transportation fuels will be discussed. Carbon dioxide which wildly used in many applications will be applied because of their convenient critical temperature and non-toxicity. The enhancement of separation efficiency when supercritical fluid is presented was due to the fact that the organic compounds have different solubility with supercritical CO_2. Therefore, the two factors affected to separation efficiency were the difference in affinity between adsorbate and adsorbents and the difference in solubility in supercritical CO_2. The former is the characteristic of adsorbents in adsorbing adsorbates and the latter can be controlled by operating parameters such as pressure and temperature. Although the dropping in adsorption capacities is because of the competition in adsorption between adsorbate and supercritical CO_2, there are some interests in higher separation efficiencies. The low separation efficiencies can be faced in conventional adsorption in separating benzene compounds and thiophenic compounds because their similarity of structure.