



## CHAPTER II BACKGROUND AND LITERATURE SURVEY

### 2.1 Sulfur Compounds in Petroleum Refining

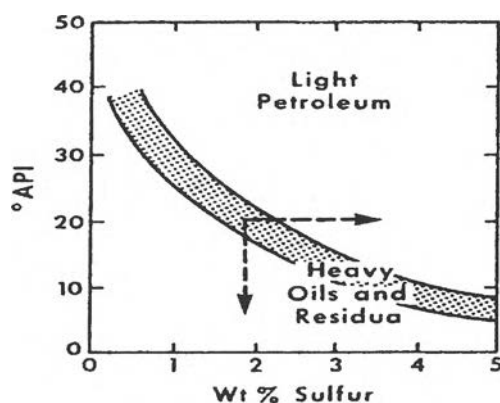
Sulfur compounds are the most influential heteroatomic components that found in crude oils (Table 2.1). Total sulfur in crude oils can vary from 0.04%w/w for light crude oils to about 8.0%w/w for heavy crude oils. In addition, the total amount of sulfur compounds depends on the sources of crude oils that are different substrates to from crude oil (Wauquier, 1995). In general, the higher density of crude oil for the lower API gravity of crude oil, the higher sulfur content (Figure 2.1).

**Table 2.1** Some characteristics of crude oils

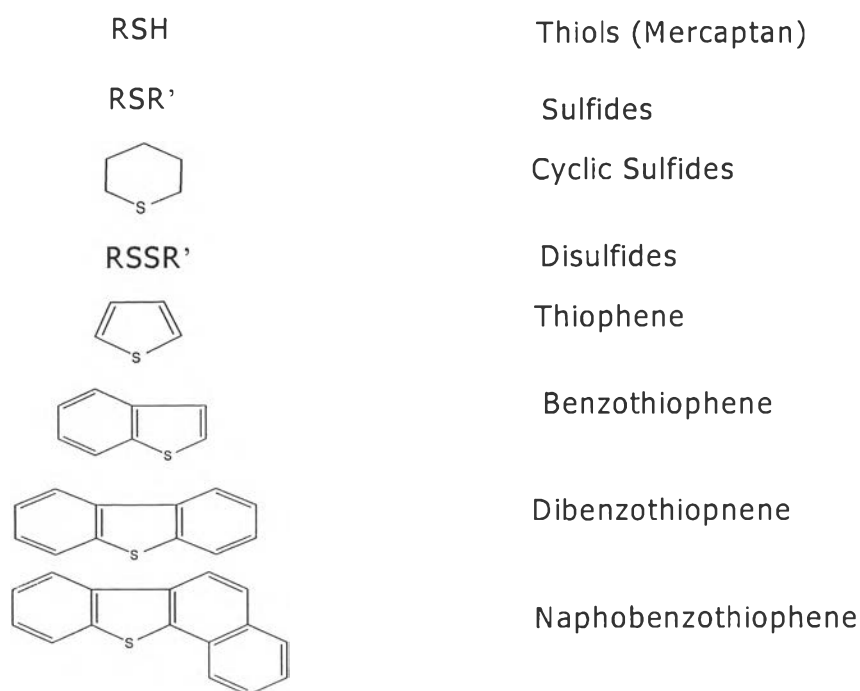
Crude oil	origin	Visc. mm <sup>2</sup> /s	Asph. wt.%	O wt.%	N wt.%	S wt.%	Ni ppm
Batiraman	Turkey	1180	22.1	0.53	0.49	7.04	99
Boscan	Venezuela	595	14.1	0.79	0.74	5.46	125
Lacq.sup.	France	81.7	13.2	0.57	0.42	4.94	19
Chauvin Source	Canada	28	6.0	0.48	0.66	2.80	35
Bellshill Lake	Canada	7.9	2.2	0.34	< 0.3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

There are many varieties of sulfur compounds in crude oils both inorganic and organic forms such as elemental S, hydrogen sulfide H<sub>2</sub>S, carbonyl sulfide COS

as shown in Figure 2.2. However, the prevailing conditions during formation, maturation, and even in situ alteration may dictate only preferred types exist in any particular crude oils. Moreover the types of sulfur in crude oils 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.

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-trimethylbenzothiophen, 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. 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.

## **2.2 Treatment Technologies for Sulfur Compounds**

Currently, there are several processes and technologies available to reduce sulfur compounds in refining processes. Each process has different advantages, disadvantages, and limitations in removing sulfur compounds. In general, typical processes include hydrotreating, caustic process, acid process, and adsorption process. Among these processes, hydrotreating is the most important process nowadays (Speight, 2002).

### 2.2.1 Hydrotreating Processes

Hydrotreating processes, in particular the hydrodesulfuization of petroleum residua, are catalytic processes. Hydrocarbon feedstock and hydrogen are passed through a catalyst bed at elevated temperatures and pressures. Some of sulfur atoms attached to hydrocarbon molecules react with hydrogen on the surface of catalyst to form hydrogen sulfide (Speight, 2002). 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. 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 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 through put; where as 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.

### 2.2.2 Caustic Process

Treating of petroleum products by 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 distilled, 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 (Speight, 1999).

#### 2.2.2.1 *Lye Treatment*

The lye treatment is carried out in continuous treaters, which consist of a pipe containing baffles or other mixing devices into which the oil lye 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.

#### 2.2.2.2 *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 stripping tower. The nature and concentration of mercaptans to be removed dictate the quantity and temperature of process.

#### *2.2.2.3 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.

#### *2.2.2.4 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.

#### *2.2.2.5 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.

#### *2.2.2.6 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.

### 2.2.3 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, nitric 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 (Speight, 1999). 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.

## 2.3 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 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, there have been used adsorption processes in petroleum industry for long times ago. 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.

### 2.3.1 Adsorbents and Selectivity for Sulfur Compounds

There are several adsorbents that can adsorb sulfur species from transportation fuels and other petroleum products. In general, the typical adsorbents are activated carbon, zeolites, silica gel, and activated alumina. Different types of adsorbent show different selectivity and capacity 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. 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. Salem and Hamid (1997) showed that the capacity of 13X zeolite for sulfur compound was approximately an order of magnitude higher than ZSM-5. 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  $\approx$  activated carbon  $\gg$  Na-Y  $\gg$  H-USY  $\approx$  modified activated alumina. The sorbent capacities for thiophene at low pressure followed the order Cu-Y and Ag-Y  $\gg$  Na-ZSM-5 > activated carbon > Na-Y > modified alumina and H-USY. Hernandez *et al.* (2003) studied the desulfurization by using Cu-Y, Ag-Y, H-Y, and Na-Y in 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-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-Y showed the highest selectivity and capacity among the adsorbents studied.

### 2.3.2 Modification and Improvement of the Adsorbents

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. 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<sup>+</sup> and Ag<sup>+</sup>. On a per cation basis, more thiophene was adsorbed by Cu<sup>+</sup> than Ag<sup>+</sup>. 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<sup>+</sup> exchange was 100% complete but Cu<sup>+</sup> exchange was only 46% complete for Ag-Y and Cu-Y, respectively. Only half of Cu<sup>2+</sup> was automatically reduced to Cu<sup>+</sup> after heat treatment at 450 °C. Takahashi *et al.* (2001) measured pore volume by using nitrogen at 77K and found that a 25% reduction in pore volume in Ag-Y compared to Na-Y. Jiang *et al.* (2003) studied activated carbon treated with sulfuric acid for adsorption of sulfur compound. They found that the adsorption

capacities of activated carbon for dibenzothiophene in heptane reached the maximum after modification by concentrated sulfuric acid at 250 °C. The amount of dibenzothiophene adsorbed on the modified activated carbon was found to be approximately 2 times that of the unmodified activated carbon.

### 2.3.3 Subsequence Treatment and Regeneration

Subsequence treatment processes may be required for deep desulfurization since one unit may not be enough to lower the sulfur content in the fuels to the governed limits. For example, the subsequent treatment process may include: reaction and extraction of sulfur compound with added chemicals, and adsorption of remaining sulfur compounds and generated new sulfur compounds with added chemicals in liquid fuels. Shiraishi *et al.* (2002) studied the reaction of sulfur compounds in light oils, with chloramine T and then removes remaining sulfur compound by using aluminum oxide. Dibenzothiophene reacts with chloramine T to form corresponding sulfimide that dissolve in methanol. But benzothiophene reacts with chloramine T to form corresponding chlorine adduct products that dissolve in methanol as well. The reaction is suppressed by an increasing the concentration of aromatics. However, there are sulfimide of alkyl-substituted dibenzothiophene remaining in light oils since the polarity of that compound. These compounds are removed successfully by sequent adsorption with sorbents such as aluminum oxide.

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: increasing temperature, lowering total pressure, stripping with an inert gas, and displacing by desorbent. As a result, several research groups in this field have studied various ways to regenerate used sorbents to their original properties. 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.