CHAPTER 1

INTRODUCTION

Petroleum consists predominantly of various hydrocarbons but also contains lesser amounts of sulfur, nitrogen and oxygen in the forms of a variety of organic compounds. Of these impurities, sulfur compounds are generally the most prevalent and of most concern in refining. The sulfur content of a crude oil varies greatly with its origin. The highly paraffinic crude from North Africa (Libya, Algeria) and from Nigeria and Indonesia may have as little as 0.2 wt% sulfur and a very low metal content (for example, ~ 3 ppm). In the Near East a light Arabian crude may contain typically 1.5 wt% sulfur, and a Kuwait crude 2.5 to 4 wt% sulfur. The metal contents are of the order of 10 to 30 ppm. The sulfur content increases progressively with the boiling point of the fraction, as illustrated in Table 1.1 for a Kuwait crude.

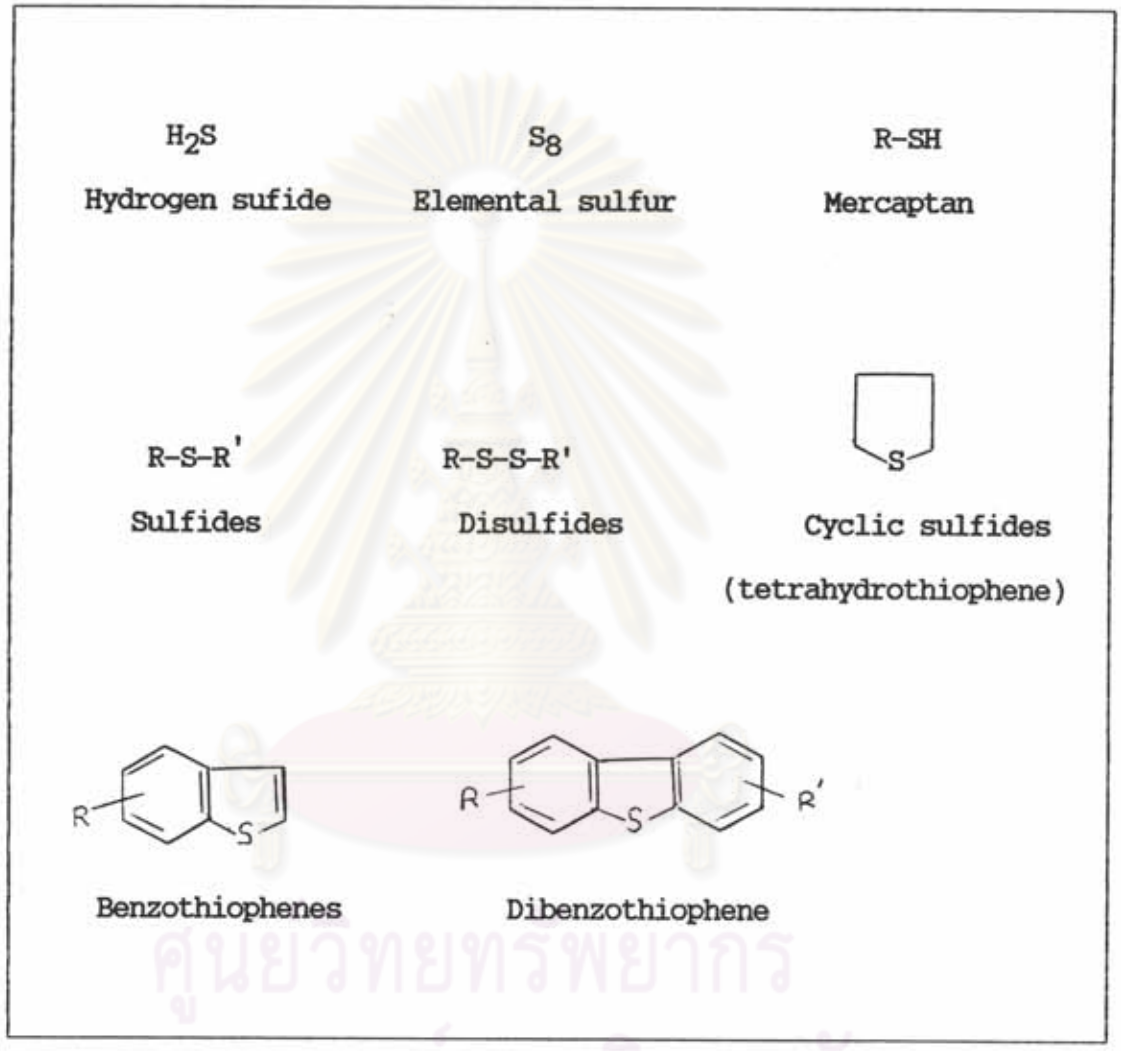
Not only do the sulfur contents of crude oils vary, but the relative amounts of various classes of sulfur compounds (Table 1.2) vary from crude to crude.

Table 1.1 Variation of sulfur content of a Kuwait crude oil with boiling point*

Fraction: boiling point range, ^{o}C (^{o}F)	Sulfur content wt%
Naphtha; C_4-150(300)	0.02
Kerosene; 150-230(300-450)	0.175
Furnace oil; 230-345(450-650)	1.23
Heavy furnace oil; 345-370(650-700)	2.37
Heavy gas oil; 350-550(660-1020)	2.91
Residue; >370(700)	4.22
Residue; >550(1020)	5.12

* F. W. B. Porter et al., British Patent 710,342,in Schuman and Shalit, 1970, p. 293

Table 1.2 Example of sulfur compounds in petroleum



Organic sulfur compounds occur in all crude oils. Hydrogen sulfide is also often present and sometimes there is trace of elemental sulfur. In the low-boiling fractions the principal sulfur compounds are organic sulfides or disulfides, mercaptans and thiophenes. In the high-boiling fractions sulfur is present largely in the form of thiophene derivatives such as benzo- and dibenzo-thiophenes. The nonheterocyclic sulfur compounds are less stable thermally, and they may react or be substantially decomposed during distillation.

Especially, in light petroleum products, such as liquefied petroleum gas, naphtha, gasoline and even kerosine, which are used as fuel in household, in the internal combustion engine and jet fuel, sulfur compounds are objectionable because of:

1. The potential to cause corrosion, the bad odor and the toxicity of light sulfur compounds.

2. The presence of sulfur compounds in gasolines tends to lower the octane number and also decrease the susceptibility of gasoline to octane number improvement by addition of tetraethyllead and tetramethyllead.

3. Sulfur poisons noble metal catalysts. In catalytic reforming of naphthas and in isomerization of C_4 to C_6 paraffins, the maximum acceptable sulfur content in the feed to a catalytic reformer is determined by the nature of the catalyst. Bimetallic reforming catalyst are especially sensitive, and the sulfur content must be limited to the vicinity of 1 ppm or less.

The techniques that are used for sulfur removal from hydrocarbons or hydrocarbon mixtures derived from petroleum or natural gas are called desulfurization. Three general techniques are used for sulfur removal as follows :

1. Catalytic hydrodesulfurization involves the reaction of sulfur compounds with hydrogen in the presence of a catalyst, resulting in their decompositon into hydrogen sulfide and hydrocarbon remnants of the original sulfur compounds. This is the most broadly applicable process for desulfurization.

2. Caustic treating, usually with aqueous sodium hydroxide, is widely practiced to remove mercaptan and organic acids from gasoline and occasionally from light distillates. Some processes combine caustic treating with air oxidation of mercaptans to convert them to disulfides. Such "sweetening" process eliminates the bad odor and corrosiveness associated with mercaptans without necessarily removing sulfur from the hydrocarbon stream being treated.

3. Adsorption on molecular sieves is widely used to remove sulfur compounds from natural gas and from light hydrocarbon streams such as propane, butane, pentane and even light gasolines. This process is effective for removing hydrogen sulfide and light mercaptans, sulfides and disulfides. It simultaneously dries the hydrocarbons and will also remove carbon dioxide from natural gas stream.

As indicated above, amine or caustic treating or molecular sieve adsorption is generally used to remove sulfur compounds from light hydrocarbon streams. Caustic treating or sweetening process is also useful for naphthas and kerosines. However, the very low sulfur

levels required in feedstocks for catalytic reforming can only be achieved by hydrodesulfurization.

In this work we want to study about hydrodesulfurization of light oils by using thiophene in toluene as the typical sample.

The scope of this work

1. To hydrodesulfurize thiophene in toluene using two self-prepared and , for comparison, one industrial catalysts and to select an effective catalyst for further investigation.

2. To investigate the effects of reaction conditions (space velocity , pressure , temperature) on the hydrodesulfurization of thiophene in toluene using the selected catalyst.

3. To obtain the suitable conditions for presulfidation of the selected catalyst.