

## **CHAPTER II**

### **BACKGROUND AND LITERATURE REVIEW**

#### **2.1 Overview of Diesel Fuel**

The diesel engine was invented in 1892 by Rudolph Diesel, who initially considered powered coal and liquid petroleum as possible fuels but coal was difficult to inject into the engine cylinder and can cause an explosion that destroyed the prototype engine. As a result, he turned to experiments with this liquid petroleum, which later became known as "Diesel Fuel". After that, Diesel sold a license of diesel engine to Adolphus Busch and Busch built the first commercial diesel engine to sell in the United State and Canada.

At the end of World War I, the diesel engine was developed to "semi-diesel" engine which used in truck in the 1930 by soldier who operated diesel engine in submarine. These truck was called "smokers" because of their dark, smoky emissions.

Diesel fuel is heavier and oilier than gasoline because of less refining so it is generally cheaper than gasoline. Diesel fuel also has a higher energy density than gasoline when compare in the same quantity.

#### **2.2 Composition of Diesel Fuel**

Diesel fuels consist of 3 compositions which are Saturate (paraffins and naphthenes), Aromatic hydrocarbons and Heteroatom-containing compounds but the former two are the main compositions. Their relative distribution depends on the feedstock and fuel processing schemes. It should be noted that refineries of oil companies generally vary the mix of hydrocarbons in the fuels they supply to suit the demand, climate and the season of the year. They include more components of low boiling range in cold climates and in winter, and conversely in hot weather.

### 2.2.1 Saturate Hydrocarbons

Saturate hydrocarbons are generally long-chain alkanes with carbon numbers in the range of C<sub>10</sub>-C<sub>20</sub> which are the major paraffinic components. Long-chain paraffins have excellent cetane number and show good combustion performance (Table 2.1), but higher-boiling n-alkanes tend to have higher cloud points and do not have good cold-flow properties.

**Table 2.1** Cetane number and auto-ignition temperature of hydrocarbons (Song *et al.*, 2000)

Compound	Carbon No.	Cetane No.	Auto-ignition T, °C
n-Octadecane	C18	103	235
1-Octadecane	C18	90	250
n-hexadecane	C16	100	202
1-hexadecane	C16	84	240
Heptamethylnonane	C16	15	472
n-Nonylbenzene	C15	50	N/A
n-Tetradecane	C14	96	202
1-Tetradecane	C14	83	235
n-Dodecane	C12	88,82	204
7-Dodecane	C12	71	N/A
3-Ethyldecane	C12	55	N/A
Dicyclohexyl	C12	47	245
4,5-diethyloctane	C12	23	N/A
2,2,4,6,6-			
Pentamethylheptane	C12	10	N/A
n-Hexylbenzene	C12	26	N/A
Diisopropylbenzene	C12	-12	N/A
n-Pentylbenzene	C11	8	N/A
1-Methylanphthalene	C11	0	529
n-Decane	C10	77	208

**Table 2.1** Continued

Compound	Carbon No.	Cetane No.	Auto-ignition T, °C
1-Decene	C10	60	235
Decalin	C10	42	250 (trans-D)
Tetralin	C10	N/A	384
n-Octane	C8	64	220
1-Octene	C8	40	230
n-Heptane	C7	56	223
Methylcyclohexane	C7	20	285

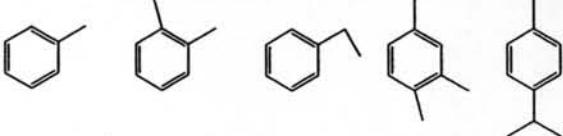
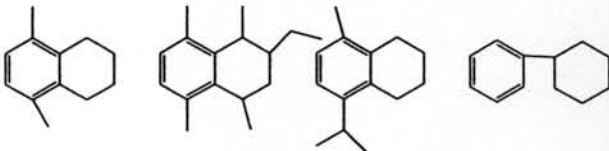
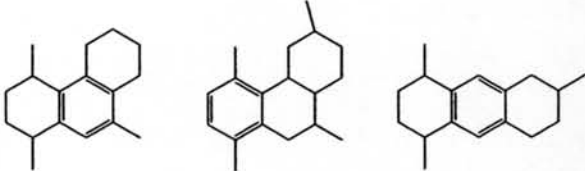
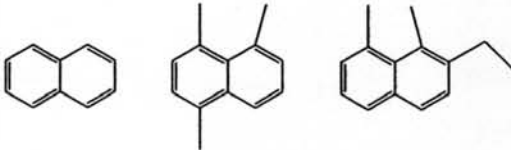
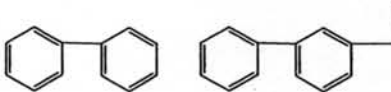
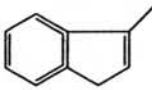
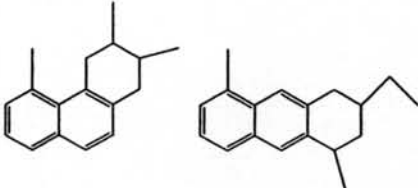
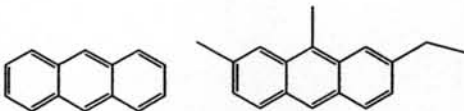
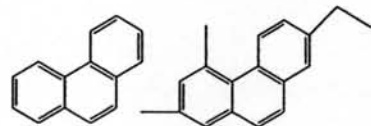
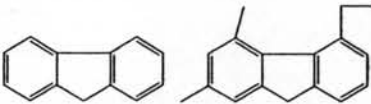
### 2.2.2 Aromatic Components

The aromatic compounds found in diesel fuels mainly fall into four groups: (i) monoaromatics, (ii) diaromatics, (iii) triaromatics, and (iv) polycyclic aromatics as shown in Table 2.2 (Stanislaus and Cooper, 1994). And the typical structures of these aromatics are shown in Table 2.3.

**Table 2.2** Aromatic compounds in Kuwait Atmospheric Gas Oil (Stanislaus *et al.*, 1994)

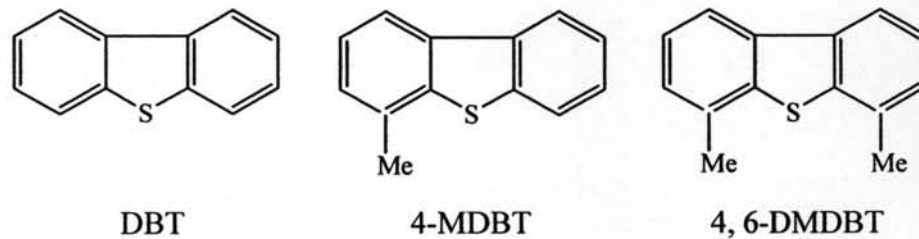
Aromatic type	Aromatic content (wt %)
1. Monoaromatics	
C <sub>3</sub> -C <sub>6</sub> alkyl benzenes	3.68
C <sub>1</sub> -C <sub>5</sub> benzothiophenes	14.24
2. Bicycloaromatics	
C <sub>0</sub> -C <sub>4</sub> naphthalenes	52.81
C <sub>0</sub> -C <sub>4</sub> dibenzothiophenes	14.38
C <sub>0</sub> -C <sub>4</sub> fluorenes	4.12
C <sub>1</sub> - benzyls+ dibenzofuran	4.07
3. Triaromatics	
C <sub>0</sub> -C <sub>4</sub> phenanthrenes	6.20
C <sub>0</sub> -C <sub>4</sub> pyrenes/fluoranthrenes	0.5
Total	100

**Table 2.3** Typical structures of some aromatic compounds present in petroleum fraction (Stanislaus *et al.*, 1994)

Aromatic Compound Type	Typical Structures
<b>1. <u>Monoaromatics</u></b>	
a) Alkyl Benzenes	
b) Benzocycloparaffins	
c) Benzodicycloparaffins	
<b>2. <u>Diaromatics</u></b>	
a) Naphthalenes and alkyl naphthalenes	
b) Biphenyl	
c) Indenes	
d) Naphthlocycloparaffins	
<b>3. <u>Triaromatics</u></b>	
a) Anthracenes	
b) Phenanthrenes	
c) Fluorenes	

### 2.2.3 Heteroatom-Containing Compounds

Heteroatom compounds are sulfur, nitrogen and metal compounds. The main heteroatom compounds in diesel fuel are sulfur compounds which have higher weight and larger ring size than in gasoline due to higher boiling range of diesel fuel. Most sulfur compounds in diesel fuels are alkylated benzothiophene-type and dibenzothiophene-type species, as shown in Figure 2.1 (Song *et al.*, 2000).



**Figure 2.1** Structure of related polycyclic sulfur compounds found in diesel fuels.

## 2.3 Diesel Emissions

Diesel exhaust contains several pollutants that can be harmful to public health, alone or in combination with other substances. These include hydrocarbons, nitrogen oxides, fine particulate matter, carbon monoxide, and toxic air contaminants known as hazardous air pollutants.

### 2.3.1 Nitrogen Oxides (NO<sub>x</sub>)

Nitrogen oxides are by-products of fuel combustion and contribute to the formation of ground-level ozone or "smog," which is highly corrosive and damages crops and forests. Health effects include coughing, shortness of breath, and decreased lung function. Besides, NO<sub>x</sub> contribute to acid rain and to the acidification of lakes and soils. They can also affect aquatic ecosystems by providing too many nutrients to aquatic plant life, which reduces dissolved oxygen levels and can ultimately harm the ecosystem.

### 2.3.2 Fine Particulate Matter (PM<sub>2.5</sub>)

Fine particulate matter is the term used for the mixture of solid particles and liquid droplets in the air. Because of its small size, fine particulate matter can be deposited deep in the lungs, where it can cause health problems. Nitrogen oxides and sulfur dioxides are also major sources of fine particulate matter. Recent studies have shown an association between particulate matter and premature mortality from respiratory and cardiovascular disease, and increased incidence of respiratory illness, particularly in children and the elderly. For adults with heart or lung conditions, exposure to fine particulate matter can cause more illness and, in some cases, premature death. More than 90 percent of the particulates found in diesel exhaust are fine particles and they are the major cause of poor visibility and haze in many parts of the United States and the world. Air pollution, largely due to particulate matter, has reduced visibility in some areas from 90 miles to only 14 to 24 miles. Visibility has been affected in urban centers and in scenic rural areas as well. Fine particulate matter can remain suspended in the air for days and can travel long distances.

### 2.3.3 Hydrocarbons (HC)

Hydrocarbons are formed by incomplete fuel combustion. When combined with NO<sub>x</sub> in the presence of sunlight, hydrocarbons can produce ground-level ozone or "smog," which can irritate eyes, damage lungs, and aggravate respiratory problems. Symptoms include coughing, shortness of breath, and decreased lung function. Many hydrocarbons are also considered hazardous air pollutants.

### 2.3.4 Carbon Monoxide (CO)

Carbon monoxide is formed by incomplete fuel combustion. Carbon monoxide reduces the flow of oxygen in the bloodstream and is of particular concern to people with heart disease.

### 2.3.5 Hazardous Air Pollutants (HAPs)

Diesel exhaust contains 40 substances that the U.S. Environmental Protection Agency lists as hazardous air pollutants - 15 of these are considered probable or known human carcinogens. Of greatest concern are acetaldehyde, benzene, 1,3-butadiene, formaldehyde, and polycyclic aromatic hydrocarbons (PAHs).

From the former information we found that the most deleterious part of diesel exhaust is black smoke, due to carbonaceous particulate matter (PM) and NO<sub>x</sub> formed from diesel fuel. The influence of fuel quality on pollutant emissions especially for PM and NO<sub>x</sub> from diesel engines can be summarized below:

PM: Increase with increasing sulfur content

Decrease with decreasing aromatic content

Increase with increasing fuel density

NO<sub>x</sub>: Decrease (generally) with decreasing aromatic content

Increase with increasing sulfur content

Nowaday, the environmental regulations in many countries, including Thailand, have been setting more and more strict standards for diesel emissions in exhaust gases. For example, Thailand recently limited sulfur content in diesel to 350 ppm, and will reduce the diesel standard further in 2012 to reach levels below 50 ppm (Table 2.4), so the new diesel fuel specifications, including a lower level of sulfur, aromatic content, and higher cetane number are demanded. High aromatic content in diesel fuel has been recognized for both lower fuel quality and the formation of undesired emissions in exhaust gases. In order to reduce the harmful emission from exhaust gases, the amount of particulate matter (PM) emissions in diesel can be reduced by decreasing the sulfur and aromatic content of the fuel which raises the cetane number (Navarro *et al.*, 2000). In addition, the quality of diesel fuel, generally shown as cetane number (CN), decreases with increasing aromatic compounds (Rojas *et al.*, 2003).

As a result of the stringent environmental regulations, lowering the aromatic content in diesel fuel by aromatic hydrogenation is becoming one of the most important technologies in the petroleum refining industry.



**Table 2.4** Current and proposed sulfur levels in diesel in Asia, EU and USA  
([http://www.gtz.de/de/dokumente/en\\_4a\\_CFVT.pdf](http://www.gtz.de/de/dokumente/en_4a_CFVT.pdf))

	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Bangladesh							5,000										
Cambodia					2,000												
Hong Kong, China		500					50										
India	5,000				2,500					500					350		
Indonesia	5,000																
Japan	500				100					50		10					
Malaysia	5,000		3,000					500 marketed									
Pakistan	10,000						5,000										
Philippines	5,000					2,000			500								
PRC	5,000		2,000														
Republic of Korea	500							430			30				10		
Singapore	3,000		500														
Sri Lanka	10,000							3,000									
Taipei, China	3,000			500			350					50					
Thailand	2,500			500					350								50
Viet Nam	10,000							2,000		500							
European Union					350					50				10			
United States	500														15		

> 500 ppm

51-500 ppm

< 50 ppm

## 2.4 Hydrogenation of Aromatic Compound

Hydrogenation is exothermic reaction so it is favored at low temperatures. However, conventional hydrotreating catalysts are active only at relatively high temperature (>300°C). It is therefore natural to consider deep hydrogenation at low temperature (<300°C). The potential candidate catalysts for low-temperature hydrotreating include noble metals. Since it is known that noble metal catalysts are easily deactivated by sulfur compounds, a two-stage processing strategy is being adopted. The first stage involves deep desulfurization of the fuels using metal sulfide catalysts to reduce the sulfur and nitrogen contents to less than 50 wppm and

1 wppm, respectively. The second stage deals with hydrogenation over a noble metal catalyst which is very active and tolerate organic sulfur levels of about 5-10 wppm.

The hydrotreating process has two different approaches:

- Single-stage process system, which combines severe HDS with HYD using single conventional CoMo, NiMo, or NiW catalysts, reaches the necessary aromatic saturation only at the H<sub>2</sub> pressure at which current HDS units operate.
- Two-stage process system, which uses hydrotreating by use of an Ni-Mo/Al<sub>2</sub>O<sub>3</sub> as a catalyst in the first reactor and a platinum-supported catalyst in the second for deep aromatic hydrogenation. This system yields a low aromatic diesel stream at moderate hydrogen pressure. This system is highly active for the reduction of aromatics, but is very susceptible to sulfur poisoning. Accordingly, the sulfur concentration at the inlet of the second reactor must be decreased to a few parts per million. Thus, the use of these catalysts is limited by the severe pretreatment conditions, unless sulfur tolerance can be greatly improved.

## 2.5 Literature Review

Argentiere *et al.*, (1997) reported on the effect of cobalt and tungsten addition to a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst on its catalytic activity, selectivity and sulfur resistance during styrene selective hydrogenation. It was found that the addition of cobalt and tungsten as a second metal was a useful way to increase the activity and the sulfur resistance of palladium for these reaction.

Silica-alumina supported Pd catalysts with a second metal such as Cu, Ru and Pt have been prepared and tested in the naphthalene hydrogenation (HYD) and dibenzothiophene hydrodesulfurization (HDS) model reaction. The test showed that the PtPd system exhibited strong Bronsted acid sites and it had the highest HYD and HDS activity; this catalyst presented the highest DBT conversion and the highest C-S hydrogenolysis activity, as illustrated by the lowest S-containing products at the reactor exit as compared with the much higher S-containing products obtained with

the monometallic Pd/ASA catalyst under the same reaction conditions. (Barrio *et al.*, 2003)

In 2001, Hu *et al.*, tried to improve the sulfur resistance of noble metal catalysts in the aromatic hydrogenation of diesel fuel by using the alloying effect of non-noble metals (Cr, W, La, Mn, Mo, Ag) with Pd on the mixed HY-Al<sub>2</sub>O<sub>3</sub> and investigated it in the presence of 3000 ppm sulfur as thiophene in the feedstock. It was found that the addition of La, Mn, Mo and Ag decreased the sulfur resistance and hydrogenation activity of the Pd catalyst, but Cr and W increased hydrogenation activity.

Rousset *et al.*, (2001) found that Pt is the most active catalyst at low sulfur concentration. In contrast, Pd became slightly more active than Pt for high sulfur content.

In the same year (2001), Guillon *et al.*, studied the addition of a second metal (Ge and Pd) to the Pt catalyst to enhance the sulfur tolerance. This promotion has also been ascribed to a change in electronic properties. It was found that the addition of germanium to platinum decreases the rate of aromatic hydrogenation, whereas the palladium-platinum system exhibited higher activity. It was concluded that the decrease in metal-S bond strength is not sufficient to obtain high aromatic hydrogenation activity in the presence of H<sub>2</sub>S.

In 1995, Lin *et al.* modified the Pt catalyst by the addition of a second metal catalyst such as Co, Mo, Ni, Re, Ag and Pd. The result indicated that the Pd-Pt catalyst had the highest sulfur resistance, and suggested that electrons transferred from Pt to Pd by bimetallic interaction. The decrease of electron density on Pt inhibits H<sub>2</sub>S adsorption and thereby enhances catalyst sulfur resistance. Besides the sulfur tolerance improvement, the Pd was also inferred to inhibit agglomeration of Pt particles during hydrogen regeneration.

To confirm that the PtPd bimetallic catalyst system is resistant to the poisoning with dosing variable amounts of sulfur (113-1,200ppm), it was found that an increase in the sulfur concentration led to a decrease in the intrinsic activity of naphthalene, tetralin and toluene hydrogenation. Moreover, the dosing variable amounts of sulfur can effect temperature, in an Arrhenius plot, whereas tetralin hydrogenation, and toluene hydrogenation for a 1,200 S ppm temperature-

independent activation energy behave differently. During the 300 to 600 S ppm, the activation energy of toluene hydrogenation decreases at high temperature. This suggests the occurrence of a pore diffusion limitation at high temperature. (Navarro *et al.*, 1999)

Yasuda *et al.* (1997) reported that the coexistence of Pt with Pd on USY zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 680$ ) greatly enhanced tetralin hydrogenation activity and improved the sulfur tolerance, which depended on the Pt/Pd ratio and reached a maximum at a Pd: Pt mole ratio of 4:1. The reaction was carried out at a hydrogen pressure of 3.9 MPa at 553 K in the presence of dibenzothiophene at a sulfur concentration of 500 wtppm. After that, Yasuda *et al.* (1999) studied the sulfur-tolerance of a Pd-Pt/ $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$  catalyst for aromatic hydrogenation; they found that the Pd-Pt/ $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$  catalyst had higher sulfur tolerance than the catalyst supported on  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and USY zeolites for the hydrogenation of tetralin in the presence of DBT and had excellent hydrogenation selectivity.

Augusto *et al.* (2001) found that the addition of potassium decreases the number and strength of the acidic sites presenting in the Pt/Y catalyst. The change in acidity is associated with the support, since the acidity of metal/zeolite catalysts originates from the zeolite rather than from the metal. Both nitrogen and sulfur poisons influenced the cis/trans selectivity of tetralin hydrogenation. In 2002, Arribas and co-workers found that the presence of Bronsted acid sites is required to achieve some reactions, for example, isomerization, ring opening, cracking and dealkylation. Furthermore, because zeolite is somewhat expensive, the use of zeolites as a support is economically less attractive.

On the other hand, zeolite-supported noble metal catalysts have been receiving more attention as aromatics hydrogenation catalysts. Fujikawa *et al.* (2001) suggested that the lower apparent activation energy for the hydrogenation of aromatics over Pt/HY catalyst is probably responsible for a stronger adsorption of the aromatics on the Bronsted acid sites of the HY zeolite. They concluded that the acidic properties of the catalyst play an important role in the kinetic behavior of aromatics hydrogenation. However, zeolites drastically increase undesirable cracking activity, which accelerates the rate of coke deposition and enhances the

yields of naphtha and gas. These circumstances are caused by too high acidity of zeolite.

The addition of fluorine can cause lower metal dispersion and the orders of impregnation affect metal dispersion. Since fluorine is an electronegative atom, the replacement of OH groups by fluorine made the metal electron deficient on the surface of catalyst. As a result, it enhanced the sulfur tolerance of the catalyst (Jongpatiwut *et al.*, 2004).