CHAPTER II
LITERATURE REVIEW

2.1 Crude Oil

Natural gas, crude oil and petroleum cuts all contain a wide variety of chemical compounds made up of two main elements namely carbon and hydrogen. Some of these compounds also contain other elements which are often considered as impurities such as sulfur, nitrogen, oxygen and some metals, for example, nickel and vanadium.

2.1.1 Hydrocarbons in General

There are a great variety of hydrocarbons, largely due to the capacity of carbon atoms to form long chains, resulting in extremely different combinations. It can be seen in Table 2.1 that there is an initial distinction between the hydrocarbon types.

2.1.2 Composition of Crude Oil

Crude oils from some wells are as clear as vegetable oil. Other wells produce green, brown or black crudes. Some taste sour or smell like rotten eggs. Some flow as easily as water, others don’t flow unless they are heated.

Table 2.2 shows the composition (mol%) and properties of various reservoir fluids and a crude oil.

Table 2.1 Different types of hydrocarbons and their physical and chemical properties (Delon, 2009)

		SATURATED HYDROCARBON *(without multiple bonds)*			**UNSATURATED HYDROCARBON** *(with double and benzoic bonds)*	
		EXISTING IN CRUDE OILS				PRODUCED BY CRACKING PROCESSES
		Paraffins		Naphthenes	Aromatics	Olefins and diolefins
		Normal-	Iso-			
Liquid specific gravity		low	low	medium	high	low
Properties under cold conditions		very poor	generally good enough	generally good	generally good	–
Combustion	**Gasoline engine**	week	good	medium	very good	good enough
	Diesel engine	very good	weak	medium	very weak	weak
Hydrogen content or H/C ratio		high	high	medium	low	medium
Storage stability		good	good	good	good	very poor

Table 2.2 Composition (mol%) and properties of various reservoir fluids and a crude oil (Riazi, 2005)

Component	Dry gas	Wet gas	Gas condensate	Volatile oil	Black oil	Crude oil
CO_2	3.70	0.00	0.18	1.19	0.09	0.00
N_2	0.30	0.00	0.13	0.51	2.09	0.00
H_2S	0.00	0.00	0.00	0.00	1.89	0.00
C_1	96.00	82.28	61.92	45.21	29.18	0.00
C_2	0.00	9.52	14.08	7.09	13.60	0.19
C_3	0.00	4.64	8.35	4.61	9.20	1.88
iC_4	0.00	0.64	0.97	1.69	0.95	0.62
nC_4	0.00	0.96	3.41	2.81	4.30	3.92
iC_5	0.00	0.35	0.84	1.55	1.38	2.11
nC_5	0.00	0.29	1.48	2.01	2.60	4.46
C_6	0.00	0.29	1.79	4.42	4.32	8.59
C_{7+}	0.00	1.03	6.85	28.91	30.40	78.23
Total	100.00	100.00	100.00	100.00	100.00	100.00
GOR[a] (scf/stb)	–	69917	4428	1011	855	–
M_{7+}	–	113	143	190	210	266
SG_{7+} (at 15.5 °C)	–	0.794	0.795	0.814	0.844	0.895
API_{7+}	–	46.7	46.5	42.1	36.1	26.6

[a] Gas-to-oil ratio (GOR represents the amount of gas produced at standard condition in standard cubic feet (scf) to the amount of liquid oil produced at the SC in stock tank barrel (stb).

Table 2.3 compares properties for 21 selected crudes. Traders characterize a crude by citing its source, API gravity and sulfur content. The source is the oil field from which the crude was produced. The API gravity is a rough indication of distillation properties, which determine how much gasoline, kerosene, etc., can be distilled from the crude. Along with other factors, the sulfur content affects processing costs. Figure 2.1 shows light crudes (those with high API gravities) often contain less sulfur and nitrogen than heavy crudes, but not always.

Table 2.3 Properties of 21 selected crude oils (Hsu and Robinson, 2006)

Crude Oil	API Gravity[b]	Specific Gravity	Sulfur (wt%)	Nitrogen (wt%)
Alaska North Slope	26.2	0.8973	1.10	0.20
Arabian Light	33.8	0.8560	1.80	0.07
Arabian Medium	30.4	0.8740	2.60	0.09
Arabian Heavy	28.0	0.8871	2.80	0.15
Athabasca (Canada)	8.0	1.0143	4.80	0.40
Beta (California)	16.2	0.9580	3.60	0.81
Brent (North Sea)	38.3	0.8333	0.37	0.10
Bonny Light (Nigeria)	35.4	0.8478	0.14	0.10
Boscan (Venezuela)	10.2	0.9986	5.30	0.65
Ekofisk (Norway)	37.7	0.8363	0.25	0.10
Henan (China)	16.4	0.9567	0.32	0.74
Hondo Blend (California)	20.8	0.9291	4.30	0.62
Kern (California)	13.6	0.9752	1.10	0.70
Kuwait Export	31.4	0.8686	2.50	0.21
Liaohi (China)	17.9	0.9471	0.26	0.41
Maya (Mexico)	22.2	0.9206	3.40	0.32
Shengli (China)	13.8	0.9738	0.82	0.72
Tapis Blend (Malaysia)	45.9	0.7976	0.03	nil
West Hackberry Sweet[a]	37.3	0.8383	0.32	0.10
West Texas Intermediate	39.6	0.8270	0.34	0.08
Xinjiang (China)	20.5	0.9309	0.15	0.35

[a] Produced from a storage cavern in the U.S. Strategic Petroleum Reserve.

[b] API Gravity is related to specific gravity by the formula:

$°API = 141.5 \div (\text{specific gravity @ } 60°F) - 131.5$.

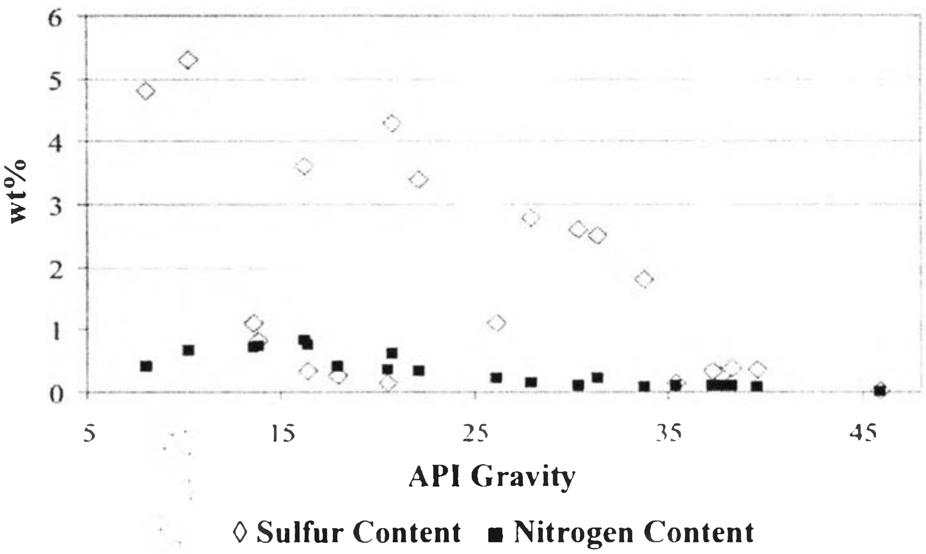


Figure 2.1 Sulfur and nitrogen versus API gravity for selected crude oils (Hsu and Robinson, 2006).

2.2 Petroleum Fractions and Products

The crude distillation units are the first major processing units in the refinery. They are used to separate the crude oils by distillation into fractions according to boiling point so that each of the processing units following will have feedstocks that meet their particular specifications. Higher efficiencies and lower costs are achieved if the crude oil separation is accomplished in two steps: first by fractionating the total crude oil at essentially atmospheric pressure; then by feeding the high-boiling bottoms fraction (topped or atmospheric reduced crude) from the atmospheric distillation unit to a second fractionator operated at a high vacuum.

The vacuum distillation is employed to separate the heavier portion of the crude oil into fractions because the high temperatures necessary to vaporize the topped crude at atmospheric pressure cause thermal cracking to occur, with the resulting loss to dry gas, discoloration of the product, and equipment fouling due to coke formation.

The operation of the crude oil distillation is shown in Figure 2.2 and typical fraction cut points and boiling ranges for atmospheric and vacuum distillation fractions are given in Tables 2.4 and 2.5.

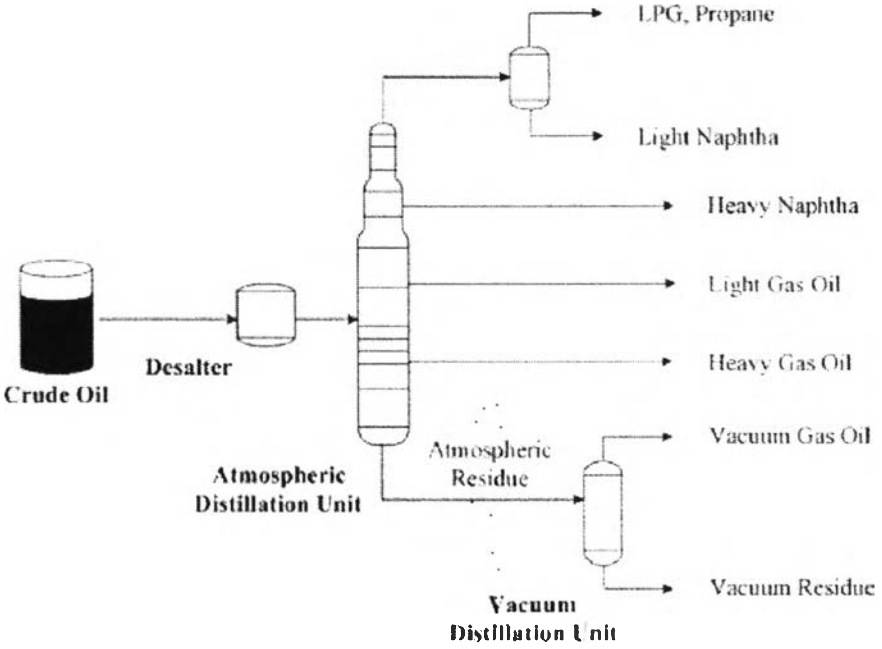


Figure 2.2 Crude distillation (Hsu and Robinson, 2006).

Table 2.4 Boiling ranges of typical crude oil fractions (Gary and Hanwerk, 2001)

Fraction	Boiling ranges, °F	
	ASTM[a]	TBP[b]
Butane and lighter	–	–
Light straight-run naphtha (LSR)	90–220	90–190
Heavy straight-run naphtha (HSR)	180–400	190–380
Kerosene	330–540	380–520
Light gas oil (LGO)	420–640	520–610
Atmospheric gas oil (AGO)	550–830	610–800
Vacuum gas oil (VGO)	750–1050	800–1050
Vacuum reduced crude (VRC)	1050+	1050+

[a] Several distillation tests are commonly referred to as ''ASTM distillations.'' These are usually used in product specification. These ASTM distillations give results in terms of percent distilled versus temperature for a simple laboratory distillation with no fractionation. The values do not correspond to those of refinery process distillations where fractionation is significant.

[b] True boiling point distillation.

Table 2.5 True boiling point (TBP) cut points for various crude oil fractions (Gary and Hanwerk, 2001)

Cut	**IBP[a] (°F)**	**EP[b] (°F)**	**Processing use**
LSR gasoline cut	90	180	Min. light gasoline
	90	190	Normal LSR cut
	80	220	Max. LSR cut
HSR gasoline (naphtha)	180	380	Max. reforming cut
	190	330	Max. jet fuel opr.
	220	330	Min. reforming cut
Kerosene	330	520	Max. kerosene cut
	330	480	Max. jet-50 cut
	380	520	Max. gasoline operation
Light gas oil (LGO)	420	610[c]	Max. diesel fuel
	480	610[c]	Max. jet fuel
	520	610[c]	Max. kerosene
Heavy gas oil (HGO)	610	800	Catalytic cracker or hydrocracker feed
Vacuum gas oil (VGO)	800	1050	Deasphalter or catalytic cracker feed
	800	950	Catalytic cracker or hydrocracker feed

[a] Initial boiling point of a cut, usually on an ASTM basis.

[b] End Point (Upper temperature limit of a distillation).

[c] For maximum No. 2 diesel fuel production, end points as high as 650 °F (343 °C) can be used.

Note: In some specific locations, economics can dictate that all material between 330 °F IBP and 800 °F EP (166 to 427 °C) be utilized as feed to a hydrocracker.

As an example, the composition of an Alaska crude oil for various products is graphically shown in Figure 2.3. The weight and volume percentages for the products are near each other. More than 50% of the crude is processed in vacuum distillation unit. The vacuum residuum is mainly resin and asphaltenes-type compounds composed of high molecular weight multi-ring aromatics. The vacuum residuum may be mixed with lighter products to produce a more valuable blend.

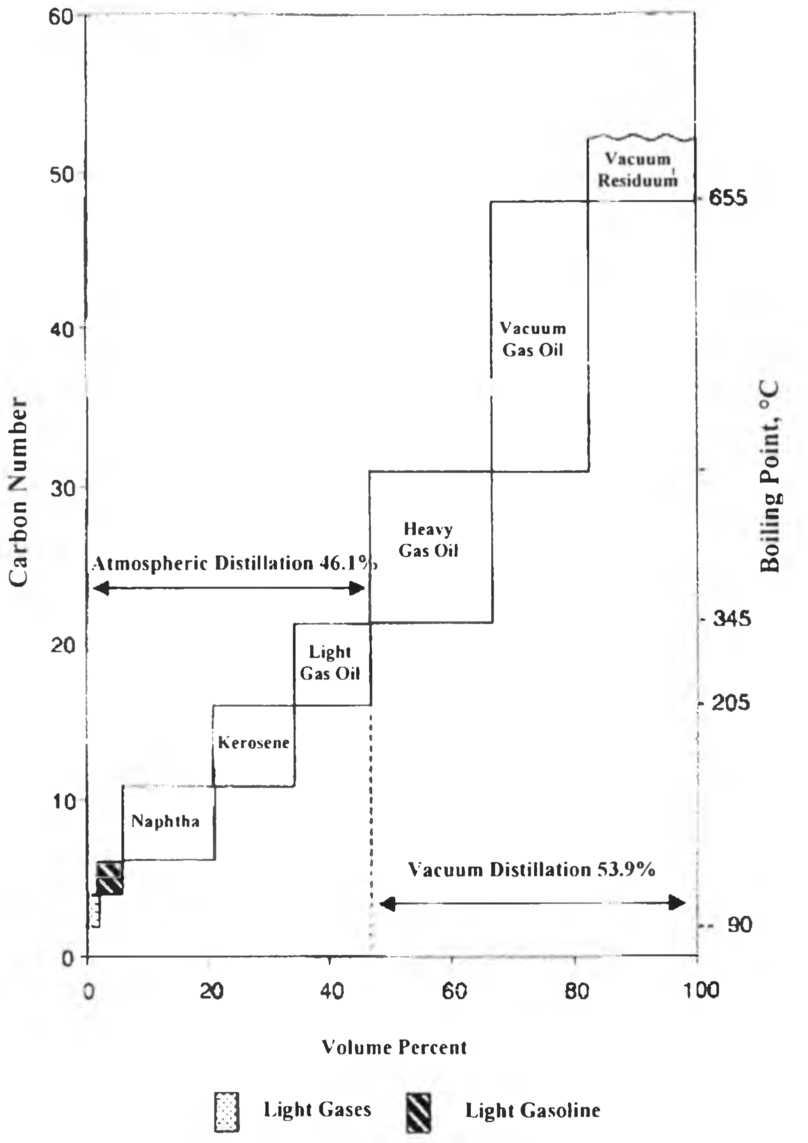


Figure 2.3 Products and composition of Alaska crude oil (Riazi, 2005).

A petroleum cuts produced after necessary separation processes is transferred through conversion processes. The conversion process consists of chemical changes that occur with hydrocarbons in reactors. The purpose of such reactions is to convert hydrocarbon compounds from one type to another. The most important reaction in modern refineries is the cracking which heavy hydrocarbons are converted to lighter and more valuable hydrocarbons. Catalytic cracking and thermal cracking are commonly used for this purpose. Other types of reactions such as isomerization or alkylation are used to produce high octane number gasoline. Then, if it is needed to be purified, finishing processes are used. Finishing is the purification of various product streams by processes such as desulfurization or acid treatment of petroleum fractions to remove impurities from the product or to stabilize it.

The destinations of the different petroleum cuts are summarized in Table 2.6 as tabulated below:

Table 2.6 Destinations for straight-run distillates (Hsu and Robinson, 2006)

Fraction	Next Destination	Ultimate Product(s)
LPG	Sweetener	Propane fuel
Light Naphtha	Hydrotreater	Gasoline
Heavy Naphtha	Cat. Reformer	Gasoline, aromatics
Kerosene	Hydrotreater	Jet fuel, No.1 diesel
Gas Oil	Hydrotreater	Heating Oil, No.2 diesel
Vacuum Gas Oil	FCC	Gasoline, LCO, gases
	Hydrotreater	Fuel oil, FCC feed
	Lube Plant	Lube basestock
	Hydrocracker	Gasoline, jet, diesel, FCC feed lube basestock
Vacuum Residue	Coker	Coke, coker gas oil
	Visbreaker	Visbreaker gas oil, resid
	Asphalt Unit	Deasphaltd oil, asphalt
	Hydrotreater	FCC feed

2.3 Hydrocarbon Feeds and Sulfur Specifications

There are many types of petroleum cuts or hydrocarbon feeds that have been mentioned above. Three of them—gasoline, diesel and jet fuels—can be classified as transportation fuels. The compositions of these fuels vary widely depending on the crude oil compositions, the refining process, the product demand and the product specifications. The approximate compositions of gasoline, diesel and jet fuel are given in Table 2.7. Branched and n-alkanes are the main ingredients of these fuels, typically 70–80%. The major alkanes in n-hexane and the main branched alkanes are C_5 and C_6 compounds. The aromatics are mainly benzene, toluene, xylenes and alkyl benzenes, totaling about 20–30%.

Table 2.7 Typical compositions of transportation fuels (vol%) (Yang, 2003)

	Gasoline[a]	**Diesel**[b]	**Jet Fuel**[c]
Boiling range (°C)	40–204	232–350	330–510
Aromatics	30.5	17	18
Olefins	1.8	5	2
n–alkanes	17.3	–	–
Branched alkanes	32	–	–
Cycloalkanes	5	–	–
Saturates	–	78	–
Paraffins	–	–	60
Naphthenes	–	–	20

[a] Siences International. Inc., "Toxicological Profile for Gasoline," Report to epartment of Health and Human Services, June, 1995.

[b] Ma *et al.*, 1994.

[c] Ma *et al.*, 2002.

As is well known to researchers and also to the common man, sulfur in transportation fuels has been a major concern from the environment point of view. However, this is not the only reason for research on desulfurization of transportation fuels. The desulfurization of transportation fuels such as diesel and gasoline is also important from the point of application in fuel cells, as liquid hydrocarbons such as gasoline can be used conveniently as a feed in the fuel cells (Bhandari *et al.*, 2006).

Consequently, the sulfur level in diesel fuel must be reduced from current maximum 500 to 15 ppmw by 2006 in the US (Kim *et al.*, 2006), and the sulfur level in diesel fuel required by European Emission Standards decreases gradually from EURO II (500 ppmw) to EURO III (350 ppmw) and rapidly decreases from EURO III (350 ppmw) to EURO IV (50 ppmw). For EURO V, the sulfur level is reduced to 10 ppmw in 2009. In Thailand, the sulfur level in diesel is regulated to decrease gradually from 350 ppm to 35 ppm by 2012 and the beginning of the year 2012 it is regulated to decrease to 5 ppm (Department of energy business, Ministry of Energy, Thailand, 2010). The regulated sulfur levels in diesel fuel are illustrated in Figure 2.4.

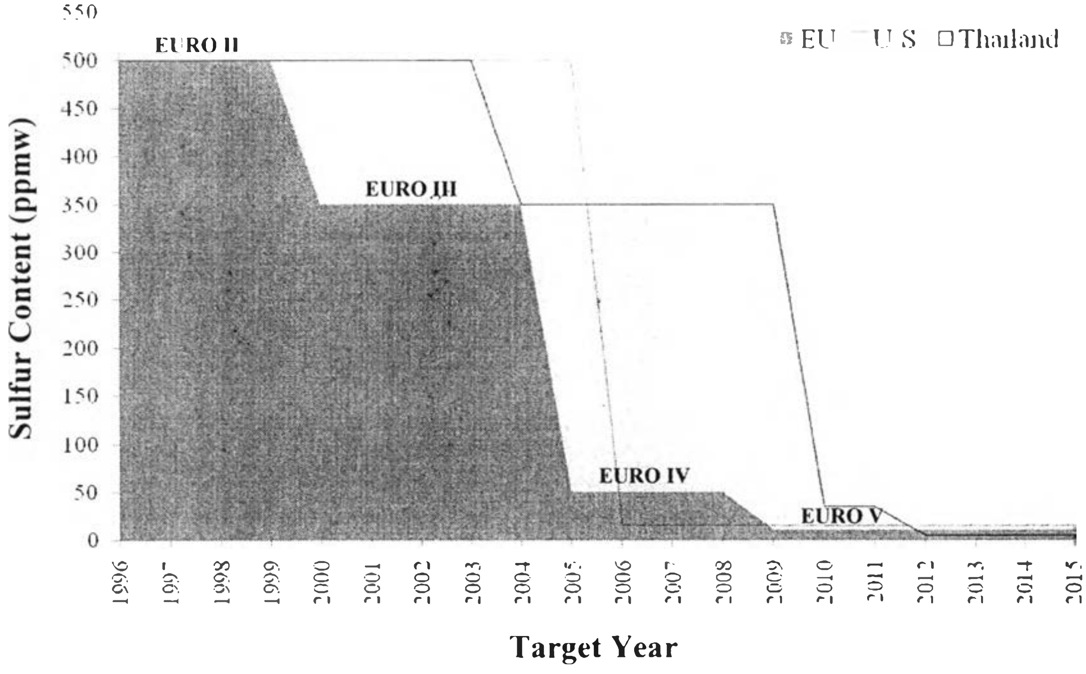


Figure 2.4 Regulated sulfur levels in diesel fuel in EU, US and Thailand.

Moreover, the U.S. Environmental Protection Agency (U.S. EPA) and the European Parliament promulgated clean-fuel regulations that are lowering the sulfur content of gasoline and diesel fuel. New sulfur-content standards for several developed countries are shown in Table 2.8, which also shows the target dates for implementation.

Table 2.8 Clean fuels: limits on sulfur (Hsu and Robinson, 2006)

Country	Fuel Sulfur Content, ppmw		
	2004 Level	Target Level	Target Date
US			
Gasoline	> 300	30	2004–2008
Diesel, on-road	500	15	July 1, 2006
	–	–	July 1, 2010
Diesel, off-road	2,000–3,500	500	2007
	–	15	2010
Canada			
Gasoline	150	30	2005
Diesel	500	15	2006
Germany			
Gasoline	10	10	2003
Diesel	10	10	2003
Sweden			
Diesel	10	10	1995
Other EU			
Gasoline	150	50	2005
	–	10	2008
Diesel	350	50	2005
	–	10	2008
Australia			
Gasoline	500	150	2005
Diesel	500	30	2008
Korea (South)			
Gasoline	100	30	2006
Diesel	300	50	2006
Japan			
Gasoline	100	10	2008
Diesel	500	50	2004
	–	10	2008

2.4 Organosulfur Compounds

Organosulfur compounds are organic compounds that contain sulfur. They are often associated with foul odours, but ironically many of the sweetest compounds known are organosulfur derivatives. Nature abounds with organosulfur compounds sulfur is essential for life. Two of the twenty common amino acids are organosulfur compounds. Fossil fuels, coal, petroleum, and natural gas, which are derived from ancient organisms, necessarily contain organosulfur compounds, the removal of which is a major focus of oil refineries (http://en.wikipedia.org/wiki/Organosulfur_compounds).

Sulfur is divalent element associated with hydrogen and carbon in 4 typed of principal compound: hydrogen sulfide, mercaptans, sulfides and thiocyclic compounds (containing sulfur in a ring). The physical constants of the principal sulfur compounds are shown in Table 2.9.

2.4.1 Hydrogen Sulfide

Hydrogen sulfide (H_2S) is not found in petroleum products but it does exist in small amounts in crude oils and in varying amounts in natural gas: 0.3 vol% in gas from the Zakum field (Abu Dhabi), and 15 vol% in gas from Lacq (France). It is also present in large quantities in the refinery as many units generate H_2S as a compulsory step in the desulfurization process.

Refineries therefore have to handle and process large quantities of H_2S and have to apply extremely strict safety regulations as it is a very toxic and dangerous gas. It is also corrosive, particularly at low temperatures when dissolved in water where it breaks down into sulfhydride acid.

2.4.2 Mercaptans

Mercaptans are composed of the functional combination **–S–H** associated with a hydrocarbon chain represented by the letter R. They occur in most petroleum cuts and they have the many drawbacks, for example, they are acid and they have an obnoxious smell. Refinery installations therefore generally have to include specific units removing these compounds.

2.4.3 Sulfides

In these compounds the sulfur atoms are linked to two hydrocarbon chains. The sulfur therefore forms an intermediary between the two chains and a distinction is made between:

- Sulfides in which there is only one sulfur atom: **R–S–R'**;
- Disulfides in which there are two sulfur atoms: **R–S–S–R'**;
- Polysulfides in which there are several sulfur atoms: **R–S– S…S–R'**.

These compounds occur in crude oils and petroleum products. Unlike mercaptans, they have the advantage of not being acid which means they are not corrosive and their low volatility greatly reduces their smell.

2.4.4 Thiocyclic Compounds (containing a sulfur atom in a ring)

This group of sulfur compounds is the most commonly found in crude oils and petroleum products and is chiefly derived from thiophene and benzothiophene. The structure of thiophene, benzothiophene and its properties is shown in Figure 2.5 and 2.6, respectively.

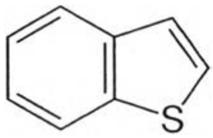
Thiophene

C_4H_4S

bp = 84 °C

$sp.gr_4^{15} = 1.070$

Figure 2.5 Structure of thiophene and its properties.



Benzothiophene

C_8H_6S

bp = 220 °C

$sp.gr_4^{15} = 1.165$

Figure 2.6 Structure of benzothiophene and its properties.

Their characteristics are similar to those of aromatic hydrocarbons: unsaturated rings and good thermal stability. They are neutral and non-corrosive.

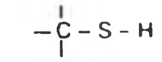
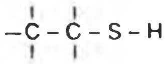
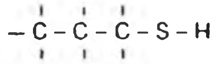
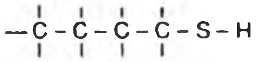
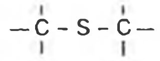
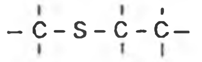
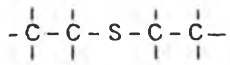
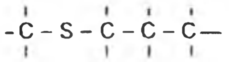
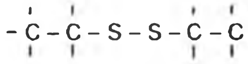
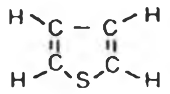
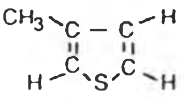
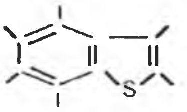
The desulfurization of petroleum products consists in destroying these compounds, which is not an easy task, particularly in the case of very heavy thiophenic compounds.

The sulfur content of liquid fuels can vary from virtually zero to as high as 7 or 8 wt%. There are many common types of sulfur compounds in liquid fuel as shown in Figure 2.7, which can be analyzed with X-ray fluorescence spectroscopy or by gas chromatography equipped with a capillary column plus a flame photometric detector.

The common types of sulfur compounds in liquid fuels are listed below.

- Gasoline range: naphtha, fluid catalytic cracking (FCC)-naphtha (Selective HDS)
    - Mercaptans (RSH); sulfides (R_2S); and disulfides (RSSR);
    - Thiophene and its alkylated derivatives;
    - Benzothiophene.
- Jet fuel range: heavy naphtha, middle distillate
    - Benzothiophene (BT) and its alkylated derivatives.
- Diesel fuel range: middle distillate, light cycle oil (LCO)
    - Alkylated benzothiophenes;
    - Dibenzothiophene (DBT) and its alkylated derivatives.
- Boiler fuel feeds: heavy oils and distillation residues
    - $\geq$ 3-ring polycyclic sulfur compounds, including DBT, benzonaphthothiophene (BNT);
    - Phenanthro[4,5-b,c,d]thiophene (PT), and their alkylated derivatives (Song and Ma, 2003).

Table 2.9 Physical constants of the principal sulfur compounds (Delon, 2009)

	Chemical formula	Structural formula	Molecular weight	Normal boiling point °C	$\mathrm{Sp\ gr}_{4}^{15}$ (liquid)
hydrogen sulfide	H_2S	H - S - H	34.1	- 60.3	
MERCAPTANS					
methylmercaptan	CH_3SH		48.1	6.0	0.873
ethylmercaptan	C_2H_5SH		62.1	35.0	0.845
n-propylmercaptan	C_3H_7SH		76.2	67.6	0.847
n-butylmercaptan	C_4H_9SH		90.2	98.5	0.847
SULFIDES					
dimethylsulfide	C_2H_6S		62.1	37.3	0.854
ethylmethylsulfide	C_3H_8S		76.2	66.6	0.848
diethylsulfide	$C_4H_{10}S$		90.2	92.1	0.841
methyl n-propylsulfide	$C_4H_{10}S$		90.2	95.5	0.847
DISULFIDES					
dimethyldisulfide	C_2H_6S		94.2	109.6	1.069
diethyldisulfide	$C_4H_{10}S_2$		122.2	152.6	0.998
dipropyldisulfide	$C_6H_{14}S_2$		150.3	126.5 at 100mm of Hg	0.964
THIOPHENIC COMPOUD					
thiophene	C_4H_4S		84.1	84	1.070
methylthiophene	$CH_3C_4H_3S$		98.2	119	1.069
benzothiophene	C_8H_6S		134.2	220	1.165

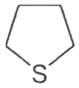
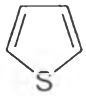
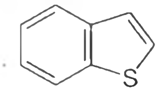
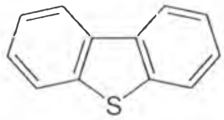
H_2S	Hydrogen sulfide
S_8	Elemental sulfur
R–S–H	Mercaptans
R–S–R'	Sulfide
R–S–S–R'	Disulfide
	Cyclic sulfide (tetrahydrothiophene)
	Thiophene
	Benzothiophene
	Dibenzothiophene (with alkyl groups at the 4- and 6-positions, that is, 4-MDBT and 4,6-DMDBT, are the refractory sulfur compounds that are most difficult to remove by HDS or sorbents aiming at bonding with S due to steric hindrance.)

Figure 2.7 Examples of sulfur compounds in petroleum.

Ma *et al.* (2002) showed GC-FPD chromatograms of a sample each of gasoline, diesel and jet fuel in Figure 2.8. The FPD detects only sulfur compounds. The dominant sulfur compounds in the gasoline were (in decreasing order) 3-MT, BT, T, 2-MT, and 2,4-DMT. No mercaptans, dialkyl sulfides and dialkyl disulfides were detected. In diesel, the dominant sulfur compounds were 4-MDBT, 4,6-DMDBT, 2,4,6-TMDBT, 3,6-DMDBT, DBT, 2,3,7-TMBT, 2,3,5-TMBT, 2,3-DMBT, and others. The sulfur compounds found in the jet fuel were 2,3,7-TMBT, 2,3-DMBT, and the minor species 2,3,5-TMBT and 2,3,6-TMBT. All these MBT have two methyl groups at 2- and 3-positions, respectively, implying that the BT with two methyl groups at 2- and 3-positions are more difficult to be removed than other sulfur compounds in hydrotreating of jet fuel.

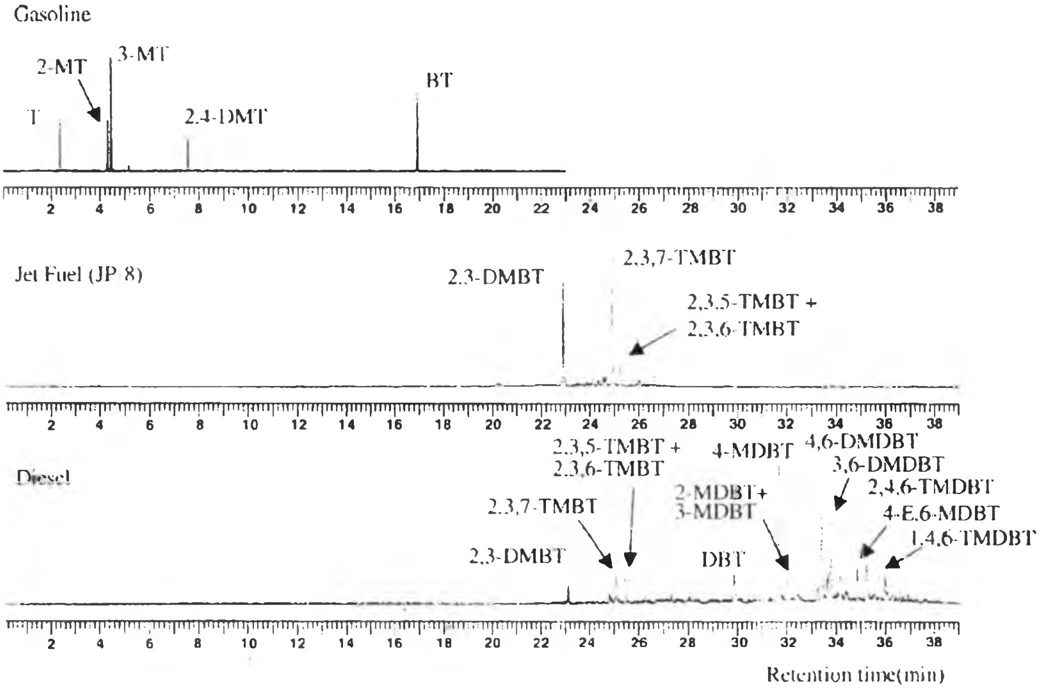


Figure 2.8 GC-FPD chromatograms of gasoline, jet fuel and diesel for identification of sulfur compounds (Ma *et al.*, 2002).

2.5 Desulfurization Process

There are several processes that can be used to remove the sulfur compounds in the liquid fuel. The classification of desulfurization technologies, according to Babich *et al.* (2003), can be based on the fate of the organosulfur compounds during desulfurization, the role of hydrogen, or the nature of the process used (chemical and/or physical).

Based on the way in which the organosulfur compounds are transformed, the processes can be divided into three groups depending on whether or not the sulfur compounds are decomposed separately from the refinery stream without decomposition, or whether they are both separated and then decomposed (Figure 2.9). When organosulfur compounds are decomposed, gaseous or solid sulfur products are formed and the hydrocarbon part is recovered and remains in the refinery streams.

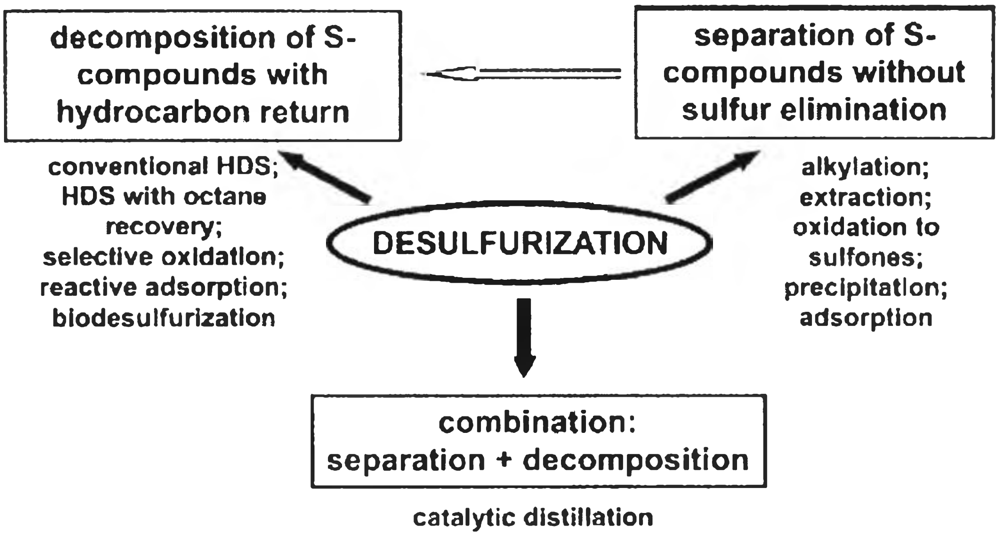


Figure 2.9 Classification of desulfurization processes based on organosulfur compound transformation (Babich *et al.*, 2003).

Depending on the role of hydrogen in removing sulfur, desulfurization processes can be also classified into two groups: "HDS-based" and "non-HDS-based". In HDS-based processes, hydrogen is used to decompose organosulfur compounds and eliminate sulfur from refinery streams, while non-HDS-based processes do not require hydrogen.

Finally, desulfurization processes can be classified based on the nature of the key physico-chemical process used for sulfur removal (Figure 2.10). The most developed and commercialized technologies are those which catalytically convert organosulfur compounds with sulfur elimination. Such catalytic conversion technologies include conventional hydrotreating, hydrotreating with advanced catalysts and/or reactor design and a combination of hydrotreating with some additional chemical processes to maintain fuel specifications.

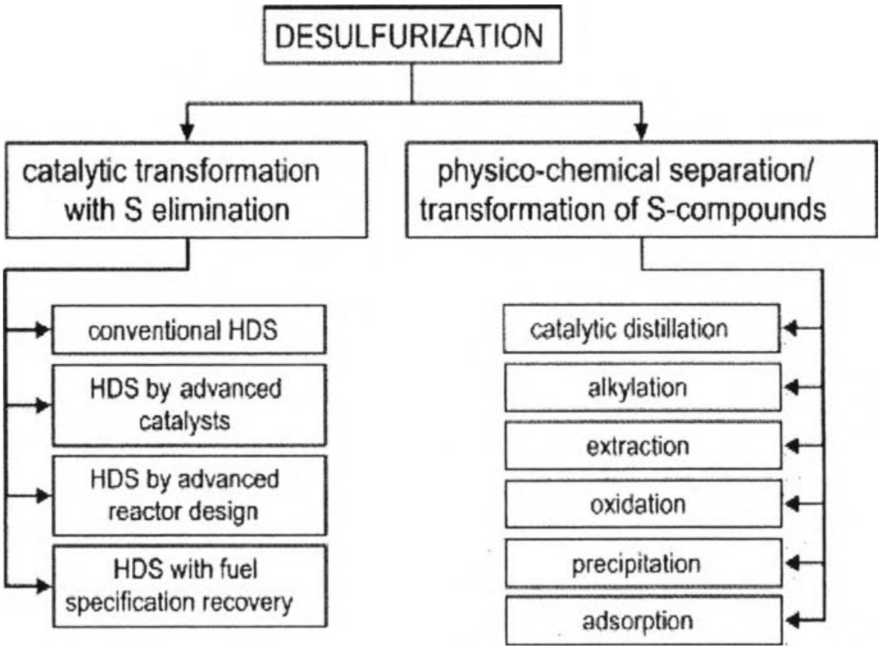


Figure 2.10 Desulfurization technologies classified by nature of a key process to remove sulfur (Babich *et al.*, 2003).

2.5.1 Conventional Hydrodesulfurization (HDS)

Conventional hydrodesulfurization (HDS) process is an efficient method of sulfur removal from gasoline and diesel with high sulfur concentrations, and is used worldwide (Xue *et al.*, 2005). The hydrodesulfurization process involves catalytic treatment with hydrogen to convert the various sulfur compounds present to hydrogen sulfide at elevated temperatures (300–340 °C) and pressures (20–100 atm H_2) using Co-Mo/Al_2O_3 or Ni-Mo/Al_2O_3 catalysts (Hernández *et al.*, 2004). The hydrogen sulfide is then separated and converted to elemental sulfur by the Claus process. Their performance in terms of desulfurization level, activity and selectivity depends on the properties of the specific catalyst used (active species concentration, support properties, synthesis route), the reaction conditions (sulfiding protocol, temperature, partial pressure of hydrogen and H_2S), nature and concentration of sulfur compounds present in the feed stream, and reactor and process design (Babich *et al.*, 2003). However, these catalysts are poisoned by H_2S and metals in feedstock. There is generally no method for regeneration other than running straight hydrogen through the reactor.

The typical process conditions for the hydrotreating of different feeds in fixed-bed hydrotreating units are shown in Table 2.10.

Table 2.10 Typical process conditions for hydrotreating different petroleum fractions (Hsu and Robinson, 2006)

	Naphtha	Kerosene	Diesel	VGO	Residue
WART[a]					
	530	550	575–600	680–700	700–725
	277	288	300–315	360–370	370–385
H_2 Pressure[b]					
psig	250–450	250–600	600–800	800–2000	> 2,000
kpa	1,825–3,204	1,825–4,238	4,238–5,617	5,617–13,891	> 13,891
LHSV	5	4	2–3	0.8–1.5	0.5
H_2/Oil Ratio[c]					
scf/bbl	350	450	800	1,200	> 3,000
M^3/m^3	60	80	140	210	> 525

[a] Approximate weighted average reactor temperature at start of run.

[b] Approximate hydrogen partial pressure at the high-pressure separator.

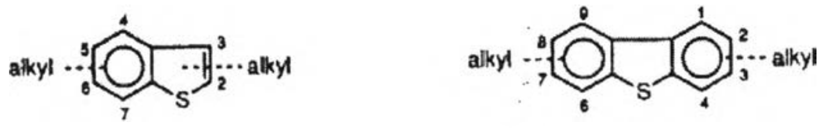
[c] Approximate hydrogen-to-oil ratio at the first reactor inlet.

2.5.2 Challenges of Ultra Deep Desulfurization

2.5.2.1 Reactivity of Organic Sulfur Compounds in HDS

Kabe *et al.* (1992) studied on deep hydrodesulfurization of polyaromatic sulfur-containing compounds (PASC) in light oil using Co-Mo/Al_2O_3 under experimental conditions. They have analyzed the sulfur compounds in a light gas oil (LGO) and hydrotreated gas oils using gas chromatography with atomic emission detector (GC-AED) and GC-mass spectrometer (GC-MS). They identified 42 alkylated benzothiophene compounds and 29 alkylated dibenzothiophene compounds in the oil. Among them, the 4,6-DMDBT was found to remain even after deep hydrodesulfurization.

Ma *et al.* (1994, 1996b, 1997) studied on hydrodesulfurization reactivities of various sulfur compounds in diesel fuel. They concluded that the sulfur compounds can be classified into four groups according to their HDS reactivities that were described by the pseudo-first-order rate constants. The first group is dominantly alkyl BTs; the second, DBT and alkyl DBTs without alkyl substituents at the 4- and 6-positions; the third, alkyl DBTs with only one alkyl substituent at either the 4- or 6-position; the fourth, alkyl substituents at the 4- and 6-positions (as shown in Figure 2.11) and they also found that the major sulfur compounds are alkyl benzothiophenes and alkyl PBT in the gas oil, and alkyl thiophenes, alkyl benzothiophenes, alkyl DBT, alkyl BNT and alkyl PT in the vacuum gas oil. The dibenzothiophenes with two alkyl substituents at 4- and 6-positions, respectively, were found to be the sulfur compounds that are the most difficult to be removed from the oils.



Alkyl BTs **DBT and alkyl DBTs**

4- or 6-MDBT **4,6-DMDBT**

Figure 2.11 Structures of related polycyclic sulfur compounds found in diesel fuels (Ma *et al.*, 1994).

Gates and Topsøe (1997) pointed out that 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) are the most appropriate compounds for investigations of candidate catalysts and reaction mechanisms.

The HDS process is effective to remove thiols, sulfides and disulfides, but it is difficult to remove thiophene, benzothiophene (BT), dibenzothiophene (DBT) and their derivatives (most importantly, 4,6-DMDBT) (Zhang *et al.*, 2008). The reactivity of organic sulfur compounds varies widely depending on their structure and local sulfur atom environment. The low-boiling crude oil fraction contains mainly the aliphatic organic sulfur compounds: mercaptans, sulfides and disulfides. They are very reactive in conventional hydrotreating processes and they can easily be completely removed from the fuel. For high boiling crude oil fractions, the organic sulfur compounds predominantly contain thiophenic rings. These compounds include thiophenes and benzothiophenes and their alkylated derivatives. These thiophene containing compounds are more difficult than mercaptans and sulfides to convert via hydrotreating thus because of this problem, the sulfur compounds that remain in the transportation fuels are mainly thiophene, benzothiophene, dibenzothiophene, and their alkylated derivatives (Hernández *et al.*, 2004).

Figure 2.12 shows the qualitative relationship between reactivities of sulfur compounds and their ring size and substitution patterns. It covers the gasoline, jet fuel and diesel fuel ranges. It illustrates that there are major differences in reactivity of sulfur compounds depending on both their pattern. In particular, differences in the position of alkyl groups on benzothiophene ring size and substitution and on dibenzothiophene can have major impacts on their reactivity due to steric hindrance. There are many different sulfur compounds in diesel fuels. The reactivities of the 1- to 3-ring sulfur compounds decrease in the order of thiophenes > benzothiophenes > dibenzothiophenes. In naphtha, thiophene is so much less reactive than the thiols, sulfides, and disulfides that the latter can be considered to be virtually infinitely reactive in practical high-conversion processes (Hsu and Robinson, 2006).

Figure 2.13 shows the relative reactor volume requirements for various degrees of sulfur removal by conventional single-stage HDS of diesel fuels. The estimation of volume requirements is based on the results from HDS kinetics studies using a commercial Co-Mo/Al_2O_3 catalyst, assuming 1.0 wt% sulfur in feed. When the total sulfur content is reduced to 500 ppmw, the sulfur compounds remaining in the hydrotreated oil are 4- or 6-MDBT. When the total sulfur content is reduced to 30 ppmw, the sulfur compounds remaining in the hydrotreated oil are 4,6-DMDBT, indicating that the less the sulfur content is the lower the HDS reactivity (Song and Ma, 2003).

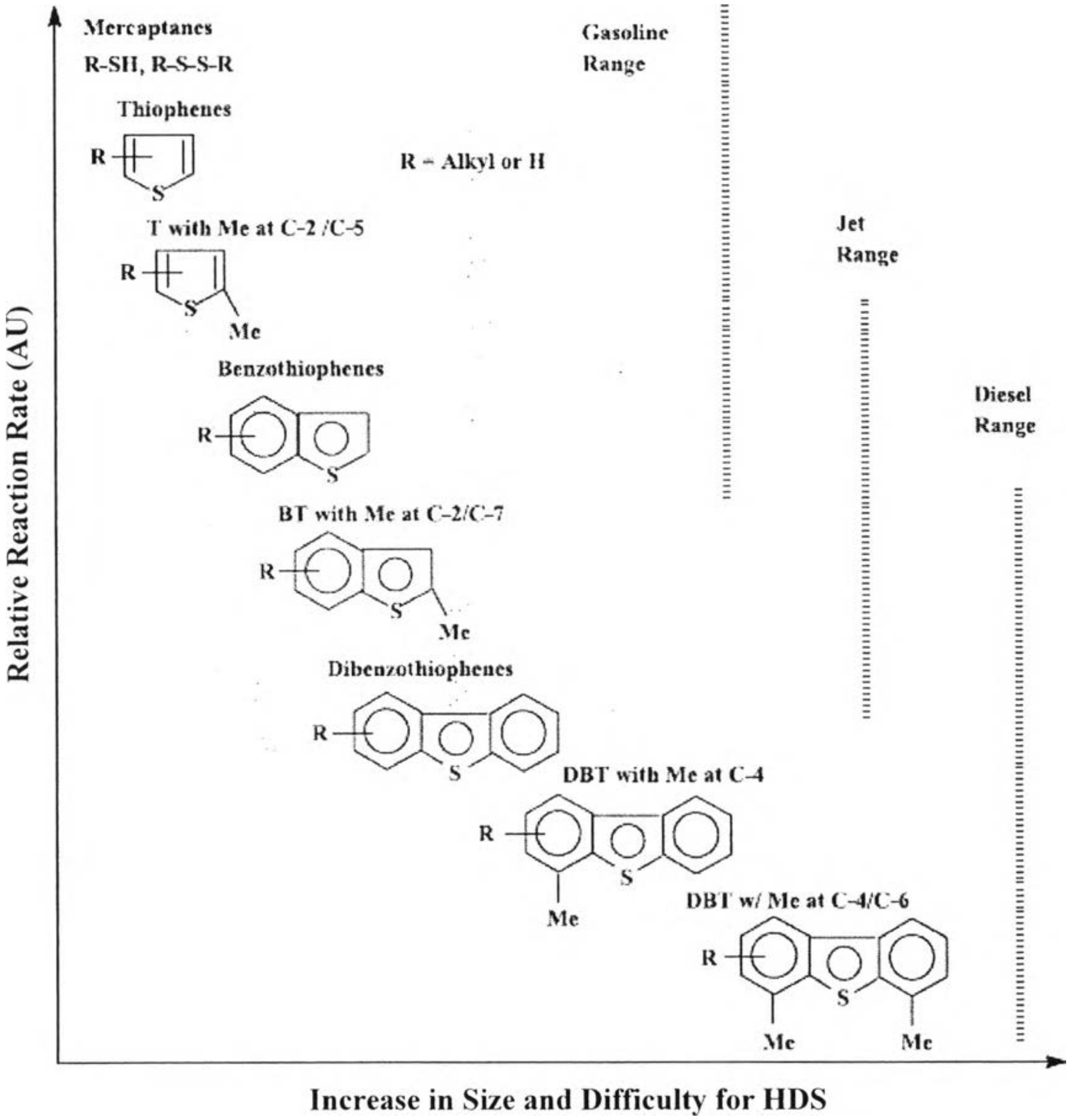


Figure 2.12 Dependence of reactivity of sulfur compounds versus their ring size and substitution patterns (for sulfur compounds in gasoline, jet fuel and diesel fuel feedstock) (Song, 2003).

To put these problems into perspective based on conventional approaches for HDS of diesel fuels, for reducing the sulfur level from current 500 ppmw to 15 ppmw (the regulation in 2006) by conventional HDS processing, the volume of catalyst bed will need to be increased by 3.2 times as that of the current HDS catalyst bed. If reducing the sulfur level to 0.1 ppm by conventional HDS processing for fuel cell application, the volume of catalyst bed will have to be increased by about seven times. As it is well known, increasing high temperature and high-pressure reactor volume is very expensive. In another scenario, with current commercial HDS processes without changing the reactor volume the catalyst activity will have to be increased by a factor of 3.2 and 7 to meet the new regulation and fuel cell applications, respectively. It might be hard to meet such a demand by making small incremental improvements in the existing hydrotreating catalysts that have been developed during the last 50 years (Song and Ma, 2003).

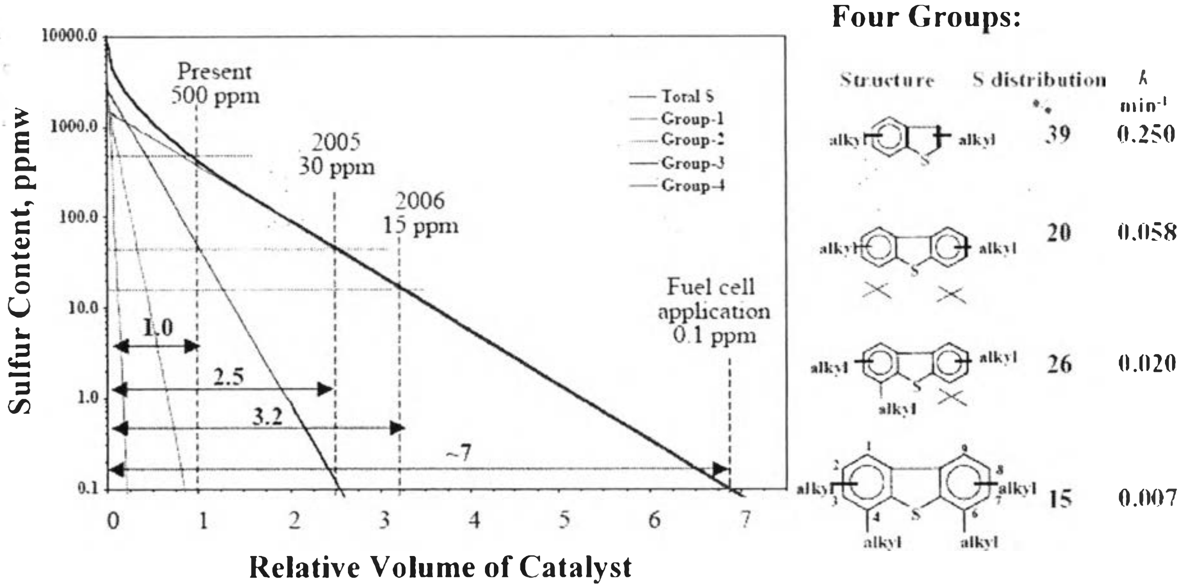


Figure 2.13 Simulated HDS of diesel to meet 15 and 0.1 ppm level on the basis of a conventional single-stage reactor, assuming 1.0 wt% S in feed; HDS kinetic model: $C_{S,total} = C_{S1o}\,e^{-k1t} + C_{S2o}\,e^{-k2t} + C_{S3o}\,e^{-k3t} + C_{S4o}\,e^{-k4t}$ (Song, 2003).

The NPRA (National Petroleum Refiners Association) estimates that imposing a 15 ppmw sulfur maximum on diesel could result in a 10% to 20% shortfall in supply. The above trends and discussion indicate that the petroleum refining industry is facing a major challenge to meet the new stricter sulfur specifications for producing ultra clean transportation fuels in the early 21st century when the quality of the crude oils continue to decline in terms of increased sulfur content and decreased API gravity (Hsu and Robinson, 2006).

2.5.2.2 Mechanistic Pathways of HDS

HDS of thiophenic compounds proceeds through two pathways: hydrogenation pathway (hydrogenation followed by hydrogenolysis) and the direct hydrogenolysis pathway (direct elimination of S atom via C–S bond cleavage). Hydrogenation and hydrogenolysis occur at different active sites. Polyaromatic compounds have been found to be the main inhibitors towards the hydrogenation pathway (Song and Ma, 2003).

Cárdenas *et al.* (2010) have proposed the reaction network of two possible reaction pathways for sulfur removal from the organosulfur compounds as illustrated for dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in Figure 2.14 and Figure 2.15, respectively. The first pathway is the sulfur atom direct extraction (hydrogenolysis) from the sulfured molecule. The second pathway is the hydrogenation of one aromatic ring followed by the sulfur atom extraction.

Both pathways occur in parallel employing different active sites of the catalyst surface. Which reaction pathway predominates depends on the nature of the sulfur compounds, the reaction conditions, and the catalyst used. At the same reaction conditions, DBT reacts preferably via the hydrogenolysis pathway whereas for DBT alkylated at the 4- and 6-positions both the hydrogenation and hydrogenolysis routes are significant (Babich *et al.*, 2003).

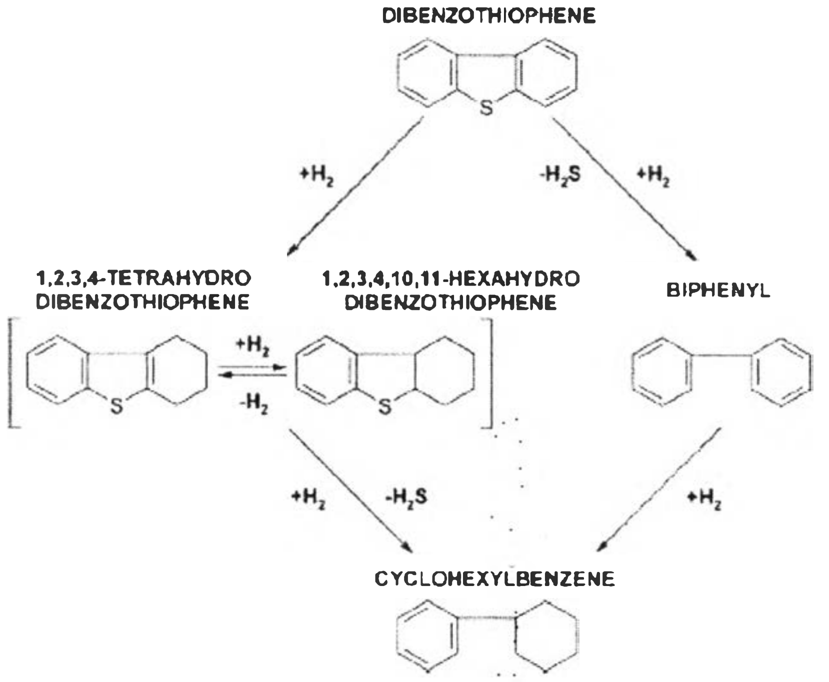


Figure 2.14 Reaction pathways for dibenzothiophene hydrodesulfurization (Cárdenas *et al.*, 2010).

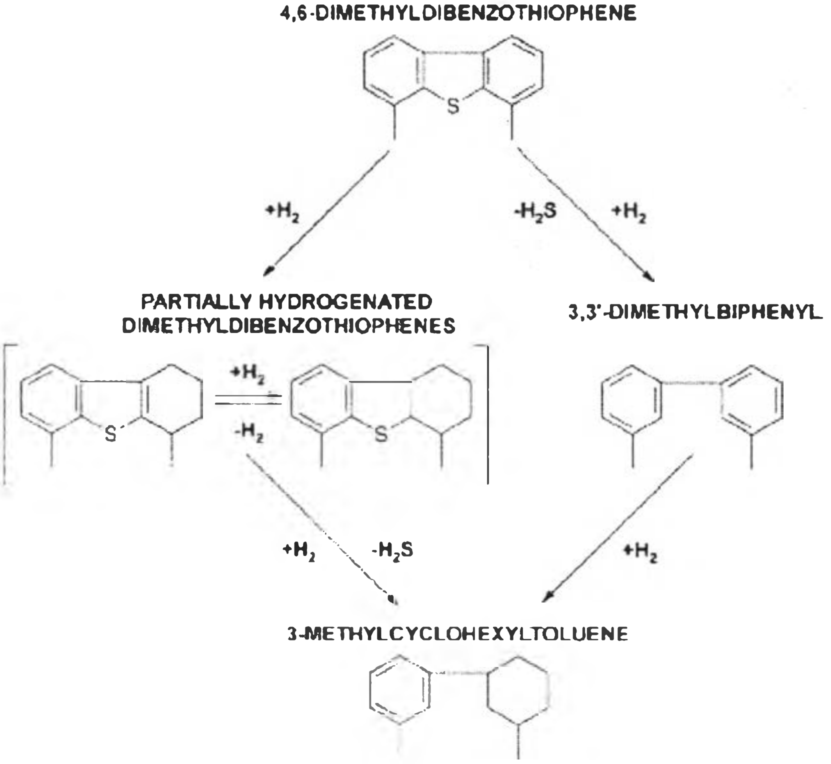


Figure 2.15 Reaction pathways for 4,6-dimethyldibenzothiophene hydrodesulfurization (Cárdenas *et al.*, 2010).

2.5.2.3 Fuel Cell Applications

Fuel cell applications required the use of a fuel with sulfur content lower than 1 ppmw in order to avoid poisoning and deactivation of the reformer catalyst. To use gasoline or diesel commercial fuels, which are the ideal fuels for fuel cells because of their high energy density, ready availability, and safety and ease for storage, the sulfur concentration should be preferably below 0.1–0.2 ppmw (Hernández *et al.*, 2005). Fuels like diesel and gasoil must be desulfurized to extremely low levels before being used as hydrogen source for modern fuel cell applications and to avoid sulfur poisoning of therein used catalysts (Rheinberg *et al.*, 2008).

a) Vision for Efficient Utilization of Hydrocarbon Resources

Figure 2.16 presents a vision on directions and important issues in research on effective and comprehensive utilization of hydrocarbon resources that are non-renewable. It has been developed by the author for directing future research in our laboratory on clean fuels, chemicals, and catalysis. There are three fundamental elements in this vision: fuel uses, non-fuel uses, and environmental issues of energy and resources. This is a personal view reflecting my judgments and prejudices for future directions. It is helpful to us for seeing future directions and for promoting responsible and sustainable development in research on energy and fuels for the 21st century (Song, 2002).

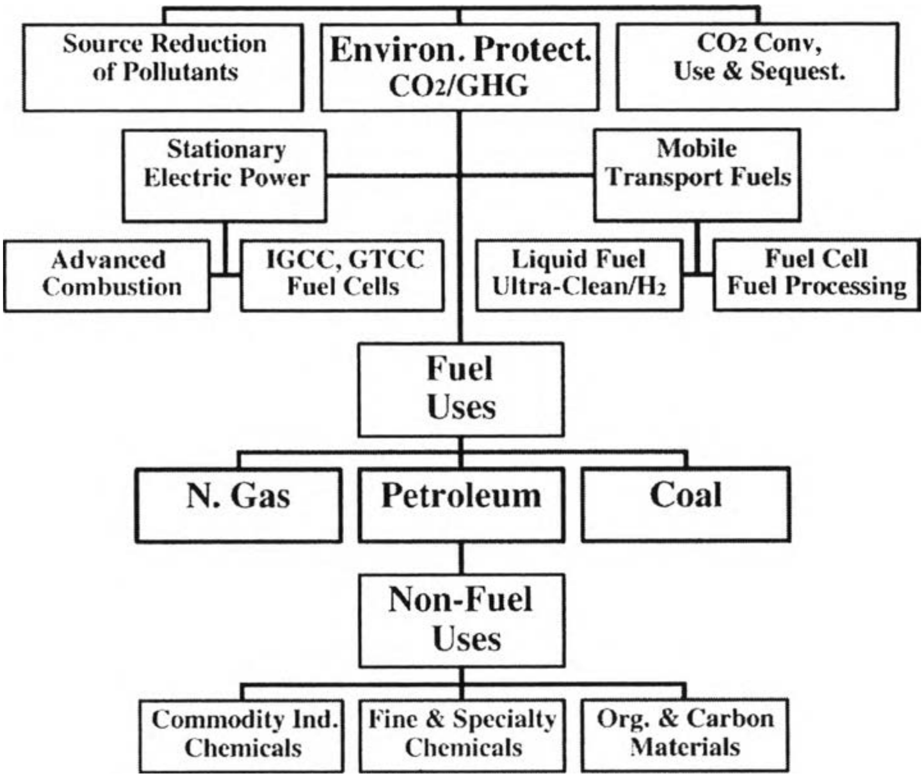
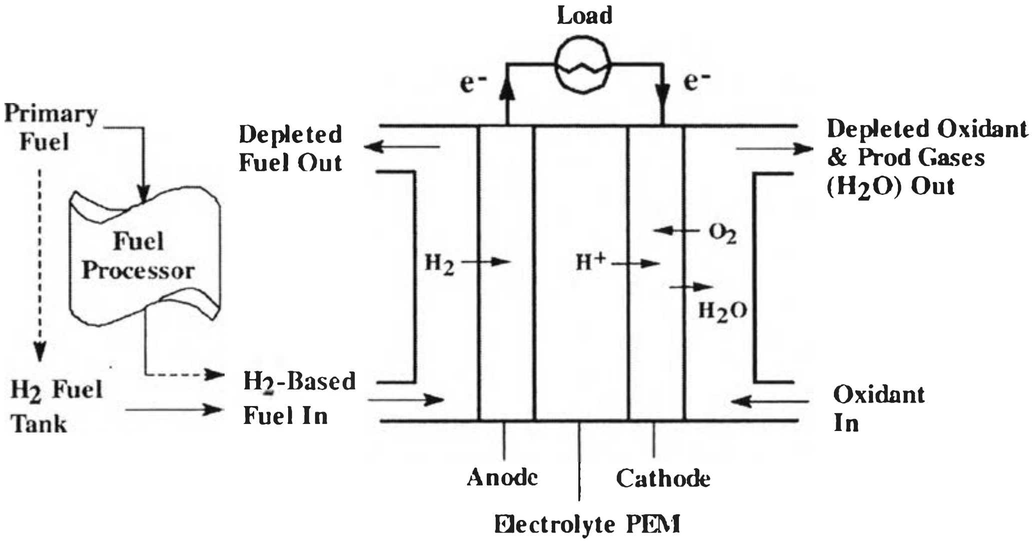


Figure 2.16 Personal vision for research towards comprehensive and effective utilization of hydrocarbon resources in the 21st century (Song, 2002).

b) Concept of Fuel Cell

A fuel cell is defined as an electrochemical device in which the chemical energy stored in a fuel is converted directly into electricity. A fuel cell consists of an electrolyte material which is sandwiched in between two thin electrodes (porous anode and cathode). Specifically, a fuel cell consists of an anode—to which a fuel, commonly hydrogen, is supplied—and a cathode—to which an oxidant, commonly oxygen, is supplied. The oxygen needed by a fuel cell is generally supplied by feeding air. The two electrodes of a fuel cell are separated by an ion-conducting electrolyte. All fuel cells have the same basic operating principle. An input fuel is catalytically reacted (electrons removed from the fuel elements) in the fuel cell to create an electric current. The input fuel passes over the anode (negatively charged electrode) where it catalytically splits into electrons and ions, and oxygen passes over the cathode (positively charged electrode). The electrons go through an external circuit to serve an electric load while the ions move through the electrolyte toward the oppositely charged electrode. At the electrode, ions combine to create by-products, primarily water and CO_2. Depending on the input fuel and electrolyte, different chemical reactions will occur (Song, 2002). The example of fuel cell is shown in Figure 2.17.



Anode (Fuel) Reaction: $H_2 = 2\,H^+ + 2\,e^-$

Cathode (oxidant) Reaction: $1/2\,O_2 + 2\,H^+ + 2\,e^- = H_2O$

Total Reaction: $H_2 + 1/2\,O_2 = H_2O$

Figure 2.17 Concept of proton-exchange membrane fuel cell (PEMFC) system using on-board or on-site fuel processor, or on-board H_2 fuel tank (Song, 2002).

c) Fuel Processing for Fuel Cell Applications

Figure 2.18 illustrates the general concepts of processing gaseous, liquid, and solid fuels for fuel cell applications. For a conventional combustion system, a wide range of gaseous, liquid and solid fuels may be used, while hydrogen, reformate (hydrogen-rich gas from fuel reforming), and methanol are the primary fuels available for current fuel cells. The sulfur compounds in hydrocarbon fuels poison the catalysts in fuel processor and fuel cells and must be removed. Syngas can be generated from reforming. Reformate (syngas and other components such as steam and carbon dioxide) can be used as the fuel for high-temperature fuel cells, for which the solid or liquid or gaseous fuels need to be reformulated. Hydrogen is the real fuel for low-temperature fuel cells, which can be obtained by fuel reformulation on-site for stationary applications or on-board for automotive applications. Synthetic ultra-clean fuels can be made by Fischer–Tropsch synthesis or methanol synthesis using the synthesis gas produced from natural gas or from coal gasification.

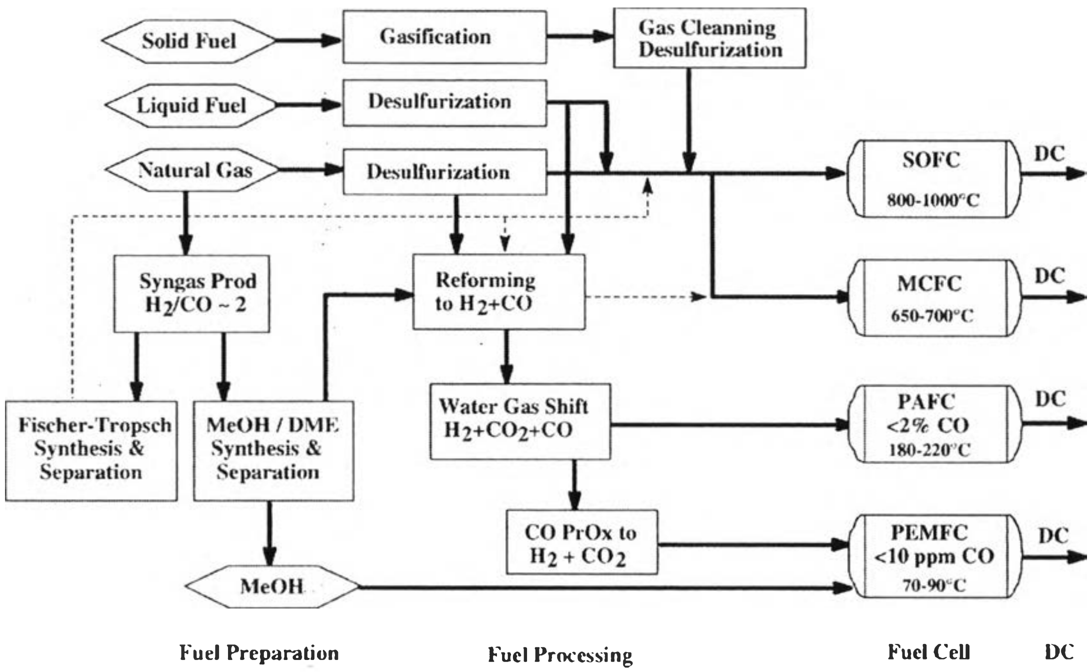


Figure 2.18 Concepts and steps for fuel processing of gaseous, liquid and solid fuels for high-temperature and low-temperature fuel cell applications (Song, 2002).

d) Fuel Cells for Transportation

Currently, the typical overall fuel efficiency of gasoline-powered cars is only around 12%, and the overall fuel efficiency of diesel-powered vehicles is better, at around 15%. These numbers, however, indicate that the majority of the energy is wasted. Therefore, new powering mechanisms (that are more efficient and clean) are also being explored by many auto manufacturers. Fundamentally, the theoretical upper limit of efficiency in the current internal combustion (IC) engines is set by a thermodynamic (Carnot) cycle based on combustion, and this must be overcome by using different conversion devices. Fuel cells hold tremendous potential in this direction. Fuel cell-powered cars are expected to be two to three times more efficient than the gasoline and diesel engines.

2.5.3 Developing New Processes

The issues of deep desulfurization are becoming more serious because of the increase in sulfur content of the crude oil and lowering of the regulated sulfur limits in diesel and gasoline (Srivastav and Srivastava, 2009). Various desulfurization techniques like hydrodesulfurization (HDS), oxidative desulfurization (ODS), bio-desulfurization (BDS) and adsorptive desulfurization are being investigated world over to produce ultra clean fuels. HDS is the most commonly used method of sulfur reduction of fossil fuels in refineries. Typically, it involves catalytic treatment with hydrogen to convert the various sulfur compounds to hydrogen sulfide. However, it requires the application of severe operating conditions and the use of especially activated catalysts for the production of fuels with very low levels of sulfur compounds. HDS is limited in treating benzothiophenes (BTs) and dibenzothiophenes (DBTs), especially DBTs having alkyl substituent on 4- and/or 6-positions. Moreover, the HDS process has reached a stage where increasing temperature and pressure are just not enough to remove last traces of sulfur without affecting the octane number. In the oxidation process, the sulfur containing compounds is oxidized to sulfone by chemical reaction using various types of oxidants namely H_2O_2, H_2SO_4, etc. The sulfone compound is then easily extracted from the fuel because of its higher polarity. Reaction selectivity, safety and cost are important concerns for the selection of oxidants, catalysts and operating conditions in ODS processing. The catalytic systems reported in literature are mostly toxic and expensive. Bio-desulfurization has drawn wide attention over the past decade. Considerable research has been done to extend the understanding of the enzymology and molecular genetics of the BDS system and to apply that into the design of the BDS bioreactor and bioprocesses (Srivastav *et al.*, 2009). Compared to the hydrodesulfurization process, the adsorptive removal of sulfur compounds seems very promising with regard to energy consumption since adsorption can be accomplished at low temperature and pressure, and the sulfur in fuels can be removed to a very low level (Jiang *et al.*, 2005).

In the adsorptive desulfurization technique, the active adsorbent is placed on a porous, non-reactive substrate that allows high surface area for the adsorption. Adsorption occurs when the sulfur molecules attach to the adsorbent and remain there separate from the fuel. Various investigators have utilized this technique for the removal of sulfur from various types of fuels and model oils by various types of adsorbents. Desulfurization by adsorption faces the challenge of developing easily remunerable adsorbent with a high capacity. Adsorbents developed must have high selectivity for the adsorption of refractory aromatic sulfur compounds that do not get removed during the HDS process (Srivastav and Srivastava, 2009).

2.5.4 Adsorptive Desulfurization

There are two types of adsorption—physical and chemical adsorption or chemisorption. The physical adsorption involves only relatively weak intermolecular forces. These forces include van der Waals forces (dispersion–repulsion) and electrostatic interactions comprising polarization, dipole, and quadrupole interactions. The chemisorption involves the formation of chemical bond between the sorbate molecule and the surface of the adsorbent (Ruthven, 1984). The different parameters of physical adsorption and chemisorption are shown in Table 2.11.

Adsorption processes consist of the selective concentration of one or more components of either a gas or a liquid at the surface of a 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 as an adsorbate's partial pressure, the adsorbate can be desorbed (Rousseau, 1987).

Adsorptive separation is achieved by one of three mechanisms: steric, kinetic, or equilibrium effect. The steric effect derives from the molecular sieving properties of zeolites and molecular sieves. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecule. A large majority of processes operate through the equilibrium adsorption of mixture and hence are called equilibrium separation processes (Yang, 2003).

Table 2.11 Parameters of physical adsorption and chemisorption (Kulprathipanja, 2009)

Parameters	Physical Adsorption	Chemisorption
Heat of Adsorption (ΔH)	low, < 2 or 3 times latent heat of evaporation	high, > 2 or 3 times latent heat of evaporation
Specificity	non-specific	highly specific
Nature of Adsorbed Phase	monolayer or multilayer no dissociation adsorbed species	monolayer only very involve dissociation
Temperature Range	only significant at relatively low temperatures	possible over a wide range of temperature
Force of Adsorption	no electron transfer, although polarization of sorbate may occur	electron transfer leading to bond formation between sorbate and surface
Reversibility	rapid, non-activated reversible	activated, may be slow and irreversible

Desulfurization by adsorption is based on the ability of a solid sorbent to selectively adsorb organic sulfur compounds from refinery steams. Based on the mechanism of the sulfur compound interaction with the sorbent, desulfurization by adsorption can be divided into two groups—adsorptive desulfurization and reactive adsorptive desulfurization. Adsorptive desulfurization is based on physical adsorption of organic sulfur compounds on the solid sorbent surface. Regeneration of the sorbent is usually done by flushing the spent sorbent with a desorbent, resulting in a high organic sulfur compound concentration flow. Reactive adsorption desulfurization employs chemical interaction of the organic sulfur compounds and the sorbent. Sulfur is fixed in the sorbent, usually as sulfide, and the sulfur-free hydrocarbon is released into purified fuel stream. Regeneration of the spent sorbent results in sulfur elimination as H_2S, S, or SO_x, depending on the process applied. Efficiency of the desulfurization is mainly determined by the sorbent properties—its adsorption capacity, selectivity for the organic sulfur compounds, durability and regenerability (Babich *et al.*, 2003).

2.5.4.1 *Adsorbents for Desulfurization*

Commercial adsorbents are divided into four major types—activated carbon, molecular-sieve zeolites, silica gel, and activated alumina. As the adsorption is a surface-related phenomenon thus the useful adsorbents are all characterized by large surface area per unit of weight (or volume). The typical range of area covers from about 100 to over 3,000 m^2/g. However, the most common commercially useful materials exhibit surface areas ranging from about 300–1,200 m^2/g (Rousseau, 1987). Table 2.12 shows examples of commercial applications of these sorbents (Yang, 2003).

Table 2.12 Adsorbents in commercial adsorption separations (Yang, 2003)

Separation	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, Ar, NH_3/H_2	Activated carbon followed by zeolite (in layered beds)
Hydrocarbons/vent streams	Activated carbon
H_2O/ethanol	Zeolite (3A)
Chromatographic analytical separations	Wide range of inorganic and polymer resin agents
Gas Purification	
H_2O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite (3A)
CO_2/C_2H_4, natural gas, etc.	Zeolite, carbon molecular sieve
Hydrocarbons, halogenated organics, solvents/vent streams	Activated carbon, silicalite, others
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite, activated alumina
SO_2/vent streams	Zeolite, activated carbon
Odors/air	Silicalite, others
Indoor air pollutants—VOCs	Activated carbon, silicalite, resins
Tank-vent emissions/air or nitrogen	Activated carbon, silicalite
Hg/chlor-alkali cell gas effluent	Zeolite
Liquid Bulk Separations	
Normal paraffins/isoparaffins, aromatics	Zeolite
p-xylene/o-xylene, m-xylene	Zeolite
Detergent-range olefins/paraffin's	Zeolite
p-Diethyl benzene/isomer mixture	Zeolite

Table 2.12 (Cont.) Adsorbents in commercial adsorption separations (Yang, 2003)

Separation	**Adsorbent**
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymer, and affinity agents
Liquid Purifications	
H2/organics, oxygenated organics, halogenated organics, etc., dehydration	Silica, alumina, zeolite, corn grits
Organics, halogenated organics, oxygenated organics, etc./H_2O—water purification	Activated carbon, silicalite, resins
Inorganics (As, Cd, Cr, Cu, Se, Pb, F, Cl, radio nuclides, etc.)/H_2O—water purification	Activated carbon
Odor and taste bodies/H_2O	Activated carbon
Sulfur compounds/organics	Zeolite, alumina, others
Decolorizing petroleum fractions, syrups, vegetable oils, etc.	Activated carbon
Various fermentation products/fermentor effluent	Activated carbon, affinity agents
Drug detoxification in the body	Activated carbon

Activated carbons and zeolites have been widely used as adsorbents in the separation and purification processes for gaseous or aqueous solution systems. Activated carbons have high adsorption capacity towards some organic and inorganic compounds due to large specific surface area, high adsorbate–adsorbent physical and chemical attraction and balanced macro-, meso- and micro-porosity while at the same time the steric hindrance of particle diffusion is minimized with regard to the sizes of the molecules being adsorbed (Bagreev *et al.*, 2004; Johns *et al.*, 1999).

Zeolites can be successfully used for the selective adsorption of polar or polarizable molecules such as water and CO_2 and sulfur-containing molecules from some petroleum fractions. These adsorbents are hydrophilic and contain large void fractions. Synthetic zeolites have a well defined crystalline lattice of metal alumina silicates which contains uniform pore sizes (Muzic *et al.*, 2010). This framework has a unique property of selectively adsorbing molecules on the basis of their size, configuration, polarity and other physical characteristics (Bakr *et al.*, 1997).

There are several published reports investigating the use of activated carbons and zeolites for sulfur removal from hydrocarbon liquids (Kim *et al.*, 2006; Bakr *et al.*, 1997; Sano *et al.*, 2005; Lee *et al.*, 2002).

a) Activated Carbon

Activated carbon material is a hydrophobic porous material with very high surface area and large pore volume. It has been widely used in deodorization, decolorization, purification of drinking water, treatment of waste water, adsorption and separation of various organic and inorganic chemicals.

Haji and Erkey (2003) studied on the desulfurization of a model diesel (DBT in n-hexadecane) by using carbon aerogels as adsorbents. They found that the saturation adsorptive capacity of a carbon aerogel with pore size of 22 nm was 15 mg of sulfur per gram of adsorbent (mg-S/g-A) and the carbon aerogel selectively adsorbed DBT over naphthalene. Sano *et al.* (2004) reported an interesting work on adsorptive desulfurization of real gas oil over activated carbon materials with surface area from 683–2,972 m^2/g. They found that using the activated carbon materials can remove sulfur and nitrogen species from gas oil (Kim *et al.*, 2006).

Activated carbon is a microcrystalline, nongraphitic form of carbon that has been processed to develop internal porosity. Activated carbon is normally made by thermal decomposition of carbonaceous material followed by activation with steam or carbon dioxide at elevated temperature (700–1,000 °C). The structures of activated carbon are stacked together in random orientation and it is the spaces between the crystals which form the micropores. The porosity yields the surface area that provides for the ability to adsorb gases and vapors from gases, and dissolved or dispersed substances from liquids. The actual distribution and the total pore volume associated with each pore size range are however sensitive to the conditions of the initial pyrolysis and activation procedures. Typical ranges are given in Table 2.13, but by special procedures, it is possible to prepare activated carbons with even higher porosity, surface area, and adsorptive capacity.

Table 2.13 Pore sizes in typical activated carbon (Ruthven, 1984)

Properties	**Micropore**	**Mesopore or Transitional Pores**	**Macropores**
Diameter (Å)	< 20	20–500	> 500
Pore volume (cm^3/g)	0. 15–0.5	0.02–0.1	0.2–0.5
Surface area (m^2/g)	100–1,000	10–100	0.5–2
(Particle density 0.6–0.9 g/cm^3; porosity 0.4–0.6)			

b) Activated Alumina

Activated alumina is a porous high-area form of aluminum oxide, prepared either directly from bauxite ($Al_2O_3 \cdot 3H_2O$) or from the monohydrate by dehydration and recrystallization at elevated temperature. The surface area is more strongly polar than that of silica gel and has both acidic and basic character, reflecting the amphoteric nature of the metal (Ruthven, 1984). The surface acidity is the most important property for both adsorption and catalysis. Unlike silica, Lewis acid sites are usually abundant on aluminas. These are the Al^{3+} sites on the surfaces. There are both tetrahedral and octahedral Al^{3+} sites. The acidity of the surface can be increased with acid, such as HCl and HF. Partial conversion of a fully hydrate alumina surface by the acid treatment would form a surface that contains both Cl^- and OH^- groups:

OH^-		OH^-		OH^-		OH^-		OH^-		OH^-
	Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}	
Cl^-		OH^-		Cl^-		OH^-		OH^-		Cl^-
	Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}		Al^{3+}	

Activated alumina is a versatile sorbent that can be tailored for many special applications. New applications continue to be developed, mainly by aluminum companies. The following are proven applications of various tailored alumina (Yang, 2003):

- Removal of HCl and HF from gases and liquids;
- Removal of acidic gases (COS, CO_2, H_2S, CS_2) from hydrocarbons;
- Removal of oxygenates and Lewis Bases;
- Removal of polar organic compounds;
- Removal of As^{5+}, PO_4^{3-}, Cl^-, and F^- from water;
- Scavenger for organic process liquids;
- Alkalized alumina for SO_2 removal.

In 2009, Srivastav and Srivastava (2009) studied the usage of commercial grade activated alumina (aluminum oxide) as adsorbent for the removal of sulfur from model oil (dibenzothiophene dissolved in n-hexane). They concluded that alumina could be used as adsorbent for the desulfurization of liquid fuels.

c) Molecular-Sieve Zeolites

The zeolites that are in commercial use today are mainly the types in Milton's invention; that is types A, X, and Y. Zeolites are crystalline aluminosilicates of group IA and group IIA elements such as sodium, potassium, magnesium, and calcium, and are represented by the chemical composition:

$$M_{x'/n}[(AlO_2)_{x'}(SiO_2)_{y'}] \cdot wH_2O$$

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, and x'/y' usually has values of 1–5.

The zeolites of most interest in catalysis are those having medium to large pore sizes, consisting of 10- or 12-ring oxygen atoms, and having relatively high Si/Al ratios. The latter may stem from the initial synthesis method or from subsequent treatments. Zeolites of high current interest industrially include zeolite Y and mordenite, which have a 12-ring system, and zeolite ZSM-5, which has a 10-ring system (Ruthven, 1984; Rousseau, 1987).

d) 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 silica-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.

2.5.4.2 Types of Metal Loading on Adsorbent

In a past few years, there were a lot of researches which concentrated on the removal of sulfur compounds from transportation fuels by using various types of metals. There are two major types of oxidation number that are usually used: 1^+ and 2^+. These metals can increase the capacity and selectivity of the adsorption of organic sulfur compounds.

For the 1^+ oxidation numbers, such as Ag^+ and Cu^+ were studied by many researchers. For example, Yang *et al.* (2001) studied Cu(I)-Y and Ag-Y as selective sorbents for desulfurization of liquid fuels. Thiophene and benzene were used as the model system and vapor-phase isotherms were measured. The results show that Cu(I)-Y and Ag-Y adsorbed significantly larger amounts of both thiophene and benzene at low pressures as a result of π-complexation with Cu^+ and Ag^+. On a per-cation basis, more thiophene was adsorbed by Cu^+ than by Ag^+. Hernández *et al.* (2004) studied the desulfurization of a commercial diesel fuel by used different adsorbents with Cu(I) in a fixed-bed adsorber operated at ambient temperature and pressure. They observed that the adsorbents tested for total sulfur adsorption capacity at breakthrough followed the order: AC/Cu(I)-Y > Cu(I)-Y > Selexsorb$^@$ CDX (alumina) > $CuCl/\gamma\text{-}Al_2O_3$ > activated carbon > Cu(I)-ZSM-5.

The 2^+ oxidation numbers, Ni^{2+}, Cu^{2+}, Fe^{2+}, and Zn^{2+} can be also used. For example, Hernández *et al.* (2004) studied the desulfurization of a commercial diesel fuel by different Ni(II)-exchanged faujasite zeolites. The results show that the adsorbents tested for total sulfur adsorption capacity at breakthrough 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). King *et al.* (2006) studied the desulfurization of gasoline by divalent copper-exchanged zeolite Y (Cu(II)-Y) zeolite. Sulfur removal was found to be greater at 150 °C than at lower temperature for Cu(II)-Y adsorbents containing as the secondary cation either Na^+ (CuNaY) or H^+ (CuHY). Overall, the CuHY zeolite showed somewhat better desulfurization performance. Bhandari *et al.* (2006) studied on sulfur removal to acceptable levels by using adsorption process at room temperature. They used Y-zeolites, ion exchanged with metal ions that are capable of π-complexation. A very high sulfur removal capacity has been observed for Ni-Y (~42 mg/g) and Cu-Y (~31 mg/g) zeolites. These along with other ion exchange zeolites such as Fe-Y and Zn-Y have been found to effectively remove sulfur from commercial diesel, although the capacity in the later case was lower than that observed with model diesel. Zhang *et al.* (2008) studied the adsorptive removal of organic sulfur compounds including dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) on various ion exchanged Na-Y zeolites with single Cu^{2+}, Zn^{2+}, Ag^+ and the combined Cu^{2+}-Zn^{2+}, Zn^{2+}-Nd^{3+}, Ni^{2+}-Nd^{3+} in model systems. It was observed that the desulfurization efficiency follows the order of direct adsorption > oxidation-adsorption > direct-oxidation. The Ag-Y and CuZn-Y are very capable of removing DBT and 4,6-DMDBT adsorption approach. The co-exchanged CuZn-Y adsorbent is a promising competitor to Ag-Y according to deep desulfurization performance for DBT and 4,6-DMDBT as well as the higher stability of adsorbent.

Moreover 3^+ oxidation number can be used, such as Ce^{3+}. Xue *et al.* (2005) observed the adsorption of thiophene and 1-benzothiophene in model gasoline using NaY-zeolites exchanged with Ag^+, Cu^{2+}, and Ce^{3+} ions and NH_4Y-zeolites exchanged with Ce^{3+} ions. The results show that the sulfur uptake increased in the order CuY-zeolite(Na) < AgY-zeolites(Na) < CeY-zeolite(Na) for both the organic sulfur compounds. CeY-zeolite(NH_4) which was prepared from NH_4Y-zeolite showed less uptake thiophene and 1-benzothiphene than CeY-zeolite(Na) probably due to its lower cerium content.

2.5.4.3 Adsorbent Preparation

a) Precipitation and Coprecipitation

The preparation of catalysts and supports by precipitation or coprecipitation is technically very important. However, precipitation is usually more demanding than several other preparation techniques, due to the necessity of product separation after precipitation and the large volumes of salt-containing solutions generated in precipitation processes. On other systems precipitation techniques are also used, for instance in the production of iron oxides, titanium oxides or zirconias. The main advantages of precipitation for the preparation of such materials are the possibility of creating very pure materials and the flexibility of the process with respect to final product quality.

Other catalysts, based on more than one component, can be prepared by coprecipitation. According to IUPAC nomenclature, coprecipitation is the simultaneous precipitation of normally soluble component with a macrocomponent from the same solution by formation of mixed crystal, by adsorption, occlusion or mechanical entrapment. However, in catalyst preparation technology, the term is usually used in a more general sense in that the requirement of one species being soluble is dropped. In many cases, both components to be precipitated are essentially insoluble under precipitation conditions, although their solubility products might differ substantially. We will therefore use the term coprecipitation for the simultaneous precipitation of more than one component. Coprecipitation is very suitable for the generation of a homogeneous distribution of catalyst components or for the creation of precursors with definite stoichiometry, which can be easily converted to the active catalyst. Such a good dispersion of catalyst components is difficult to achieve by other means of preparation, thus coprecipitation will remain an important technique in the manufacture of heterogeneous catalysts in spite of the disadvantages associated with such processed. These disadvantages are the higher technological demands, the difficulties in following the quality of the precipitated product during the precipitation, and the problem in maintaining a constant product quality throughout the whole precipitation process, if the precipitation is carried out discontinuously.

The investigations of crystallization and precipitation processes from solution often have to rely on indirect and theoretical methods. Figure 2.19 depicts a general flow scheme for the preparation of a precipitation catalyst.

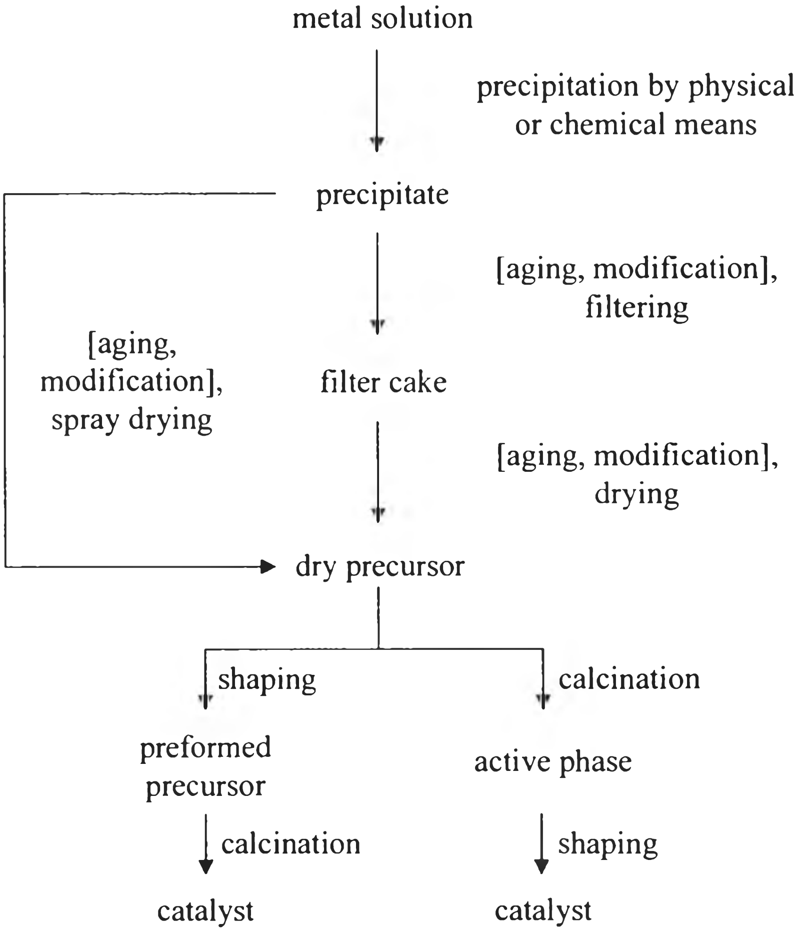


Figure 2.19 Preparation scheme for precipitated catalyst. Optional preparation steps are indicated by square brackets (Ertl *et al.*, 1997).

b) Sol-Gel Process

The sol-gel process involves first the formation of a sol followed by that of a gel. A sol, which is a liquid suspension of solid particles ranging in size from 1 nm to 1 micron, can be obtained by the hydrolysis and partial condensation of precursor such as an inorganic salt or a metal alkoxide. The further condensation of sol particles into a three-dimension network produces a gel, which is a diphasic material with a solid encapsulating a solvent. Alternatively, a gel can be produced by destabilizing a solution of performed sols. In either case the materials are referred to aquasol (or aquagel) when water is used as a solvent, and alcosol (or alcogel) when alcohol is used. The encapsulated liquid can be removed from a gel by either evaporative drying or drying with supercritical extraction. The resulting solid products are known as xerogel and an aerogel, respectively. The single most important characteristic of the sol–gel preparation of catalytic materials in its ease of control that translates into the following advantages:

- The ability to maintain high purity (because of purity of staring materials)
- The ability to change physical characteristics such as pore size distribution and pore volume
- The ability to vary compositional homogeneity at a molecular level
- The ability to prepare samples at low temperatures
- The ability to introduce several components in a single step
- The ability to produce samples in different physical forms

Figure 2.20 shows the four key steps in taking a precursor to a particular product form via sol–gel preparation: formation of gel, aging of gel, removal of solvent, and heat treatment.

c) Ion Exchange

Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species. The support containing ion A is plunged into an excess volume (compared to the pore volume) of a solution containing ion B that is to be introduced. Ion B gradually penetrates into the pore space of the support and takes the place of ion A, which passes into the solution, until equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution.

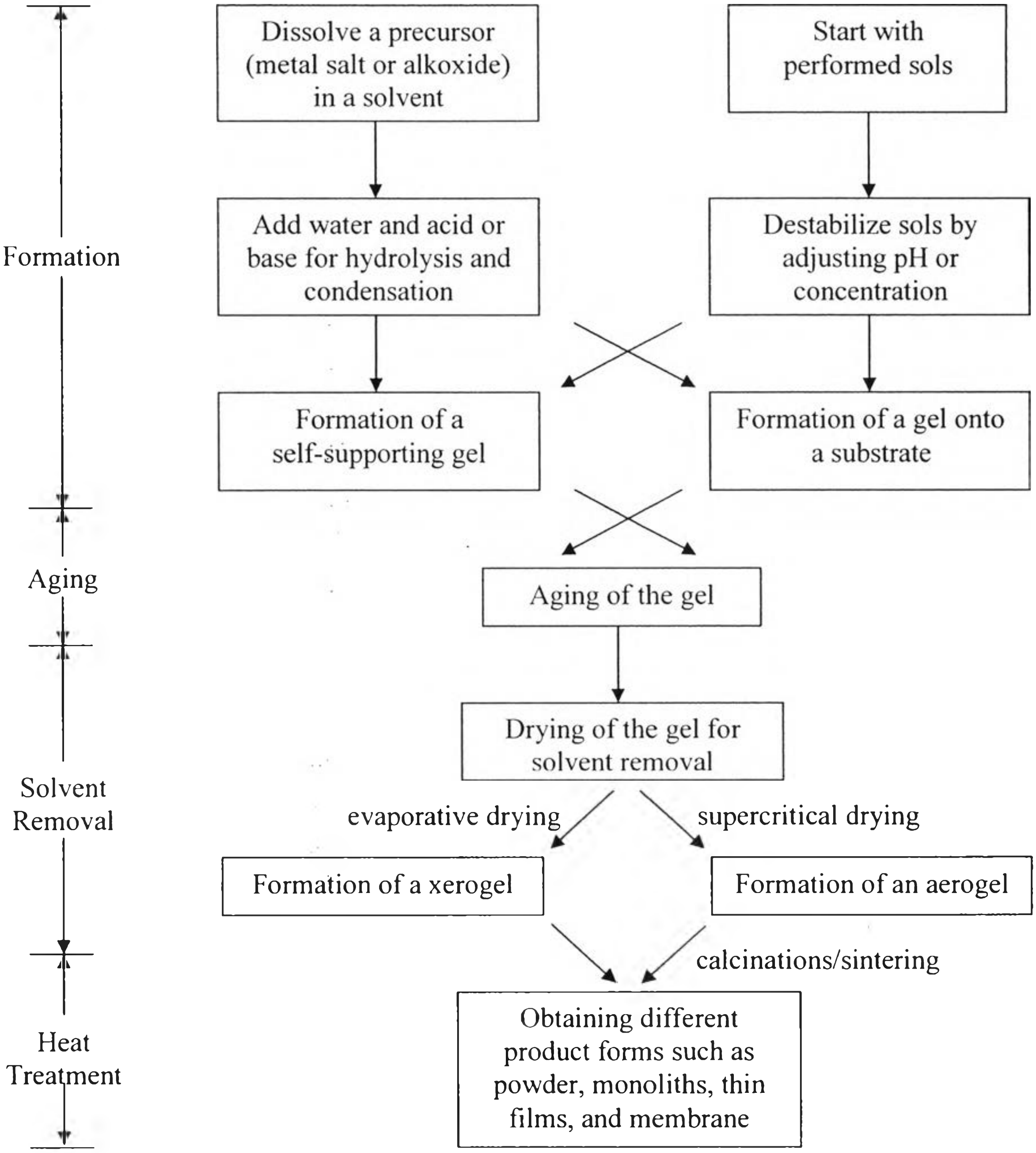


Figure 2.20 Schematic diagram showing the various steps of a sol–gel process (Ertl *et al.*, 1997).

Almost all solid mineral supports are oxides. They behave like ion exchangers when their surface bears electric charges. Two categories may be distinguished: natural exchangers which are composed of framework bearing electric charges neutralized by ions of opposite sign and amphoteric oxides (Ertl *et al.*, 1997).

d) Impregnation

Preparation of impregnated catalysts usually involves filling the pore structure of shaped, porous support body with a solution of catalyst component(s), removing the solvent, and activating the catalyst. The impregnating solution may be a simple water solution of one or more soluble salts of the metal(s) and counter-ions to be deposited, or it may be a complex mixture incorporating solubilizing agents and/or reactants, such as reducing agents that function during as activation step.

Incipient wetness impregnation is a commonly used technique for the synthesis of heterogeneous catalysts. Typically, the active metal precursor is dissolved in an aqueous or organic solution. Then the metal-containing solution is added (the solution may be sprayed into the support in blending operation) to a catalyst support containing the same pore volume as the volume of solution that was added. Capillary action draws the solution into the pores. The resulting mixture appears dry to the eye, thus the name dry impregnation has been applied. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface. The maximum loading is limited by the solubility of the precursor in the solution. The concentration profile of the impregnated compound depends in the mass transfer conditions within the pores during impregnation and drying.

This method works well with supports that have relatively large, open-ended pores, even with aqueous solutions having a relatively high surface tension. Careful attention must be paid to the viscosity of the solution, which affects how much solution can be adsorbed by the solid. Certain hydrotreating catalysts containing transition metals on alumina are examples of the use of this manufacturing method.

For catalyst supports with extremely small pores or a closed-end pore structure, it may be difficult to fill the support completely with impregnating solution by the dry impregnation method. In this case, immersion of the support in a solution containing the catalytically active components usually is more effective. Unless the solvent used has a high vapor pressure or contains dissolved gases, a complete pore volume impregnation usually can be aided by the use of vacuum. In this case, the bare support is placed in suitable vessel, the air is withdrawn, and sufficient solution is introduced to cover the support while it is under vacuum. Air, or in some cases another gas, is then admitted to the vessel until at least atmospheric pressure is established, which forces the liquid into the evacuated pore structure of the support. Excess liquid is drained from the wet support and the excess solution is discharged. Liquids are removed from the impregnated support by controlled heating with or without the use of reduced pressure. Depending on the nature of the finished catalyst, the impregnated support may or may not be treated further or calcined in subsequent steps (Grant, 1992).

2.5.4.4 Dispersing Agent

By definition, dispersing agent is an additive, exhibiting surface activity, which is added to a suspending medium to promote uniform and maximum separation of extremely fine solid particles, often of colloidal size. It is noted that although dispersing agents achieve results similar to compatibilizers, they function differently in that they reduce the attractive forces between fine particles, which allow them to be more easily separated and dispersed (http://old.iupac.org/goldbook/ DT07266.pdf).

In year 2009, Rinaldi *et al.* studied the effect of citric acid (CA) addition on the HDS of thiophene over Co–Mo/B_2O_3/Al_2O_3 catalysts. And characterized the catalysts by means of a variety of physicochemical techniques such as LRS, Mo K-edge EXAFS, NO adsorption capacity measurements, and UV–vis spectra. They concluded that the addition of citric acid considerably increases the HDS activity of Co–Mo/B_2O_3/Al_2O_3 catalysts up to CA/Mo mole ratio = 1, but a further addition of citric acid causes no activity increase.

For the following year, they studied on the MoO_3/Al_2O_3 catalysts using citric acid (CA) as a chelating agent by a simultaneous impregnation method or by a post-treatment method. The catalyst was tested for the HDS of thiophene. The catalysts were characterized by means of LRS, XRD, Mo K-edge EXAFS and XANES, NO adsorption capacity, and surface area measurements. They concluded that the addition of citric acid by the post treatment method is very effective to greatly improve the edge dispersion of MoS_2 particles on the catalysts and thus the HDS activity of the resulting CA/Mo/Al and Co/CA/Mo/Al catalysts.

2.5.4.5 Regeneration of Adsorbent

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 permits 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.

Wang and Yang (2007) studied the desorption of $PdCl_2$/activated carbon after saturated with the model jet fuel by using ultrasound-assisted sorbent regeneration. The desorption was conducted in a static bath of solvent at room temperature and 50 °C. The results showed that the amount of sulfur desorbed depended on the time and temperature. With increasing desorption time, the amount of sulfur desorbed reach a constant value. They also found that ultrasound was an effective technique for regenerating spent $PdCl_2$/activated carbon. Kaewboran (2005) investigated the desorption of NaX after the desulfurization of the sulfur compounds such as 3-MT and BT in simulated gasoline and DBT in simulated diesel by heating technique at 400 °C. The result was 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. Hernández *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%. Hernández *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. Hernández *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.

2.5.5 Π-Complexation Sorbents

The π-complexation bond is typically a weak bond that can be formed between the sorbent and sorbate. The sorbents that are used for separation and purification based on π-complexation are called π-complexation sorbents. Development of π-complexation sorbents began only recently. A number of sorbents have already been used commercially, and tremendous potential exists for future applications in separation and purification, both for the chemical/petrochemical industry and environmental applications. All major industrial adsorption processes are based on van der Waals and electrostatic interactions between the sorbate and sorbent. Chemical bonds have yet to be exploited in a significant way. Chemical complexation has been studied and used on a large scale in a number of other separation and purification processes by using mass separating agents.

Chemical complexation bonds are generally stronger than van der Waals interactions (thus giving rise to higher selectivities), many of them are weak enough to be reversible (i.e., to be broken by simple engineering means). The π-complexation is a special class of chemical complexation. For π-complexation sorbents, it pertains to the main group (or d-block) transition metals (and there are 27 elements). When interact with a gas or solute molecule, these metals and their ions can form the usual σ bonds with their s-orbitals and, in addition, their d-orbitals can back-donate electron density to the antibonding π-orbitals of the molecule to be bonded (Yang, 2003) (see Figure 2.21, 2.22 and 2.23).

During the last decade, π-complexation sorbents have been developed for many applications, including desulfurization, olefin/paraffin, diene/olefin, and aromatics/aliphatics separations. For desulfurization, transition-metal ion exchanged zeolites have used to selectively remove organosulfur molecules from commercial fuels like diesel and gasoline.

Molecular orbital calculations have shown that the π-complexation bonds between Cu^+ or Ag^+ and thiophene are stronger than that with benzene (Yang, *et al.*, 2001). Moreover, it was determined that the π-complexation bond was stronger for substituted thiophenes over non-substituted ones and thus π-complexation sorbents are selective for sulfur removal from transportation fuels (Hernández *et al.*, 2005).

In 2005, Hernández and coworkers used a CuCl/γ-Al_2O_3 sorbent prepared by incipient wetness impregnation methods for desulfurization of a commercial diesel fuel (297.2 ppmw S). They found that these cuprous π-complexation sorbents selectively adsorb thiophenic compounds over aromatics and olefins (as predicted by the high separation factors), which resulted in the observed desulfurization capability. CuCl/γ-Al_2O_3 is a promising sorbent for selective removal of all sulfur compounds from a commercial jet fuel and a BP diesel.

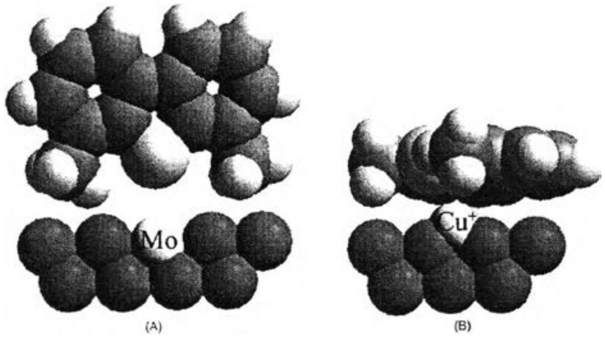


Figure 2.21 Schematic representation for desulfurization of 4,6-DMDBT with molybdenum-based (A) and copper(I)-based (B) adsorbents. Case (B) corresponds to π-complexation (Hernández *et al.*, 2005).

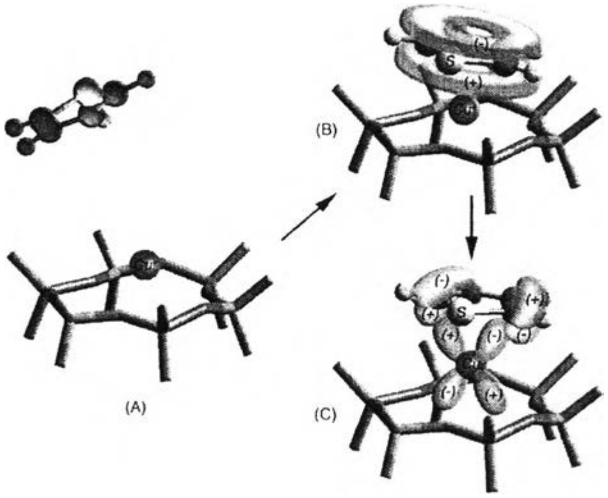


Figure 2.22 Copper ions occupying faujasite 6-ring windows sites (A); σ-donation of π-electrons of thiophene to the 4s orbital of copper(I) (B); d–π* backdonation of electrons from 3d orbitals of copper(I) to π* orbitals of thiophene (C). Here 3d represents d_{xy}, d_{yz} or d_{xz}, or 3 of the 53d orbitals (Hernández *et al.*, 2005).

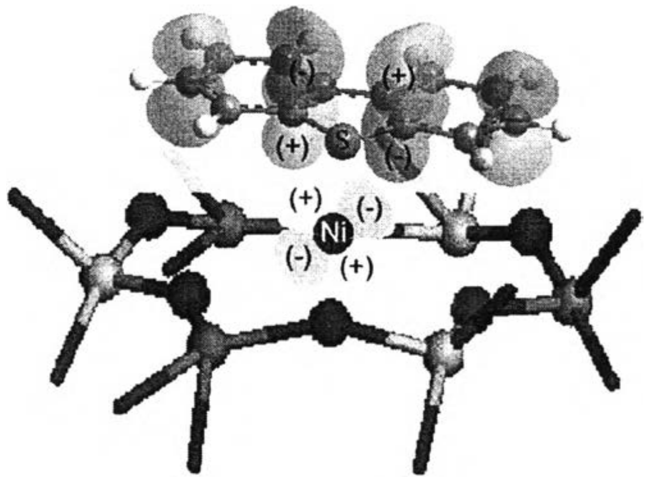


Figure 2.23 Means of interaction for a DBT molecule with NiY, corresponding to π-complexation (Juan *et al.*, 2009).

2.5.6 Fixed-Bed Adsorption

Fixed-bed adsorption processes are ubiquitous throughout the chemical process and other industries. The phenomenon of adsorption is an attraction of adsorbate molecules to specific interaction between adsorbate molecules (aromatic rings or specific atoms) and the adsorbent surface. Figure 2.24 illustrates the breakthrough curve used to represent the adsorption process.

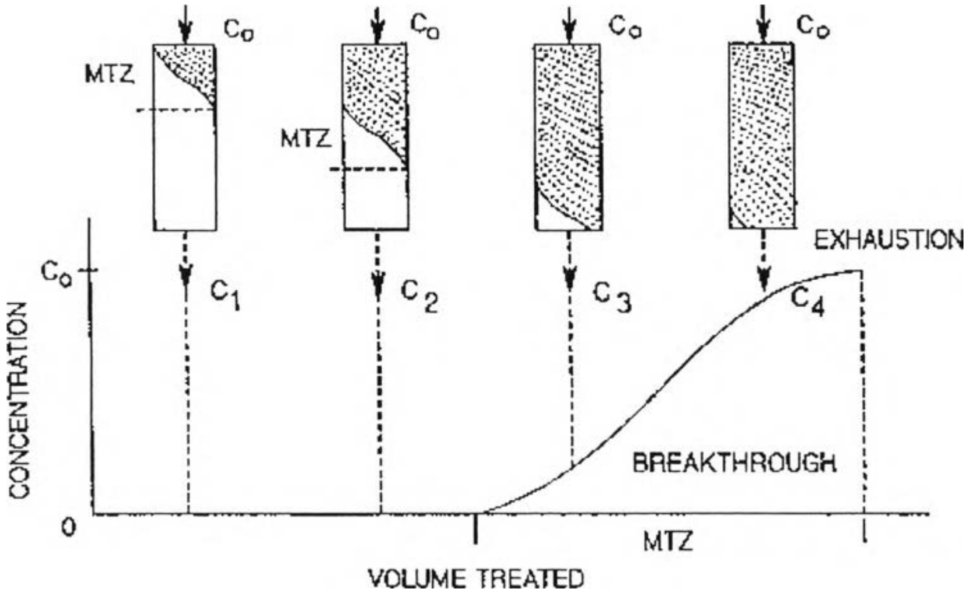


Figure 2.24 Idealized breakthrough curve of a fixed-bed adsorber (http://www.activated-carbon.com/solrec3.html).

Figure 2.24 plots the relationship between outlet concentration of the adsorbate from the fixed-bed adsorber and volume treated which is the function of time. The mass transfer zone (MTZ) is the area within the adsorbate bed where adsorbate is actually being adsorbed on the adsorbent. The MTZ typically moves from the influent end toward the effluent end of the adsorbent bed during operation. That is, as the adsorbent near the influent becomes saturated (spent) with adsorbate, the zone of active adsorption moves toward the effluent end of the bed where the adsorbate is not yet saturated. The MTZ is sometimes called the adsorption zone or critical bed depth.

The length of the MTZ can be defined as LMTZ. When LMTZ is equal to bed depth, it becomes LCRIT, or the theoretical minimum bed depth necessary to obtain the desired removal. As adsorption capacity is used up in the initial MTZ, the MTZ advances down the bed until the adsorbate begins to appear in the effluent. The concentration slowly increases until it equals the influent concentration. In cases where there are some very strongly adsorbed components, in addition to a mixture of less strongly adsorbed components, the effluent concentration very seldom reaches the influent concentration because only the components with the faster rate of movement through the adsorber are in the breakthrough curve.

Dynamic desorption capacity is influenced by many factors, such as flow rate, temperature, bed length, and concentration of the bed. The adsorption column may be considered exhausted when the effluent adsorbate concentration equals 95–100% of the influent concentration. As the concentration wave moves through the bed, most of the mass transfer is occurring in a fairly small region. This mass transfer zone moves down the bed until it breaks through. The shape of the mass transfer zone depends on the adsorption isotherm (equilibrium expression), flow rate, and the diffusion characteristics. Usually, the shape must be determined from the experiment. The shape of the wave front may change as it moves through the bed, and the mass transfer zone broadens or diminishes. Unfavorable and linear isotherms tend to broaden. Favorable Langmuir may broaden at first, but quickly achieve a constant pattern front, an asymptotic shape. This means that the mass transfer zone is constant with respect to both position and time (Ho Nhoc, 2007).

2.6 Inverse Gas Chromatography (IGC) Characterization

Inverse chromatography can be considered as a dynamic sorption technique. Unlike in analytical chromatography the stationary phase is the sample under investigation while a substance in the mobile phase acts as a probe molecule. This means the roles of the phases are inverted and this is where the name inverse chromatography comes from. An empty column is filled with the (porous) material under investigation (adsorbent) and the probe molecule (adsorbate) in the mobile phase probes the surface of the adsorbent (Thielmann, 2004).

2.6.1 IGC Theory

Inverse chromatography can be utilized in the gas phase as well as in the liquid phase. Although there is a significant interest in the field of inverse liquid chromatography (ILC) only little work was done so far compared to the numerous publications on inverse gas chromatography (IGC) found in literature.

IGC is usually used as gas–solid chromatography (in older literature often referred to as GSC), meaning the probe is a gas or a vapor interacting with the solid sample. A less frequently-used but also interesting variation of IGC is gas–liquid chromatography (in older literature often referred to as GLC) where the probe is again a gas or a vapor but the stationary phase is a liquid. Of course only liquids with a considerable viscosity, which have been “coated” on an inert carrier material, can be investigated.

IGC measurements can be carried out using a pulse or frontal technique. In a pulse experiment a certain amount of the probe molecule is injected. This pulse is transported by the mobile phase (carrier gas) through the system to the column with the solid sample. Subsequently, adsorption and desorption occurs and the result is a peak in the chromatogram. An alternative is the frontal technique. In this case the probe molecule is added continuously to the carrier gas and the chromatogram shows a breakthrough curve. The benefit of the frontal technique is that equilibrium can be always established due to its continuous nature while pulse chromatography requires the assumption of a fast equilibration of the probe molecule adsorbing on the surface.

Whether or not a pulse experiment represents equilibrium values depends strongly on the carrier gas flow rate. Generally it can be said that the lower the flow rate the more likely a system is in equilibrium (Mukhopadhyay and Schreiber, 1995). On the other hand low flow rates mean longer experimental times and broader peaks. The latter might reduce the accuracy of the retention time determination.

After the injection of the probe molecule adsorption takes place at the sample in the column followed by desorption. These interactions cause retention, similar to analytical chromatography. For this reason the primary information of an IGC experiment is the retention time, or to be more accurate the gross retention time.

The retention time is measured by typical chromatographic detection methods such as flame ionization (FID) or thermal conductivity (TCD) detector. The FID has the benefit of a higher sensitivity but is limited to mainly organics while the TCD is more versatile but very limited in sensitivity.

As far as the columns are concerned, the literature describes a vast amount of different column length and diameters for different applications. However, there are some criteria that help to select the right column length and diameter. The diameter should be generally rather small to keep gas-phase diffusion effects to the minimum. On the other hand, it can be beneficial to have wider diameters if materials with small particle sizes have to be packed in order to avoid a big pressure drop. The column length is not as crucial as the bed length of the packed stationary phase. Usually packed beds are supported on a porous filter or hold in place with glass wool plugs. For this reason the column can be longer than the packing. However, it is advisable to keep the column length close to the typical bed length for an application to avoid additional peak broadening due to gas phase diffusion.

The length of the packed bed depends entirely on the uptake capacity of the sample and the amount of vapor injected. This is particularly important in the case of pulse experiments. It must be insured that the retention is strong enough (good separation between probe and tracer peak) to obtain reproducible and accurate results. This can be cross-checked by repeating the experiments with different column masses. If the final results (the parameters measured) are mass-independent it can be concluded that enough mass has been used in the column in relation to the amount of probe molecule injected. The quality of the results depends of course significantly on the technical sophistication of the apparatus used. Simple conversions of regular gas chromatographs usually do not deliver the required accuracy and reproducibility without mayor modifications and improvements of the experimental set-up. Critical system components include the column oven temperature stability and uniformity, the control of the carrier gas flow rate, the injection system (for reproducible injection quantities) as well vapor generation system (temperature stability and accuracy). Generally it can be concluded that the more sophisticated the technology the shorter the required column length, and therefore, the faster the experiment without any compromise in accuracy and reproducibility (Thielmann, 2004).

2.6.2 Topological Index

In 1997, Eric Brendlé and Eugène Papirer have proposed the work on the topological index, χ_T. This index is a modification of the Wiener's index for the evaluation of the retention data of non-polar and polar solutes used in inverse gas chromatography. It has been shown to be particularly well suited for the determination, first, of the dispersive component (γ_s^d) of the surface energy of solids, such as pyrogenic silicas presenting a rather smooth surface (on the scale of the probe molecule), and second, of a morphology index IM χ_T that encounters of structural or other inhomogeneities of solid surfaces that exhibit nanorugosity.

In the same year, they also investigated the application of their index (χ_T) for the evaluation of the specific interaction (γ_s^s) potential of chosen solutes and solids, using IGC at infinite dilution conditions. It has been shown that their index was well suitable for the determination.

2.7 Previous Studies on the Use of Adsorbents for Selective Sulfur Removal at PPC

At The Petroleum and Petrochemical College, Chulalongkorn University (PPC), Thailand, there have been several studies on sulfur adsorption using various kinds of adsorbents. In 2007, Ho Nhoc studied the desulfurization of transportation fuels by adsorption process using the ion-exchanged zeolites which prepared by exchanging NaX and NaY zeolites with Ni^{2+} and Cu^{+} cations using both LPIE and SSIE methods. These adsorbents were evaluated for their efficiency in removing 3-MT and BT in both binary and ternary systems of isooctane and benzene (or toluene) as model fuels. In the static adsorption, the sulfur adsorption capacity increased in the order NiY (LPIE at 135 °C) < NiX (LPIE at 45 °C) < NiY (SSIE) for both sulfur compounds. Furthermore, the adsorption data of sulfur compounds in isooctane and benzene revealed that the removal rate and the overall sulfur uptake capacity of the adsorbents were significantly reduced when benzene was used, which can be attributed to the competitive π-complexation forming with the adsorbent between the aromatic (benzene) and sulfur compound. The equilibrium capacity under dynamic conditions for 3-MT adsorption increased in the order of NaY < NiY < NiX < NaX < Cu(I)Y; while the selectivity for 3-MT over toluene exhibited the following trend NaY < NiY < NaX < NiX < Cu(I)Y. In addition, the pre-adsorbed water was found to have detrimental effect on the π-complexation bonding between adsorbent and sulfur compounds.

Prateepamornkul (2008) studied the adsorptive capacity and selectivity of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) in simulated diesel fuels containing polyaromatic or nitrogen compounds on activated carbon and alumina, modified with Cu^{+} and Ni^{2+} using different preparation methods. Direct impregnation by using $CuCl/CH_3CN$ was found to be unsuitable due to the stability and low solubility of Cu^{+}. Impregnation was therefore performed with an aqueous solution of $CuCl_2$ following by a reduction step of $CuCl_2$ into CuCl using H_2. For Ni^{2+}, an aqueous solution of $NiCl_2$ was used. A suitable feed flow rate and granulometry of the adsorbent was found to be 0.4 cm^3/min and 100 to 400 μm, while the optimum temperature was 60 °C and 90 °C for Ni^{2+} and Cu^{+} impregnated alumina, respectively. The adsorption capacity at the sulfur breakthrough followed the order non-impregnated macroporous alumina < Cu^+/macroporous alumina < non-impregnated mesoporous alumina < Cu^+/mesoporous alumina < Ni^{2+}/macroporous alumina < Ni^{2+}/mesoporous alumina < Cu^+/AC < non-impregnated AC. The breakthrough capacity of DBT was higher than 4,6-DMDBT for both of Ni^{2+} and Cu^+/mesoporous alumina. Moreover, the breakthrough capacity of DBT without polyaromatic and nitrogen compounds was higher than that with polyaromatic and nitrogen compounds.

Atireklapwarodom (2009) studied the sulfur adsorption efficiency of Ni^{2+} and Cu^+ based mesoporous sorbents for the desulfurization of simulated diesel via π-complexation by using breakthrough experiment. Macroporous activated alumina (M-Al_2O_3), mesoporous activated alumina (m-Al_2O_3), and activated carbon (AC) impregnated with Cu^+ and Ni^{2+} was investigated to remove dibenzothiophene (DBT) in simulated diesel (80 wt% dodecane + 20 wt% toluene + 150 ppmw S). The adsorbents were prepared by incipient wetness method by using aqueous solution of $CuCl_2$ (very soluble in water) and $NiCl_2$, then followed by a reduction step of Cu^{2+} to Cu^+ by H_2. She found that the breakthrough capacity was greater with the lower feed flow rate (0.4 cm^3/min) to increase the contact time between DBT and the adsorbent, while the optimum temperature is room temperature (30°C). Quite all the breakthrough curves obtained for DBT showed a very broad shape, indicating that strong diffusion limitations seem to occur. An effort will therefore have to be done to optimize the experimental conditions, mainly by increasing the contact time and reducing the particle size of the adsorbent. For all among the adsorbents studied, the breakthrough capacity decreased in order of 43 wt% of Cu^+/AC > AC > 100% monolayer of Cu^+/m-Al_2O_3 (300-500 μm crushed after impregnation) > non-impregnated m-Al_2O_3 > 50% monolayer of Ni^{2+} /m-Al_2O_3. She recommended that the amount of metal within the porosity of the solid was too high.