

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Lubricating oil

The lubricating oil is usually a mixture of lubricating base oil and additives. There are essentially two sources from which the base lubricant fluids are obtained. There are the refining of petroleum crude oil and the synthesis of relatively pure compounds with properties, which are suitable for lubricant purposes.

##### 2.1.1 Source of Lubricating Base Oil [11]

The manufacture of lubricating base stocks consist of a series of separation or subtractive processes which remove undesirable components from the feedstock leaving a lubricating base stock that meets performance requirements. Essentially five steps are involved.

1. Vacuum distillation : this process which separates the atmospheric residue mixture into a series of fractions representing different molecular weight ranges. The residue contains the heavier base oils such as the bright stocks.

2. Propane deasphalting : the highest boiling portions of most crude oils contain resins and asphaltenes. These materials must be separated prior to introduction into the extraction process.

3. Furfural extraction : solvent extraction (Furfural in this case) separates aromatic compound from nonaromatic compounds. The resultant product shows an increase in thermal and oxidative stability as well as an improvement in viscosity and temperature characteristics, as measured by a higher viscosity index (VI)

4. MEK dewaxing: this process is to remove wax by methyl ethyl ketone (MEK) to reduce the pour point of the base stock.

5. Hydrofinishing : some base stocks require a finishing process to improve the color, oxidation, or thermal stability of the base stock. The hydrofinishing process consists of a bed of catalyst through which heated oil and hydrogen are passed.

### **2.1.2 Lubricating Base Oil Composition [11,12]**

Materials suitable for the production of lubricating oil are comprised principally of hydrocarbon containing from 25 to 35 or even to 40 carbon atom per molecule.

The lubricating oil fraction is a complex mixture consisting primarily of one lone carbon atom chain to one or both ends of which a ring system or short branch may be attached. Monocycloalkanes and monoaromatics usually have several short (e.g. methyl) branches on the ring. Most of the compounds are paraffin naphthenes with cycloparaffinic ring attached to paraffinic chain. It also contains small amounts of heterocyclic compounds containing sulfur and nitrogen atoms (e.g. thionaphthene, indole, quinoline and carbazole) and various oxygen containing compounds, including naphthenic acids, which account for most of the chemically bound oxygen in petroleum fractions.

Aromatic compounds usually have cycloparaffinic ring attached to them along with long paraffinic chain. Polyaromatics usually have all their ring in the single condensed nucleus which also might have short branch attached. Polycyclic saturates may be separated by alkyl chains. Aromatic compounds may also be in the form of biphenyls and their derivatives. Thus the lubricating oil are made mainly of three general types:

- Straight and branched chain paraffinic compounds.
- Polycyclic and fused-ring saturated hydrocarbon based on cyclopentane prototype ring structures, collectively known as naphthenes.
- Aromatic, both mono and polynuclear, which are unsaturated ring structure.

Alkanes, alicyclics and aromatics of the same molecular weight have markedly different physical and chemical properties. Physical characteristics will affect the viscometrics of the lubricant. The chemical stability of each class of oxidation and degradation while in use will also be very important.

### **2.1.3 Lubricating Oil Additive [13]**

Lubricating oils are produced by blending base lubricating oil and additives. The lube oil base stocks are prepared from crude oils by distillation and special processing to meet the desired qualification. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improved

existing properties. Additives can be classified as materials which either impart or enhance a desirable property of the lubricant into which they may be incorporated.

#### *2.1.3.1 Dispersants-metallic types*

These compounds have been described in the literature as “detergent”. Since their function appears to be one of affecting a dispersion of particulate matter rather than one of “cleaning up” any existing dirt and debris, it is more appropriate to categorize them as dispersants.

Material of this type are generally molecules having a large hydrocarbon “tail” and a polar group head. The tail section, olephilic group, serves as a solubilizer in the base fluid while the polar group serves as the element which is attracted to particulate contaminants in the lubricant.

These additives such as petroleum sulfonates, synthetic sulfonates, thiophosphonates, phenates, and phenol sulfide salts.

#### *2.1.3.2 Dispersants-ashless types*

A development of major importance in the additive field has been the discovery and use of ashless dispersants. These materials may be categorized into two broad types: high molecular weight polymeric dispersants for the formulation of multigrade oils and lower molecular weight additives for use where viscosity improvement is not necessary.

These additives are much more effective than the metallic dispersants in controlling sludge and varnish deposits which are involved in intermittent and low temperature gasoline engine operation. The compounds useful for these purposes are

again characterized by a “polar” group attached to a relatively high molecular weight hydrocarbon chain. These compounds are N-substituted long chain alkenyl succinimide, high molecular weight esters for examples.

### ***2.1.3.3 Polymeric dispersant additives***

These ashless dispersants may serve a dual function. They can be both a viscosity index improver and a dispersant and consist of two general types of molecular configuration, i.e., those whose structure is similar to the ones employed as viscosity index improvers to insure oil solubility, and those containing “polar” compounds to impart the dispersancy characteristic.

### ***2.1.3.4 Oxidation and bearing corrosion inhibitors***

The function of an oxidation inhibitors is prevention of deterioration associated with oxygen attack on the lubricant base fluid. These inhibitors function either to destroy free radicals (chain breaking) or to interact with peroxides which are involved in the oxidation mechanism. These compounds are phenolic inhibitors, zinc dithiophosphates for example.

### ***2.1.3.5 Anti-wear additives***

Wear is loss of metal with subsequent change in clearance between surfaces moving relative to each other. If continued, it will result in engine malfunction. Amout the principal factors causing wear are metal to metal contact, presence of abrasive particulate matter, and attack of corrosive acids. Metal to metal contact can be prevented by addition of film-forming compounds which protect the

surface either by physical absorption or by chemical reaction. Abrasive wear can be prevented by effective removal of particulate matter by filtration of both the air entering the engine and the lubricant during operation. Corrosive wear by acidic blow-by products, can be controlled by the use of alkaline additives.

#### ***2.1.3.6 Viscosity improvers***

Viscosity improvers or viscosity index improver, as they are quite often referred to, comprise a class of materials which improve the viscosity-temperature characteristics of the lubricating oil. This modification of the rheological property results in an increase in viscosity at all temperatures which significantly improves the viscosity index of the lubricating oil.

#### ***2.1.3.7 Pour point depressants***

Pour point depressants prevent the congelation of the oil at low temperature. This phenomenon is associated with the crystallization of the paraffin wax which is most often present in the mineral oil fractions. The pour point depressants do not prevent wax from crystallizing from the oil, but amount of oil occluded on the crystal. The reduction in volume of the crystal permits flow of the lubricating oil.

### **2.1.4 Basic Function of Lubricating Oil [1,11]**

The basic functions of a lubricating oil are :

#### ***2.1.4.1 Friction reduction***

Simply stated, friction reduction is accomplished by maintaining a film of lubricant between surfaces which are moving with respect to each other, thereby preventing these surfaces from coming in contact and subsequently causing surface damage.

One of the most important properties of a lubricating oil is its viscosity. It forms lubricating films under both thick and thin film conditions. Viscosity affects heat generation in bearings, cylinders and gears related to fluid internal friction. It governs the sealing effects of oils to reduce the rate of oil consumption. It determines that machines may be started under varying temperature conditions, particularly at cold temperature. For any given piece of equipment, satisfactory results are obtained only with the use of an oil of proper viscosity under the operated condition.

#### ***2.1.4.2 Heat removal***

In heat removal, lubricant acts as coolant, removing heat generated either by friction or other sources such as via combustion process or by transfer from contact with substances at a higher temperature. In performing this function, it is important that the lubricating oil remains in a relatively unchanged condition. Changes in thermal and oxidative stability which materially decrease its efficiency in this respect. Additives are generally employed for the solution of such problems.

#### ***2.1.4.3 Containment of contaminants.***

The ability of a lubricant to remain effective in the presence of outside contaminants is quite important. Among these contaminants are water, acidic

combustion products, particulate matter, etc., which generally find their way into lubricants employed in various applications. Here again additives are generally the answer in accomplishing these objectives.

### **2.1.5 Necessary Properties of a Lubricant [14]**

Lubricants are formulated by blending base oils and additives to meet a series of performance specifications. These specifications relate to the physical and chemical properties of the oil. Base oils have a range of properties that can be measured and used to predict performance. Analysis and testing of lubricants and related products are based on standards [International Organization for Standardisation (ISO), American Society for Testing and Materials (ASTM), Institute of Petroleum (IP), etc.] which are often identical.

#### ***2.1.5.1 Physical properties***

##### **(a) Viscosity**

Viscosity is the most significant property of a lubricating oil. The primary purpose of a lubricant is to reduce friction and minimize wear by separating lubricate surfaces with an oil film. Viscosity is a measure of resistance to flow. It

decreases with increasing temperature and increase with large increasing pressure. The extend of the viscosity change depends on the crude source of the oil and the molecular weights of the constituent components.



### (b) Viscosity index (VI)

Viscosity index is a reflection of an oil's resistance to viscosity change with fluctuation in temperature. The higher the viscosity index of an oil, the more resistant it is to a viscosity change caused by temperature fluctuation. All lubricating oils thin out or have lower viscosity as the temperature is increased. Likewise, oils become thicker or more viscous as the temperature is reduced. However, not all oils respond to the same degree to temperature changes.

Lubricating oils are subjected to wide variations of temperature in service. At high temperatures the viscosity can drop to a point where the oil is so thin that the oil film may break, allowing metal surfaces to touch, resulting in excessive wear. At the other extreme, the temperature can be so low that the oil becomes viscous and does not allow proper circulation to the parts being lubricated.

Take an automobile, for example. During startup the oil can be quite cold, particularly during winter. But the oil must not be so viscous that the drag on the engine makes starting difficult. During warm-up the oil must be able to flow to all the moving parts. Finally, after the engine has reached its normal operating temperature, the oil must not be so thin that oil consumption is high or the lubricating film can no longer carry the load. Most motor oils have a viscosity index of 100 or higher. Where temperature variations are less or for continuous operation at constant temperature, viscosity index is less critical.

### (c) Pour point

As a lubricating oil is chilled, it eventually reaches a point where it will no longer flow under the influence of gravity. This condition is brought about

either by the thickening (more viscous) that always accompanies a reduction in temperature or by crystallization of wax dissolved in the oil, restricting the flow of the liquid portion. The lowest temperature to which an oil can be chilled and still be poured from a container is called the "pour point".

The pour point is related to the ability of the oil to start lubricating when a cold machine is placed into operation. Engines that are stopped and started under low temperature conditions require an oil that will flow readily when cold.

#### (d) Flash point

The flash point is a measurement of the flammability of a petroleum product. The flash point is the temperature at which enough vapor is produced to be burned in an instantaneous flash when exposed to a source of ignition. Normally, this test is used to determine the storage and operating temperatures and the type of storage that will preclude the possibility of a fire.

Flash point is also useful in evaluating used oils. A drop in flash point indicates contamination by dilution of the motor oil with unburned fuel. An increase indicates evaporation of the oil. This property is determined by the open-cup method, usually called the Cleveland Open Cup method and abbreviated COC.

#### (e) Neutralization number

The neutralization number measures the organic acid content of base oils and acids produced by oxidation in storage or service. The acid numbers are expressed in milligrams of potassium hydroxide (KOH) needed to neutralize a gram of sample. The neutralization number is important in oils of critical service, such as

turbine oils and insulating oils. With new oils, neutralization test results serve as a guide to mechanical condition, change in operating conditions, or product deterioration due to oxidation.

(f) Metal content

The heavier oils contain relatively high proportions of metals either in the form of salts or as organometallic constituents, which are extremely difficult to remove. A variety of tests have been designated for the determination of metals on petroleum products. Inductively coupled plasma (ICP) spectrometry has made the determination of metals very easy and used oil can be scanned for 22 elements in a few minutes.

### *2.1.5.2 Chemical properties*

All petroleum products are subject to chemical attack by oxygen. Attack is promoted by high temperatures, catalysts, and the presence of water of acids. Oil oxidation results in two general classes of degradation products:

1. Oil-insoluble materials, i.e., resins, varnish, or sludge
2. Oil-soluble products, primarily acids and peroxides

Resistance to oxidation is important in the performance of a lubricant. Acids formed may be corrosive to metals. Varnish may deposit on sliding surfaces, causing them to stick or wear. Sludge may plug screens or passages or the rings on cylinders, causing them to be ineffective. Resistance to oxidation is extremely important for a steam-turbine oil because of the serious consequences of a bearing

failure. Transformer oils, gear oils, hydraulic fluids, heat transfer oils, and crankcase oils also require a high degree of oxidation stability to ensure a satisfactory service life.

The most important chemical aspect of lubrication is the degree to which atmospheric oxygen can react with lubricants under various operating conditions. Since the degradation of lubricants by oxidation can be lead to the development of corrosive organic acids and a marked increase in viscosity of the lubricant, all which seriously impart the efficiency of the lubricant.

The thermogravimetric balance (TG) is one of recently technique developed to evaluate thermal behavior of different chemical component. Loss in weight for most of the tested samples was found to be negligible up to a temperature of 300 °C. Higher than 300 °C, the sample weight begins a rapid and continuous loss. In the presence of oxygen, that decomposition reaction occurred, the reaction observed at temperature around 350 °C or higher which leads to retard decreasing in weight loss. These temperatures can be named oxidation point.

### **2.1.6 Synthetic Lubricants [1,15]**

Synthetic lubricants have been used for many years in the early 1930s. Synthetic hydrocarbon and ester technologies were being simultaneously developed in Germany and the US. In the US, the development of a process for the catalytic polymerization of olefins led to the formulation of automotive crankcase lubricants with improved low temperature performance. These products were not commercialized due to the inherent cost of new synthetic base fluids and to

improvement in the performance of lubricants based on mineral oils. In Germany, low temperature performance was one of the driving forces behind the development of similar products by Zene although the main objective was to overcome the general shortage of petroleum base stocks.

With the exception of special circumstances of World War II, synthetic lubricants did not become commercially significant until after the war. In general, the improved properties of lubricants achieved with the early synthetic base stocks could be obtained more cost effectively by improved formulations based on mineral oils. However, the requirements for lubricants, particularly military and aero-engine lubricants, to perform over increasing temperature ranges has stimulated the continuing development of synthetic lubricant technology. Synthetic lubricants are now found in all areas of lubrication such as automobiles, trucks, marine diesels, transmissions and industrial lubricants, as well as aviation and aerospace lubricants.

Many compounds have been investigated as possible base stocks for synthetic lubricants. Gunderson and Hart [15] identified over 25, of which seven types are of major importance:

- Polyalphaolefins
- Alkylated aromatics
- Polybutenes
- Aliphatic diesters
- Polyolesters
- Polyalkylene glycols
- Phosphate esters

Other materials such as silicones, borate esters, perfluoroethers and polyphenylene ethers are also of importance, but their applications are restricted due either to high cost or to performance limitations.

Some of the primary applications for synthetic lubricants are listed in Table 2.1

**Table 2.1** Primary applications for synthetic lubricants [15]

Field of service	Synthetic fluids used
<b>Industrial</b>	
Circulating oils	Polyglycol, SHF, Synthetic ester
Gear lubricants	Polyglycol, SHF
Hydraulic fluids (fire resistant)	Phosphate ester, Polyglycol
Compressor oils	Polyglycol, Synthetic ester, SHF
Gas turbine oils	SHF, Synthetic ester
Greases	SHF
<b>Automotive</b>	
Passenger car engine oils	SHF, Synthetic ester
Commercial engine oils	SHF, Synthetic ester
Gear lubricant	SHF
Break fluids	Polyglycol
<b>Aviation</b>	
Gas turbine oils	Synthetic ester
Hydraulic fluids	Phosphate ester, Silicones, SHF
Greases	Silicones, Synthetic ester, SHF

SHF : Synthesized hydrocarbon fluids such as polyalphaolefins, alkylated aromatics and polybutenes.

## **2.1.7 Lubricants and Their Environmental Impact [13]**

### ***2.1.7.1 Collection of waste lubricant***

Waste lubricant that is collected is usually disposed of either by burning as fuel or incineration as waste, or is reclaimed. Some lubricants, such as industrial oils, can be treated relatively easily and recycled, whereas automotive engine oils require more sophisticated treatment to produce re-usable base fluids of acceptable quality.

#### **(a) Used industrial lubricants**

There are many potential sources of used industrial products but reprocessing is not an option for a large number of these synthetic and fatty oil based products. Some products, such as transformer oils and hydraulic oils, can be readily collected from large industrial concerns and segregated. Consequently, contamination can be avoided. These oils may be regenerated to a recognized standard and returned to the original source.

#### **(b) Used automotive lubricants**

These will include mono- and multigrade crankcase oils from petrol and diesel engines, together with gear oils and transmission fluids. Used industrial lubricants that have been inadequately segregated will also be included. Apart from the degradation products from the in-service use of the oil, a wide range of contamination is possible. This includes:

- Water- combustion by-product, rain water/salt water ingress



- Fuels- residual components of gasoline and diesel fuel
- Solids- soot, additive and wear metals, rust, dirt, etc.
- Chemicals- used oil can be used as an unauthorized means of hazardous waste disposal
- Industrial oils- inadequate segregation of oil types can allow contamination by fatty or naphthenic products

#### ***2.1.7.2 Treatment of collected lubricant***

##### **(a) Production of fuel oil blending component**

Used lubricant is excellent source of energy, but contains contaminants which, when burnt, can create environmental pollution and operational problems. Simple processing (e.g. settling and filtration/centrifugation) is sufficient to remove coarse solids and water, and a mild chemical treatment (e.g. caustic soda solution) may also be used to reduce concentrations of other contaminants. Disposal of waste products may be a problem.

##### **(b) Reclamation of lubricating oils**

Some specific types of industrial oils can be readily segregated and are suitable for relatively simple reprocessing before being returned to their original service. Typical processing methods involve filtration and removal of water or volatile decomposition products under vacuum.

### (c) Production of re-refined lubricant base oils

When dealing with oils from multiple sources, complex processes are needed to remove the wide range of contaminants and additives that will be present. The objective is to produce base oils that can then be used as substitutes or alternatives to virgin mineral base oils. The main re-refining technologies such as acid/clay treatment, solvent extraction and distillation/hydrotreatment.

- *Acid/clay treatment*

This has been the principle re-refining process in the commercial use (e.g. Meinken process), In the acid/clay process, the used oil is first treated with 98% sulphuric acid; the resulting acid sludge is then separated and the remaining oil is clay treated, neutralized and filtered. Process yield from modern used engine oils are low and large quantities of acid sludge and oil-soaked clay are generated. These wastes are difficult and costly to dispose of in an environmentally acceptable manner.

- *Solvent extraction*

Propane or other solvents can be used to selectively extract the base lube material from the used oil (e.g. IFP process) Solvent extraction plants are expensive to build and operate, and generate significant amounts of waste materials and hazardous by-products.

- *Distillation/hydrotreatment*

This technology is the most recent (e.g. KTI and Mohawk processes). After pre-treatment and thin-film distillation, the base oil fraction is hydrotreated under moderate conditions. A final distillation step yields a range of base oil streams of different viscosity. The hydrotreatment process is comparatively sophisticated, capital intensive and requires skilled operation, although operating costs are not exceptionally high.

## **2.2 Cracking Processes**

Cracking processes are assigned in three fundamental classes :

1. Thermal cracking
2. Catalytic cracking
3. Hydrocracking

### **2.2.1 Thermal Cracking [16,17]**

Thermal cracking , where free radicals (lacking one hydrogen atom on carbon atom in the hydrocarbon molecule) are intermediate species which cracked by a  $\beta$ -scission mechanism.

The most successful present explanation of thermal cracking of hydrocarbon is Rice free radical theory as modified by Kossiakoff and Rick. This will be called the "RK-theory" as follows to explain the cracking of normal paraffin:

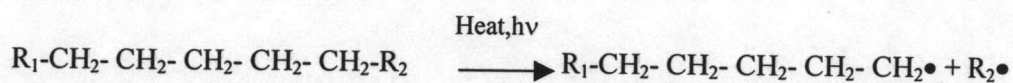
The normal paraffin molecule loses a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approach each other. Radical isomerization is a change of the position of hydrogen atom, usually to yield a more stable radical in order of tertiary > secondary > primary free radical.

Cracking of either the original or isomerized radical then takes place at a carbon-carbon bond located in the  $\beta$  position to the carbon atom lacking one hydrogen atom. Cracking at the  $\beta$  position gives directly an alpha olefin and a primary radical (lacking one hydrogen atom on primary carbon atom); in this step no change of position of any hydrogen atom with respect to the carbon skeleton.

The primary radical derived from this step may immediately recrack at the  $\beta$  bond to give ethylene and another primary radical, or it may first isomerize. In the absence of radical isomerization, only primary radicals are derived from cracking reaction of normal paraffin; primary radicals thus give only ethylene as the olefin product. Radical isomerization reduces the amount of ethylene, but it still remains the major product. By successive cracking, the radicals ultimately are reduced to methyl or ethyl fragments. These radicals then react with feed stock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction.

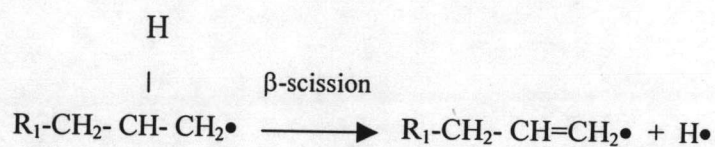
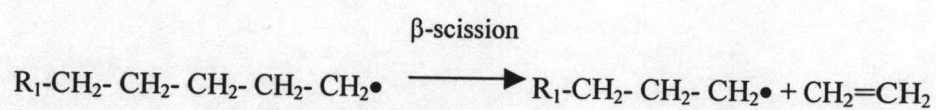
A schematic representation of linear paraffin cracking is as follows;

### 1. Initial step

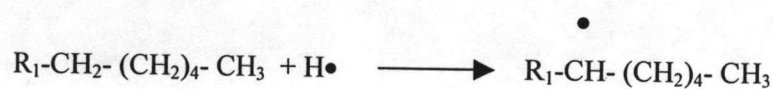


### 2. Propagation step

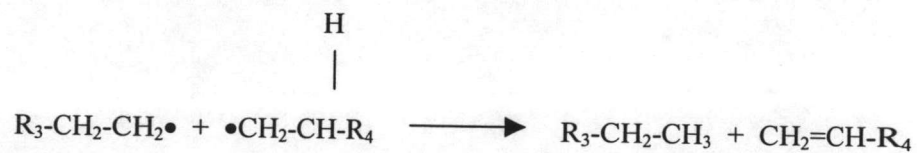
#### 2.1 $\beta$ -scission



#### 2.2 Chain transfer



### 3. Termination step



### 2.2.2 Catalytic Cracking [18-21]

The chief purpose of catalytic cracking is to break high molecular weight hydrocarbons into smaller fragments of suitable volatility to permit their use as fuels. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because of more gasoline having a higher octane and less heavy oil and unsaturated gases and products

Commercial cracking catalysts can be classified into three classes:

1. Activated natural clays
2. Amorphous synthetic silica-alumina
3. Crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves

Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are :

1. Higher activity
2. Higher gasoline yields at a given conversion
3. Product of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons
4. Lower coke yield
5. Increased isobutane production

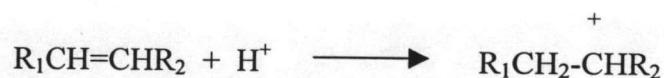
A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer lived and accordingly more selective than free radicals. Acid catalysts such as amorphous silica-alumina and crystalline zeolites promote the formation of carbonium ions.

The mechanism of the reactions occurring during catalytic cracking is quite well understood, and can be summarized as follows. Small amount of alkenes are formed by dehydrogenation, and these react with protons on the acidic catalyst to give carbonium ions. Now the sequence of stability of these ions is primary < secondary < tertiary; movement of a hydride ion (H<sup>-</sup>) changes a primary into a secondary ion, while methyl group migration forms tertiary ions. Long chain carbonium ions are unstable with respect to small ones, and carbon-carbon bonds are broken by  $\beta$ -scission to give an alkene with a primary carbonium ion. This and other unit steps are set out in the following.

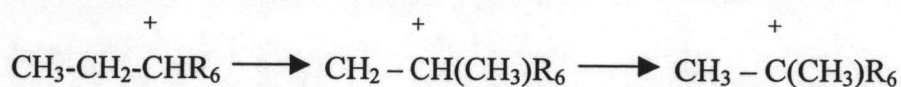
Dehydrogenation of alkene



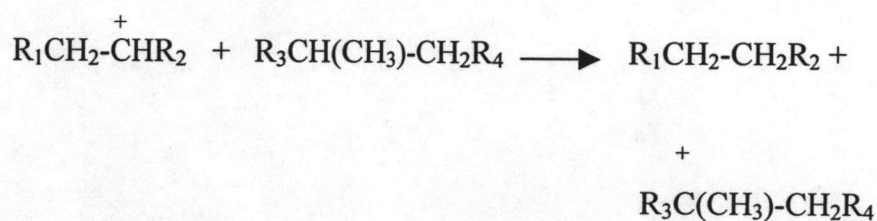
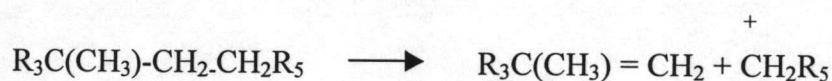
Formation of carbonium ion



## Methyl group migration



## Hydride transfer

 $\beta$ -Scission

## 2.2.3 Hydrocracking [22, 23]

A simplified description of hydrocracking is the decomposition of hydrocarbons on the acid site of the catalyst's support, followed by hydrogenation of the cracking products on the metallic sites. The first stage of this process is analogous to catalytic cracking.

In reality, the process of hydrocracking is a lot more complex, because it also includes hydrogenation of aromatic hydrocarbons, opening of naphthenic rings, and isomerization. The activity of two functions of the catalyst and the operating conditions of the process determine the conversion of these various reactions.



Basically, the aim of hydrocracking as well as other cracking processes, is the transformation of the heavy fractions of crude oil into light fractions. The use of this process is determined by the high quality of some of the products obtained, such as the jet fuel and the lubricating oils of high viscosity index. It is more expensive than catalytic cracking due to the high price of hydrogen and operation at high pressure. In addition, the role of hydrocracking increased due to the new requirements for gasoline, imposed in the U.S., by the 1990 Clean Air Act, now applied also in other countries. Hydrocracking gasolines have a low content of aromatic hydrocarbons and limited content of volatile hydrocarbons.

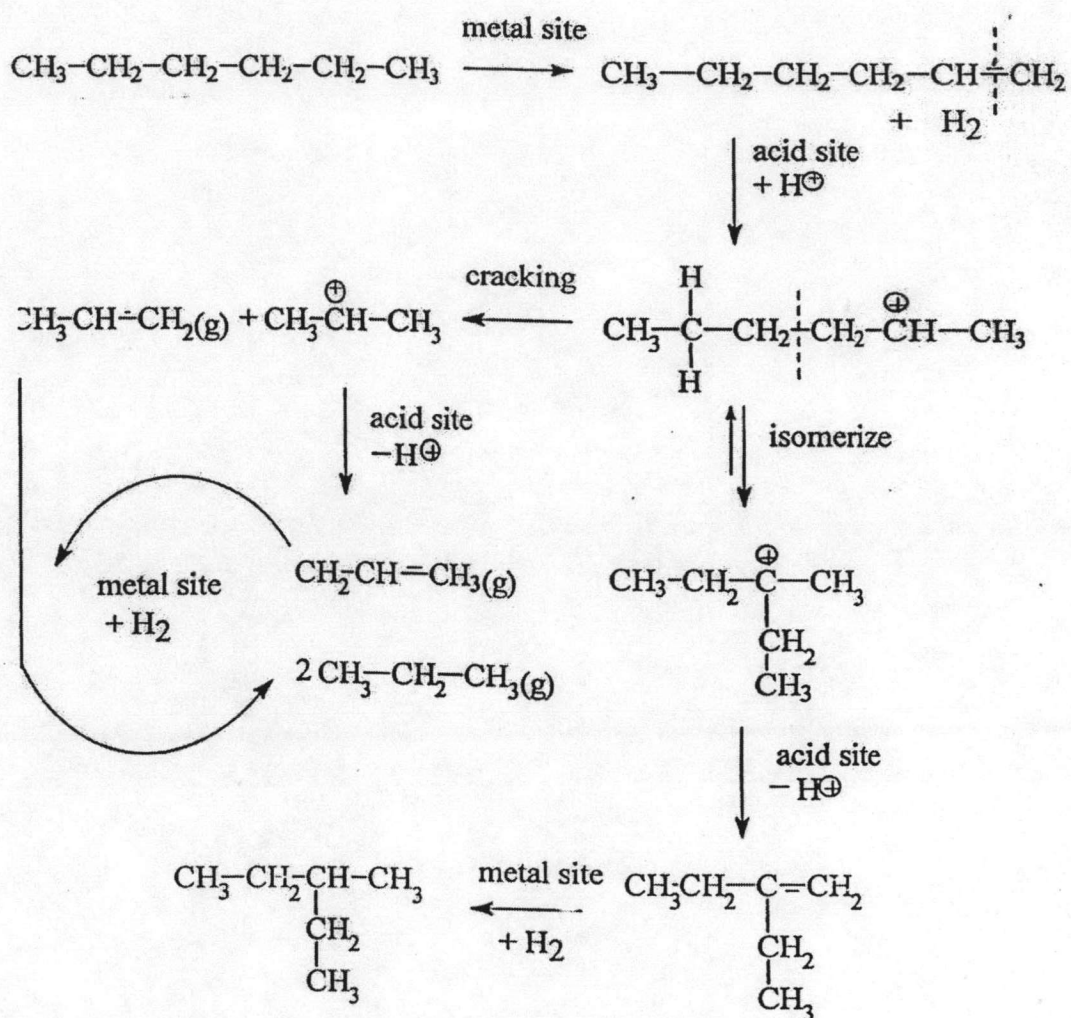
The bifunctional hydrocracking catalysts have to promote the following main reactions to the required extents:

1. Cracking, according to mechanisms similar to those prevalent in catalytic cracking
2. Hydrogenation of the unsaturated hydrocarbon obtained from the cracking reaction
3. Hydrogenation of the aromatic rings
4. Hydrogenolysis of the naphthenic structures

In the first reactions, the metallic sites contribute to the initiation reaction of dehydrogenation to alkenes, which are later transformed into ions on acid sites. The second and the third reactions take place on the metallic sites. Both types of sites seem to participate in the fourth reaction.

The reaction mechanism of bifunctional catalyst and an example are shown in Figure 2.1

Alkanes will be strongly chemisorbed and dehydrogenated readily to olefins on a transition metal. Diffusion will take the olefin to an alumina acidic site, where it will be chemisorbed as a carbonium ion and undergo cracking and/or polymerization. In turn, the new olefin products will contact with metal sites after diffusion, where rehydrogenation tends to occur, releasing new alkane species. Many isomerization reactions occur under the conditions of catalytic cracking such as skeleton or double bond isomerization, dehydrocyclization and aromatization. These isomerizations take place during the cracking to produce isomerized olefins that are rapidly hydrogenated. A carbocation will undergo rearrangement of the carbon skeleton to form a more stable carbocation, a primary carbocation may rearrange to form a secondary carbocation or a tertiary carbocation. Depending on the conditions, principally temperature, carbonium ions can be precursors to polymerized or cracked derivatives of the original reactant. The control factor is mainly thermodynamic. Low temperatures favour polymerization but high temperature favour cracking.



**Figure 2.1** Reaction mechanism of hydrocracking of hexane [23]

The catalysts commonly used in this process are Mo and W on alumina support. Ni and Co are also used as promoters to improve activities. The most common catalyst is CoMo oxide on alumina. Other catalysts, NiMo and NiW on alumina oxides, may also be used.

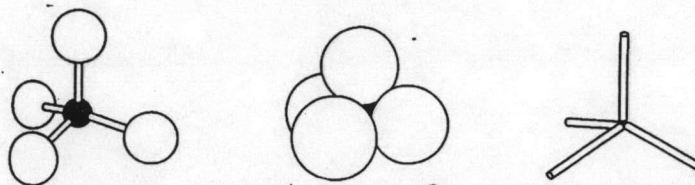
### 2.3 Zeolite catalyst [23, 24]

The crystalline solids of primary catalytic interest, called aluminosilicates, incorporate Al, Si, and O. Naturally occurring minerals and many solids prepared in the laboratory exemplify this class. Several of the more than 100 synthetic aluminosilicates find wide application as industrial catalysts. The zeolites are structurally unique in having cavities or pores with molecular dimensions as a part of their crystalline structures.

#### **Silicate and ZSM-5**

Before consideration of the structure of zeolites, it is helpful to consider a group of solids having the simpler composition  $\text{SiO}_2$ . Later, the group will be expanded by replacement of some of the Si atoms with Al. The compound  $\text{SiO}_2$  is stable in the gas phase, having a structure with two  $\text{Si}=\text{O}$  bonds resembling that of  $\text{CO}_2$ . There is a large free-energy driving force for self-association of the  $\text{SiO}_2$  molecules, with conversion of the  $\text{Si}=\text{O}$  bonds into  $\text{Si}-\text{O}$  bonds. Many geometries of the resulting condensed structures exist, two of the best known being quartz and cristobalite, and another being silicalite, which is closely related to a zeolite.

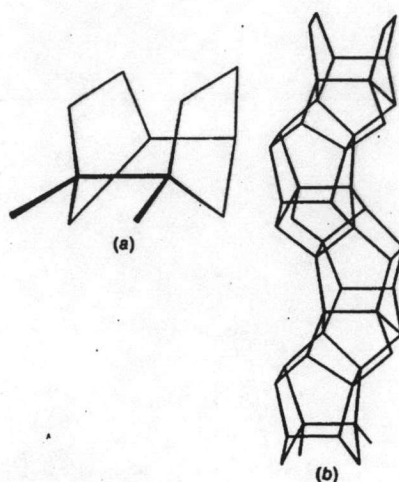
The  $\text{SiO}_4$  tetrahedron in a crystalline network is represented in the Figure 2.2.



**Figure 2.2** The  $\text{SiO}_4$  tetrahedron in a crystalline network [23]

The second structure (a space-filling model based on close-packed spheres) is the most accurate representation. But the third, in which the Si atom is represented as a point and the O atom as a line, is the most convenient for showing the complex structure of zeolites. The  $\text{SiO}_4$  unit is a building block, and the ways these are assembled define the structures of the crystalline solids with composition  $\text{SiO}_2$ .

The  $\text{SiO}_4$  tetrahedra can be combined in many arrays with sharing of O atoms. When they are arranged as shown in Figure 2.3(a), the result is the secondary building block of silicalite. Here, to emphasize the geometry, the third form of representing the structure is used, showing the Si atom as an intersection of lines; the O atom is located at the center of each line. When some of the Si atoms in this structure are replaced by Al atoms, the resulting aluminosilicate is referred to as ZSM-5, a zeolite and an industrially important catalyst.

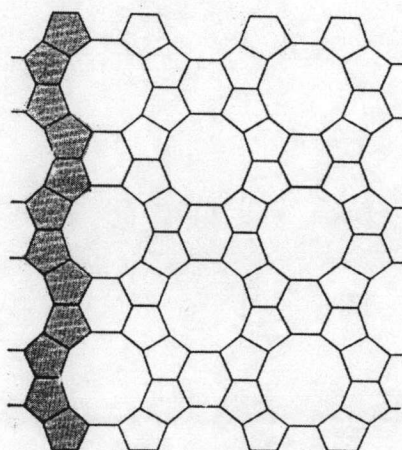


**Figure 2.3** (a) The secondary building block of silicalite, formed from  $\text{SiO}_4$  tetrahedra. (b) The chain-type building block, formed from the secondary building blocks by sharing of oxygens by linked  $\text{SiO}_4$  tetrahedra. [23]

In silicalite and ZSM-5, the tetrahedra are linked to form the chain-type building block shown in Figure 2.3(b). The chains can be connected to form a layer, as shown in Figure 2.4. Rings consisting of five O atoms are evident in this structure; the name *pentasil* is therefore used to describe it. Also evident in Figure 2.4 are rings consisting of 10 oxygen atoms; there are important because they provide openings in the structure large enough for passage of even rather large molecules. The layers can be linked in two ways, the neighboring layers being related either by the operation of a mirror or an inversion. The former pertains to the zeolite ZSM-11, the latter to silicate or ZSM-5; intermediate structures constitute the pentasil series.

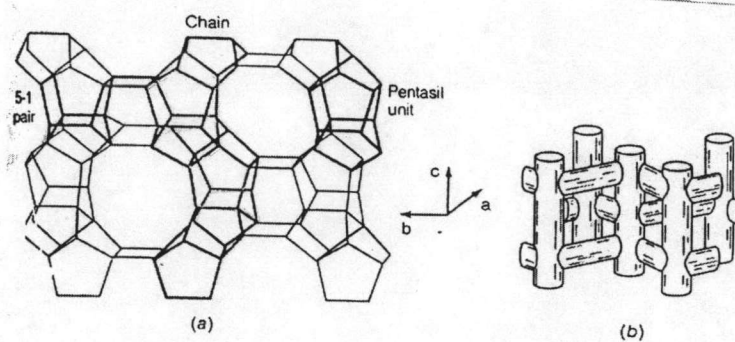
The three-dimensional structure of silicate (and ZSM-5) is represented in Figure 2.5(a). The 10-membered rings provide access to a network of intersecting

pores within the crystal. The pore structure is depicted schematically in Figure 2.5(b); there is a set of straight, parallel pores intersected by a set of perpendicular zigzag pores. Many molecules are small enough to penetrate into this intracrystalline pore structure, where they may be catalytically converted.



**Figure 2.4** Schematic diagram of silicalite layers, formed by linking of the chains shown in Figure 2.3(b) through sharing of oxygen in linked  $\text{SiO}_4$  tetrahedra. The shaded portion denotes one of the chains. [23]

ZSM-5 can be synthesized from an aqueous gel prepared from sodium aluminate, silica sol, NaOH,  $\text{H}_2\text{SO}_4$ , and tetrapropylammonium bromide. After standing at  $95^\circ\text{C}$  for 10 to 14 days, the mixture gives a yield of 80 to 90 percent ZSM-5; the composition of the solid is approximately  $1.8(\text{TPA})_2\text{O} \cdot 1.2\text{Na}_2\text{O}_3 \cdot 1.3\text{Al}_2\text{O}_3 \cdot 100\text{SiO}_2 \cdot 7\text{H}_2\text{O}$ . The tetrapropylammonium bromide may play the role of a template whereby the zeolite crystallizes around it.



**Figure 2.5** Representation of three-dimensional structure of silicalite (ZSM-5)

(a) Structure formed by stacking of sequences of layers shown in Figure 2.4. (b) Schematic representation of the intracrystalline pore Structure.[23]

The aluminosilicate structure is ionic, incorporating  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ , and  $\text{O}^{2-}$ . When some of the  $\text{Si}^{4+}$  ions in the  $\text{SiO}_4$  tetrahedra in this framework are replaced by  $\text{Al}^{3+}$  ions, as in ZSM-5 and other zeolite, an excess negative charge is generated. A compensating source of positive charge must be added, namely, cations in addition to the framework  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$ . These nonframework cations play a central role in determining the catalytic nature of zeolites. The zeolites are ion exchangers. Bringing an aqueous salt solution in contact with zeolite leads to incorporation of cations from the salt into the zeolite, replacing some of the nonframework cations initially present. Ion exchange is the simplest and most important method for modifying the properties of a zeolite. The name of zeolites specify the cations; for instance, in NaZSM-5, the cations are  $\text{Na}^+$ , in HZSM-5, they are  $\text{H}^+$ . Some cations (e.g., Ti, Ga, and Fe) have been incorporated in zeolite frameworks.



## **2.4 Bifunctional catalyst [21]**

Bifunctional catalyst widely used in hydrogenation and cracking reaction. This catalyst mainly consisted of two components, there are metallic component and supported catalyst.

### **2.4.1 Metallic component**

Catalysts developed for hydrogenating are comprises of at least one or more metal, metal oxide or group VIB and VIII on a carrier support which comprises one or more oxide of elements of group II, III, and IV.

Generally, the metals employed will be chromium (Cr), molybdenum (Mo) or tungsten (W), metals of group VI and iron (Fe), cobalt (Co) or nickel (Ni), metals of group VIII. Ni or Co is regarded as the active hydrogenation component, with W acting as a promoter, which increase the catalytic activity. The metallic component can be employed either as the metals or as the oxide of such a metal.

The critical factor for catalytic activity is that transition metals have valency (i.e. outer) electrons in their atoms, which are d-orbitals. These electrons are available for sharing into chemisorption bonds. The general predictions for chemisorption on transition metals are summarized as follows:

(a) The strength of the M-H bond decreases with an increase in the atomic number of the metal (M) along a particular transition series in the periodic table..

(b) The number of M-H bonds per unit area surface at maximum surface coverage increases with increasing atomic number.

## 2.4.2 Supported Catalysts

Supported catalysts represent the largest group of heterogeneous catalysts and are of major economic importance, especially in refinery technology and the chemical industry. Supported catalysts are heterogeneous catalysts in which small amounts of catalytically active materials, especially metals are applied to the surface of porous, mostly inert solids-the so called supports. The supports can have special forms such as pellets, rings, extrudates, and granules.

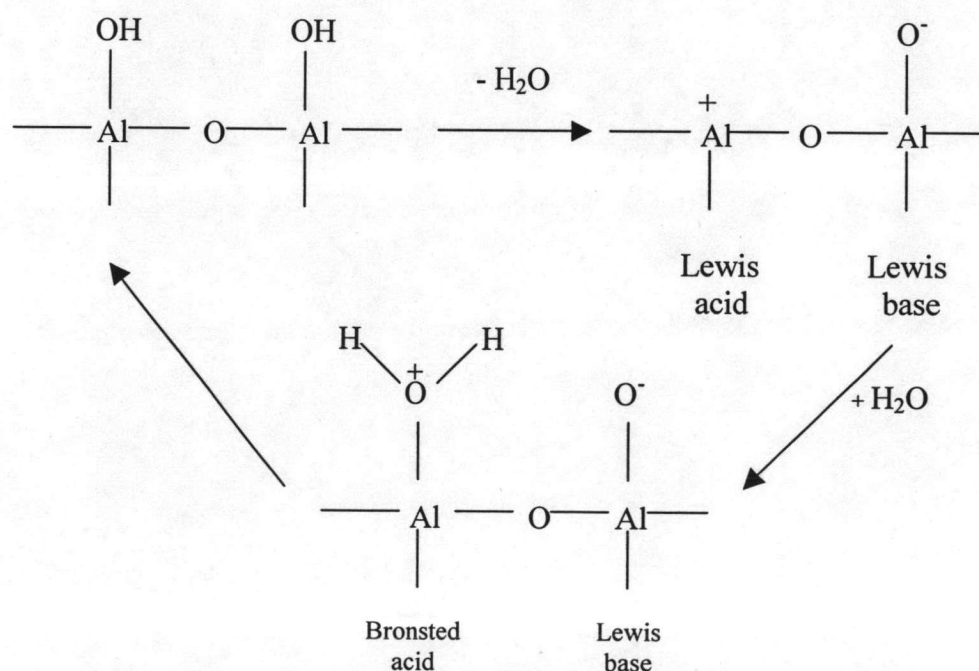
The main function of the catalyst support is to increase the surface area of the active component. Catalytic activity generally increases with increasing catalyst surface area, but a linear relationship cannot be expected since the reaction rate is often strongly dependent on the structure of the catalyst surface. However, in many reactions, the selectivity decreases when the catalytic surface is enlarged. The choice of the appropriate catalyst support for a particular active component is important because in many reactions the support can significantly influence the reaction rate and the course of the reaction. The nature of the reaction system largely determines the type of catalyst support. Typical catalyst supports are porous solids such as aluminum oxides, silica gel, MgO, TiO<sub>2</sub>, ZrO<sub>2</sub>, aluminosilicates, zeolites, activated carbon, and ceramics.

### 2.4.2.1 Alumina

The term alumina is used to describe various hydrated and anhydrous aluminium oxides. Most commercially available aluminas are prepared from the mineral bauxite (a mixture of hydrated aluminas and several non-alumina impurities)

and are available at > 99% purity. Thermally stable high-surface-area forms of alumina can be prepared, with acidic or basic surfaces. These may be used as acid or base catalysts or supports for other catalytic materials.

Alumina ( $\text{Al}_2\text{O}_3$ ), the acidic component in a dual function catalyst, exists in several distinct forms: the gamma form or the alpha form, depending on the method of preparation and subsequent treatment. Activated aluminas are amphoteric, containing either acidic or basic sites of various strength. As shown in Figure 4.6, if  $\gamma$ -alumina is heated above 800 K, the residual water is driven off to generate a catalytically inactive form known as  $\alpha$ -alumina. Activated alumina is often used as supports, where they provide a large surface area on which catalysts (metal) can be highly dispersed.

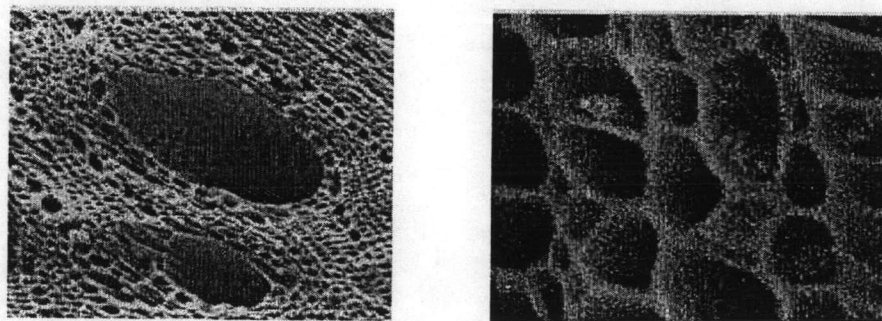


**Figure 2.6** Acidic and basic site on alumina

#### 2.4.2.2 Activated carbon [24]

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area. If we take a look at a cross section structure of activated carbon particle, it looks like a beehive. It consist principally of carbon (87 to 90%) but also contains such element as hydrogen, oxygen, sulfur and nitrogen as well as various compound either originating from the raw material used in its production or during its manufacture. Activated carbon has the ability to adsorb various substance both from the gas and liquid phases.

The reason that activated carbon is such an effective support material is due to its large number of cavernous pores. These provide a large surface area relative to the size of the actual carbon particle and its visible exterior surface. An approximate ratio is 1 gram = 900 m<sup>2</sup> of surface area. The scanning electron microscope images of activated carbon were shown in Figure 2.7.



**Figure 2.7** Scanning electron micrograph of pores of activated carbon [24]

(a) Molecular, crystalline and porous structure of activated carbon.

The graphite-like microcrystalline structure is the basic structure unit of activated carbon, as in the case of carbon black. The ordering of carbon atoms in an elementary microcrystalline indicates considerable similarity to the structure of pure graphite, the crystals of which consist of parallel layers of condensed regular hexagonal ring space 0.335 nm. apart. Such interlayer spacing is diagnostic of interaction by means of Van Der Waals forces. The length of the carbon-carbon bond in individual layers is 0.142 nm. Each carbon atom bonds with the three adjoining ones by means of covalent bonds, and the fourth delocalized  $\pi$ -electron may move freely in a system of conjugated double bonds of condensed aromatic ring. The formation of the crystalline structure of activated carbon beings early during the carbonization process of the starting material. Thus sets of condensed aromatic ring of various members, which are the nascent center of graphite-like microcrystallites, are formed. Although their structure resembles that of a crystal of graphite there exist some deviations from that structure. Thus, among other things, the interlayer distances are unequal in crystals of activated carbon and range from 0.34 to 0.35 nm. Again, the orientations of the respective layers generally display devistions, such deviations from the ordering characteristic of graphite, called a turbostratic structure. Disordering of the crystal lattice may be caused to a considerable degree both by its defects (vacant lattice sites) and by the presence of built-in heteroatoms. It is resulted from the kind of the raw material used, the nature and quantity of its impurities as well as the methods and conditions of the production processes of the active carbon. The average activated carbons have a strongly developed internal

structure (the specific surface often exceeds 1000 and sometimes even 1500 m<sup>2</sup>/g), and they are usually characterized by a polydisperse capillary structure, featuring pores of different shapes and sizes. Bearing in mind the values of the effective radii and the mechanism of adsorption of gases.

#### (b) Chemical nature of the surface of activated carbon

The chemical nature of activated carbon significantly influences their adsorptive, electrochemical, catalytic, acid-base, redox, hydrophilic-hydrophobic, and other properties. It is determined decisively by type, quantity and bonding of various heteroatoms, especially oxygen. Heteroatoms may be combined both with peripheral carbon atoms at the corners and edges of crystallites and in intercrystalline spaces and even in defect zones of particular planes constituting the crystallites. Most heteroatoms are grouped at the surface of activated carbon. Apart from their different locations, the heteroatoms are strongly differentiated in terms of their chemical reactivity. Surface-bound heteroatoms are believed to adopt the character of the functional groups typical for aromatic compounds. The surface functional groups often consist of more than one type of heteroatom, e.g. oxygen and hydrogen together as -OH or -COOH. Surface functional groups can originate from the starting material from which a particular activated carbon is produced. Substantial quantities of oxygen can be introduced during the production process itself, e.g. during activated carbonaceous materials by oxidizing gases, such as water vapor and air. Activated carbon used predominantly for practical purposes generally includes some percentage by weight of chemically-bond oxygen and usually much smaller

quantity of hydrogen combines with surface carbon atoms either directly or through oxygen.

## **2.5 Literature review**

Moliner et al. [8] studied pyrolysis of lube oil waste (LOW), coming from automation and industry, under different temperatures and pressures. Pyrolysis runs were carried out in bench scale pyrolysis unit. The results obtained from pyrolysis of a LOW at temperature from 600 to 700 °C and pressure from 0.1 to 1 MPa were achieved. Pyrolysis of waste lubricating oil yields important quantities of valuable products such as C<sub>1</sub>-C<sub>3</sub> alkanes, C<sub>2</sub>-C<sub>4</sub> olefins, and BTX. Total conversion of waste lubricating oil can be achieved at low severe conditions of pyrolysis. The relative distribution of product yields can be changed as a function of the pyrolysis conditions. The selection of pyrolysis conditions depends on the final use of the pyrolysis products. In the petrochemical feedstocks, a temperature window of 650-700 °C and pressure of 0.1 MPa should be used. At these conditions most of the hydrogen contained in waste lubricating oil is transferred to C<sub>2</sub>-C<sub>4</sub> olefins and BTX. In the hybrid approach, which produces gas fuel and liquid feedstocks, a temperature of 700 °C and a pressure of 0.5-1 MPa should be used.

Ramdoss et al. [25] studied the kinetic of coal coprocessing with petroleum waste has been studied experimentally and modeled mathematically. Experiments were carried out in a tubing bomb micro-reactor at temperature of 375 to 425 °C, at reaction times of 15-120 min, with 10% coal loading and with 1250 psig pressure.

Coal conversion as high as 98% were obtained during coprocessing. More than 70% conversion to oil is achieved at high temperatures and grease loadings. A combined parallel and series reaction schemes was assumed for coal liquefaction. The model predictions are good for experimental conditions other than those used to determine the model parameters.

Yang et al. [26] studied liquid-phase cracking of vacuum gas oil (VGO) performed over NiMo supported nonacidic catalysts under 713 K and 8.0 MPa of hydrogen in a batch reactor, which is termed hydro-thermal cracking. Compared with VGO thermal cracking under the same reaction conditions the new process showed the suppresses naphtha yield (from 22.4 to 13.5 wt.%) and VGO conversion (from 65.7 to 64.0 wt.%) and increased the middle distillate yield (from 44.3 to 49.3 wt.%). At the same conversion level, the yield ratio of middle distillates to naphtha for this new process was two time higher than that for VGO hydrocracking. The VGO hydrocracking over USY-supported NiMo proceeded at much lower temperatures but gave higher naphtha yields. Both the thermal cracking and the hydro-thermal cracking of n-dodecyl benzene yielded toluene as the major aromatic product, whereas its hydrocracking over NiMo/USY yielded benzene as the major aromatic product. The reaction mechanism of this new process was assumed to consist of thermal cracking of hydrocarbon molecule via the free radical chain mechanism and the catalytic hydroquenching of free radicals.

Serrano et al. [27] studied the potential application of Al-containing MCM-41 for the catalytic degradation of polyolefinic plastics and used lubricating oils and



compared with the behavior of ZSM-5 zeolite and commercial amorphous  $\text{SiO}_2\text{-Al}_2\text{O}_3$ . For all the studied raw plastics, MCM-41 presents significant higher activity than the amorphous catalyst, and even superior to that of ZSM-5 for the degradation of pure polypropylene, a mixture of three polyolefins (high density polyethylene + low density polyethylene + polypropylene) and a lube distillate. On the contrary, the ZSM-5 zeolite leads to higher conversions in the degradation of pure polyethylenic plastics and shows a slower deactivation during the lube oil cracking. Regarding the product distribution, while ZSM-5 leads mainly to light hydrocarbon ( $\text{C}_2\text{-C}_5$ ), MCM-41 cracks these wastes into liquid fractions (gasoline and middle distillates), which suggest the cracking pathway is not the same with these two materials, being governed by their pore size and/or their acid strength.

Yoon et al. [28] investigated coprocessing of common thermoplastics of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and acrylonitrile-butadiene-styrene (ABS) with waste lubricating oil. Statistical pentagonal design experiments in a micro-reactor system (40 ml capacity) were done to find out the optimum conditions for cracking of the plastic/waste oil mixtures into oils. From these experiments, oil yields of common thermoplastics such as PE, PP and PS reached nearly complete conversion under their respective optimum pyrolytic conditions suggesting the case of thermal cracking of each polymer into oils. Meanwhile, both PET as a condensation polymer and ABS as a graft copolymer gave relatively lower yields in oil compared to the afore mentioned common thermoplastics.

Nerin et al. [9] studied the pyrolysis of four industrial waste oil (automotives, hydraulic, machine and cutting oil), which carried out at atmospheric pressure and temperature of 600 °C. . Liquid and gases fractions have been analyzed, organic products by gas chromatography and metals concentration by Graphite Furnace Atomic Absorption Spectrometry (GFAAS). The gases obtained are mainly formed by methane and light olefins, C<sub>2</sub>-C<sub>4</sub>, and the liquids contain an aromatic fraction of high industrial value. The behavior of metals was also very different from one oil to another. Lead was the most affected metal in all of them, with a decrease ratio (concentration before and after pyrolysis) from 165 for machine oil to 32 for the hydraulic oil. Pb, Cr, Cu, Ni, Pb and V were identified and quantified in each fraction. The results show that the automotive and machine waste oils are the better ones concerning the liquid yields. However, the hydraulic and cutting oils show a high conversion to gas products. The relationship between the type of waste oil and the products obtained is discussed.

Kim and Kim [10] investigated the pyrolysis of waste automobile lubricating oil experimentally and modeled mathematically. Experiments were carried out in the tubing bomb microreactor. The yields of liquid fuel, gas product and coke were investigated at temperature from 420 to 440 °C and reaction times from 5 to 50 min. Liquid products were identified and quantitatively determined by gas chromatography. The yield of liquid oil at various residence times and temperatures was 95-98 wt% and the formation of gas and coke was relatively insignificant. The liquid products were broadly distributed in the carbon number of C<sub>5</sub>-C<sub>25</sub>, which were consisted of mainly C<sub>5</sub>-C<sub>11</sub> and C<sub>12</sub>-C<sub>25</sub>. A lump model of combined series and

parallel reactions for oil formation was proposed to represent the pyrolysis mechanism. Conversion data fitted first order kinetics for  $C_5$ - $C_{11}$  and  $C_{12}$ - $C_{25}$ . The reaction rate constants were found to be in agreement with the experimental data that the predominant reaction pathway was waste automobile lubricating oil to  $C_{12}$ - $C_{25}$  formation rather than that to  $C_5$ - $C_{11}$ .

Lazaro et al. [29] studied the pyrolysis of a lubricating oil waste with or without coal yields important quantities of valuable products such as  $C_1$ - $C_3$  alkanes,  $C_2$ - $C_4$  olefins and BTX. However, information on molecular structures of tars obtained is only available in terms of analyzes in the GC-MS ranges. This range corresponds to an upper limit of approximately 300 u; aromatics of mass greater than 300 u do not normally elute from high-temperature GC columns. For this reason, an oil tar, a coal tar and a tar obtained by the co-pyrolysis of the coal and oil (50:50 wt%) have been characterized by an array of techniques. The tar from the coal/oil mixture is much more similar to the tar from oil than to the tar from coal, reflecting the synergy in the co-pyrolysis reaction.

Maria et al. [30] studied the kinetics of the global primary thermal decomposition of raw waste lubricant oils in helium atmosphere conditions and with different proportions of helium:oxygen by TGA. In addition, pyrolysis and partial oxidation runs were carried out in a tubular reactor at 723 and 1123 K, where the volatiles and semivolatiles evolved were quantified by gas chromatography. Primary thermal devolatilization of waste oils is independent of the presence of oxygen, and consists mainly in a vaporization process, as was confirmed analyzing the flue gas

evolved from a pyrolysis process at 773 K. This can be modeled satisfactorily assuming that the oil is formed by two independent fractions: a main one (92.6%) which simply evaporates, and a second one which decomposes yielding gases. The volatile gases evolved undergo through pyrocracking reactions at higher temperature (1123 K), yielding light olefins (40%), methane and aromatic compounds, and coke in typical incineration conditions. When air is present, these flue gases formed during the pyrolysis are burnt.