

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Lubricating Oil [23]

2.1.1 Lubricating Base 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 which are suitable for lubricant purposes.

2.1.2 Petroleum Crude Oil and Its Components

Crude oil was formed many millions of years ago, and it is believed that it originated from the remains of tiny aquatic animals and plants that settled with mud and silt to the bottom of ancient seas. As successive layers built up, those deposits were subjected to high pressures and temperatures and as a result underwent chemical transformations leading to the formation of the hydrocarbon and other constituents of crude oil. They are found in a variety of types ranging from light colored oils, consisting mainly of gasoline, to black, nearly solid asphalts. These crudes are very complex mixtures ranging from methane with one carbon atom to compounds containing 50 or more carbon atoms. Crude oil consists of a very complex mixture of saturated and unsaturated hydrocarbons with minor amounts of non-hydrocarbons consisting chiefly of sulfur, nitrogen and oxygen. There are typical of hydrocarbons in crude oil.

2.1.2.1 Hydrocarbons

(a) Paraffinic hydrocarbons: These have saturated straight and branched-chain structures. The paraffinic hydrocarbons have high viscosity index and low pour point.

(b) Aromatic hydrocarbons: These are both mono and polynuclear hydrocarbons based on the six-membered benzene ring. They have a low viscosity index and low pour point.

(c) Naphthenic hydrocarbons: These are polycyclic and fuse-ring saturated hydrocarbons based on five or six-member ring. They are extremely stable compounds.

(d) olefinic hydrocarbons: These are unsaturated molecules. They are more chemically active than the other three classes. They are subject to oxidation or polymerization forming gums.

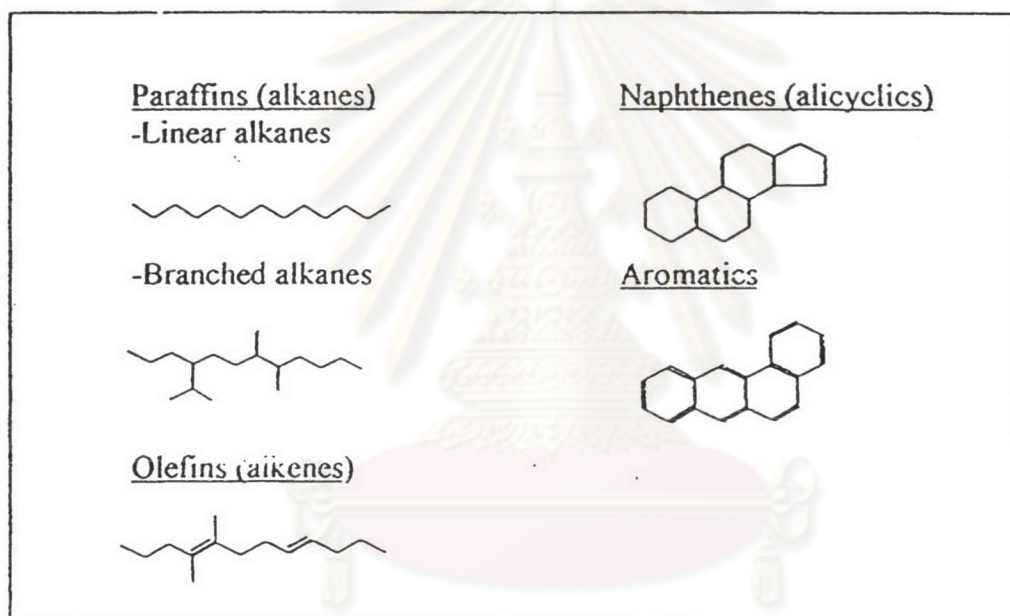


Figure 2.1 Examples of hydrocarbons [23].

2.1.2.2 Non-hydrocarbons

crude oils also contain varying amounts of compounds of sulfur, nitrogen, oxygen, varying metals such as vanadium, nickel, water and salts. Almost all of sulfur and nitrogen are heterocyclic molecules. In the production of lube oil, these compounds, including olefin and aromatic are removed. All of these materials can cause problems in refining or in subsequent products applications.

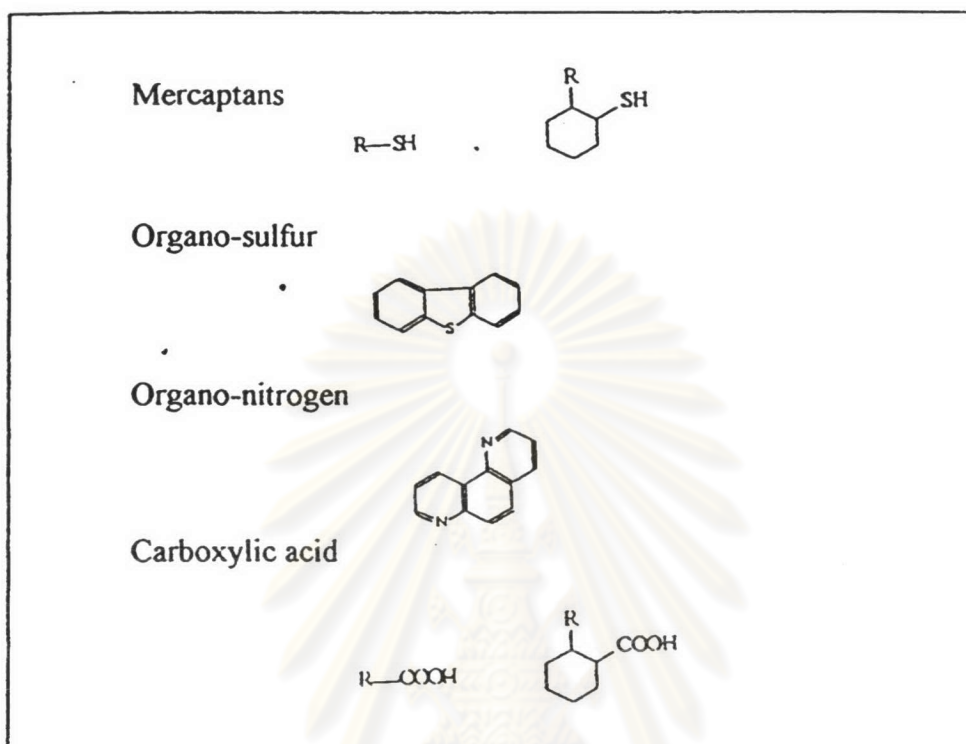


Figure 2.2 Examples of non-hydrocarbons [23]

2.1.3 Source of Lubricating Base Oil

2.1.3.1 Refining of Petroleum Crude Oils

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. A simplified diagram of such a process is shown in Figure 2.3 Essentially five steps are involved.

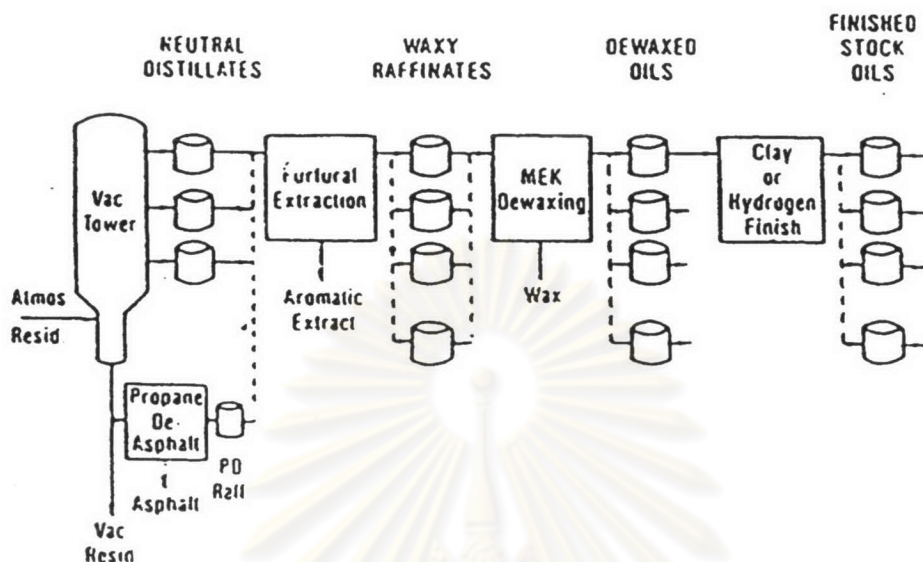


Figure 2.3 Lube processing [23].

(a) Vacuum distillation

The process which separates the atmospheric residue mixture into a series of fractions representing different molecular weight ranges or viscosity ranges from the 90-100 neutrals to the 500 neutrals. The residue contains the heavier base oils such as the bright stocks.

(b) Propane deasphlting

The highest boiling portions of most crude oils contain resins and asphaltenes. These materials must be separated prior to introduction into extraction process.

(c) Furfural extraction

Solvent extraction (furfural in this case) separates aromatic compounds 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)

(d) MEK dewaxing

This process is to remove wax to reduce the pour point of the base stock. In this case illustrated, methyl ethyl ketone (MEK) is mixed with the waxy oil. The mixture is cooled to a temperature between 100 °F (-12 °C) and 20 °F (-6 °C) below the desired pour point. The wax crystals which formed are then removed from the oil by filtration.

(e) Hydrofinishing

Some base stocks, particularly premium 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. This process removes some of the color and unstable component such as nitrogen and sulfur in the oil.

2.1.4 Base Oil Composition, Properties and Structure Relationship

The petroleum fraction used as lubricant generally contains compounds containing 18 or more carbon atoms. The lubricating fraction is a complex mixture consisting primarily of five characteristic classes-paraffin naphthenes, condensed naphthenes, aromatic naphthenes, naphthalenes (two ring aromatics) and multi-ring aromatics. It also contains small amounts of hetrocyclic compounds containing sulfur and various oxygen containing small amounts of hetrocyclic compounds containing sulfur and nitrogen atoms (e.g. thionaphthene, indole, quinoline and carbazole) and various oxgen containing compounds, including naphthenic acids, which account for most of the chemically bond oxygen in petroleum fractions.



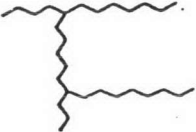
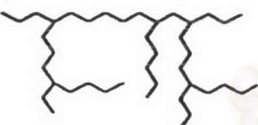
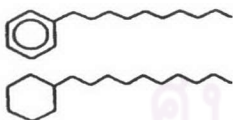
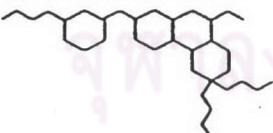

Alkanes, alicyclics and aromatics of the same molecular weight have markedly different physical and chemical properties. Physical characteristics will affect the viscometrics of the lubricant. The chemical stability of each class to oxidation and degradation while in use will also be very important. The effect of different types of compounds on lubricating oil's properties can be seen in Table 2.1

Table 2.1 shows qualitatively that the highly desirable structures for lubricant base oils are the highly branched isoparaffin and monocyclic hydrocarbons, saturated or unsaturated, with long aliphatic chains and preferably five carbon atoms in the ring.

The linear alkanes (normal paraffins) have good viscosity/ temperature characteristics. They are wax-like and therefore their concentrations must be minimized, especially in those oils for application at low temperature. On the other hand, branched-chain paraffins can be very desired constituents in a lubricant because of their good stability and viscosity/ temperature properties. Alicyclics and aromatics have rather higher density and viscosity for their molecular weight compared to the alkanes. However, their viscosity/ temperature characteristics and oxidation stability are in general rather poor. Single ring alicyclics or single ring aromatics with long alkyl side chains, in contrast, share many properties with branched alkanes and can in fact be very desirable base oil components.

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Table 2.1 Lubricating oil properties of some typical hydrocarbon structures [23].

Structure	VI	Freezing point	Resistance to oxidation	Value as base oil
Linear paraffin 	Very high	High	Good	Nil
Isoparaffin with linear chains 	High	Medium	Good	Medium
Isoparaffin with isomerized chain 	High	Low	Good	High
Highly substituted isoparaffin 	Medium	Low	Good	Medium
Single ring with long aliphatic chain 	High	Low	Good	High
Polycondensed naphthenes 	Low	Low	Medium	Nil
Polycondensed aromatics 	Very low (<0)	Low	Weak	Nil

2.1.5 Lubricating Oil Additives

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.

2.1.5.1 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.

Materials of this type are generally molecules having a large hydrocarbon “tail” and a polar group head. The tail section, oleophilic 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.

2.1.5.2 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.

2.1.5.3 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.

2.1.5.4 Oxidation and Bearing Corrosion Inhibitors

The function of an oxidation inhibitor 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 examples.

2.1.5.5 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. Among 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-by products, can be controlled by the use of alkaline additives.

2.1.5.6 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 temperature which significantly improves the viscosity index of the lubricating oil.

2.1.5.7 Pour Point Depressants

Pour point despressants prevent the congelation of the oil at low temperature. This phenomenon is associatated with the crystallization of the paraffin wax which is most often present in the mineral oil fractions. The pour point despressants 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.

2.1.6 Basic Function of Lubricating oil

The basic functions of lubricating oil are:

2.1.6.1 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 from coming contact and subsequently causing surface damage.

2.1.6.2 Heat removal

In heat removal, lubricating acts as coolant, removing heat generated either by friction or other sources such as via combustion process or 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.

2.1.6.3 Containment of contaminants

Another function of lubricating oil is to remain effective in the presence of outside contaminants. These contaminants are water, acid combustion products, particulate matter, ect., which generally find their way into lubricating oils employed in various applications.

2.1.7 Necessary Properties of a Lubricant

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.

2.1.7.1 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 increases with large increasing pressure. The extend of the viscosity change depends on the crude source of the oil and the molecular weights of the consttuent components.

The instrument used to determine the viscosity of an oil is called a viscometer. In general two types are used: the Saybolt and kinematic viscometers. Kinematic viscosity is the more common and is measured by the time required for a given volume of an oil at a

specified temperature to flow through a capillary tube under gravitational force. Test temperatures are usually at 40 and 100 °C for centistokes unit.

(b) Viscosity Index

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, 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 temperature 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) Color (ASTM D 1500)

The color test was performed by following the ASTM D 1500 method. The oil's color is normally not an indication of its lubricating properties. It is, however, a guide to the presence of contaminants or to the degree of deterioration in storage. It is also an indication of the intensity of refining. Absence of color (water white) is important in certain

applications such as in textile machinery lubrication to avoid indelible staining of the textile. Absence of color is also important to users of waxes, and white oils where extremely high purity is required.

(f) Sulfur Content

Sulfur content in lubricating oil will vary to some extent the instrumentation used and the nature of the oils. Sulfur content is measured by using X-ray fluorescence spectrometric method.

(g) Neutralization number

The neutralization number measures the organic acid content of base oils and the 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.

(h) Sulfated Ash

The sulfated ash of a lubricating oil is the residue, in percent by weight, remaining after burning the oil, treating the initial residue with sulfuric acid, and burning the treated residue. It is a measure of the noncombustible constituents (usually metallic materials) contained in the oil.

New, straight mineral lubricating oils contain essentially no ash forming materials. Many of the additives used in lubricating oils contain metallo organic components, which will form a residue in the sulfate ash test so the concentration of such materials in an oil is roughly indicated by the test. Thus, during manufacture, the test gives a simple method of checking to ensure that the additives have been incorporated in approximately the

correct amounts. However, since the test combines all metallic elements are in the oil in the correct amounts. With used oils, an increase in ash content usually indicates a buildup of contaminants such as dust and dirt, wear debris, and possibly other contamination such as lead salts, which are derived from the combustion of leaded gasolines in internal combustion engines.

(i) Water Content

The removal of water is necessary to prevent condensation of the water and the formation of ice or gas hydrates. Water in liquid phase causes corrosion problems in equipment, particularly when carbon dioxide and hydrogen sulfide are present in the gas. The water content of petroleum products is important in the refining, purchase, sale, and transfer of products. The simplest method covers the determination of water in petroleum products by distillation method.

(j) 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.

2.1.7.2 Chemical Properties

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

- A. Oil-insoluble materials, *i.e.*, resins, varnish, or sludge
- B. 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.

There are several accelerated tests to measure an oil's resistance to oxidation which are designed to correlate with field performance.

C. Oxidation Stability

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 lead to the development of corrosive organic acids and a marked increase in viscosity of the lubricant, all which seriously impair the efficiency of the lubricant.

The thermogravimetric balance (TG) is one of the techniques developed to evaluate the thermal behavior of different chemical components. 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 a temperature around 350 °C or higher which leads to a retardation in weight loss. These temperatures can be named oxidation points.

- Oxidation point; *i.e.*, temperature at which the rate of weight loss decreases due to the formation of high molecular weight oxygenated compounds.

- Oxidative compounds; *i.e.*, weight of oxygenated compounds which remains in the pan of balance at the oxidation point. Higher than point, the oxidative compounds state to carbonize and finally evaporate as CO₂.

2.1.8 Environmental considerations of used lubricating oil [1]

There are three basic disposal methods for used lubricating oils:

- Disposal as toxic/hazardous waste
- Re-refining to produce base oils
- Used fuel

Of the three basic methods of disposal or recycling of used oils, the most efficient in term of energy conservation, in that it displaces an equivalent amount of oil, is the use of the material as a fuel. The flue gas components of principal environmental concern are PCBs, PAHs, dioxins and heavy metals. Some pretreatment of the oil will be required to ensure that emission standards for these materials are not exceeded when waste oil is used as fuel. Should this not be possible, the oil must be considered a hazardous waste and treated accordingly.

Disposal waste oil as hazardous waste requires that it be incinerated at high temperature to ensure complete oxidation of PAHs, PCBs and PCTs.

With regard to re-refining, the process is able to generate a product of sufficiently high quality; the principal environmental consideration concerns the disposal of the byproducts of the refinery process. The effluents/waste products from some re-refining process can be highly toxic and / or potentially carcinogenic. If these wastes are not

disposal properly, they represent a potential hazard to the environment, which is at least as serve as that of untreated oils.

2.1.9 Economic Aspects of Lubricating Oil need of Thailand [24]

As the growth of industries in Thailand, lubricating oil is a choice of demands for a necessary chemical used in the production processes. The more productions, the more quantity of oil is needed. Thailand's economic data can be shown in the following Tables.

Table 2.2 Import of petroleum crude oils in 1992 to 2003 [25].

Year	Quantity (million liters)
1992	16,148
1993	18,794
1994	21,336
1995	26,558
1996	36,844
1997	42,348
1998	39,446
1999	40,535
2000	39,242
2001	41,386
2002	42,279
2003	45,025

Table 2.3 Monthly import of lubricating oils in 1993 to 1994 [24].

Month	Quantity (million liters)	
	1993	1994
January	6.397	6.482
February	4.792	7.863
March	12.454	7.548
April	10.503	14.169
May	5.793	5.795
June	8.337	10.853
July	10.192	8.414
August	8.897	4.200
September	2.673	5.885
October	8.146	16.635
November	7.197	0.675
December	10.005	13.465

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Table 2.4 Forecast of lubricating base oil demand [24].

Year	Quantity (million liters)
1989	272.3
1990	326.4
1991	345.3
1992	382.0
1993	417.6
1994	458.0
1995	504.4
1996	547.3
1997	593.9
1998	644.2
1999	699.0
2000	758.4

Form these Tables, it can say that the more growth in industrial productions, more demand of lubricating oil Thailand. Then, if some used lubricating oil can be recycled to the new process, we can save some quantities of oil in use.

2.2 Thermal cracking [26]

Thermal cracking, where free radicals (lacking one hydrogen atom on carbon atom in hydrocarbon molecule) are intermediate species which crack, by a β -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:

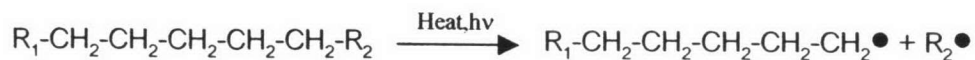
The normal paraffin molecule a hydrogen atom by collision and reaction with a small free hydrocarbon radical or a free hydrogen atom, thereby becoming a free radical itself. This radical may immediately crack or may undergo radical isomerization prior to cracking. Radical isomerization presumably occurs through a coiled configuration of a single radical, in which the hydrogen donor and acceptor carbon atom much closely approaches 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 take place at carbon-carbon bond located in the β position gives directly an alpha olefin and 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 β position 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 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 feedstock molecules to produce new free radicals and are themselves converted to methane or ethane. Thus, cracking is propagated as chain reaction.

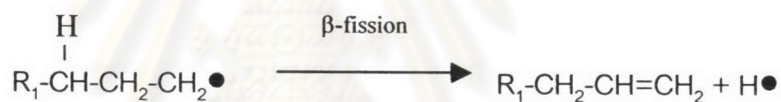
A schematic representation of polyethylene cracking is as follow;

1. Initiation Step



2. Propagation Step

2.1 β -fission



2.2 Chain transfer



2.3 Termination Step



2.3 Catalytic cracking [26]

Catalytic cracking is the most important and widely used refinery process for converting heavy oil into more valuable gasoline and lighter product. 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 are product.

Commercial cracking catalysts can be divided into three classes:

1. Acid-treated natural aluminosilicates
2. Amorphous synthetic silica-alumina
3. Crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves.

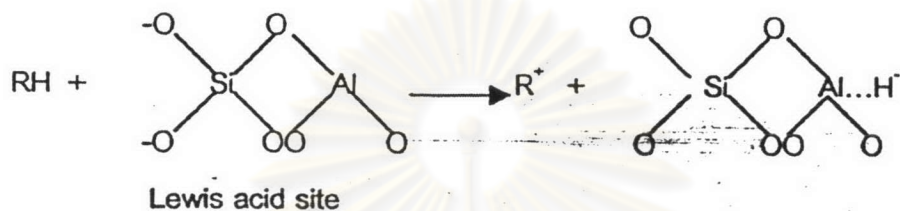
Most catalysts used in commercial units today are either class (3) or mixtures of classes (2) and (3) catalysts. The advantages of the zeolite catalysts over the natural and synthetic morphous catalysts are:

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

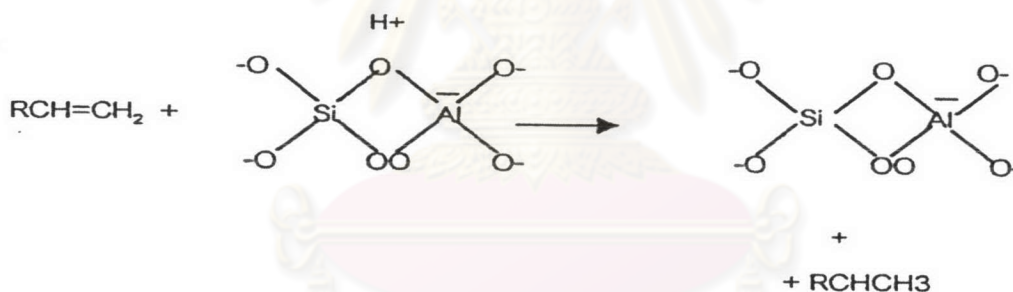
A major difference between thermal and catalytic cracking is that reactions through catalytic cracking occur via carbonium ion intermediate, compared to the free radical intermediate in thermal cracking. Carbonium ions are longer-lived and accordingly more selective than free radicals. Acid catalysts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

zeolites promote the formation of carbonium ions. The following illustrates the different ways by which carbonium ions may be generated in the reactor.

1. Abstraction of a hydride ion by a lewis acid site from a hydrocarbon



2. Reaction between a Bronsted acid site (H^+) and an olefin



3. Reaction of a carbonium ion formed step 1 or 2 with another hydrocarbon by abstraction of a hydride ion



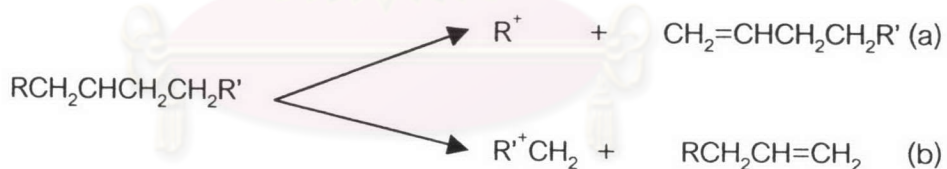
Abstraction of a hydride ion from a tertiary carbon is easier than from a secondary, which is easier than from a primary position. The formed carbonium ion can rearrange through a methide-hydride shift similar to what has been explained in catalytic reforming.

This isomerization reaction is responsible for a high ratio of branched isomers in the products.

The most important cracking reaction, however, is the carbon-carbon beta bond scission. A bond at a position beta to the positively charged carbon breaks heterolytically, yielding another carbonium ion. This can be represented by the following example:



The carbon-carbon beta scission may occur on either side of the carbonium ion, with the smallest fragment usually containing at least three carbon atoms. For example, cracking a secondary carbonium ion formed long chain paraffin could be represented as follows:



If R=H in the above example, then according to the beta scission rule (an empirical rule) only route (b) becomes possible, and propylene would be a product:

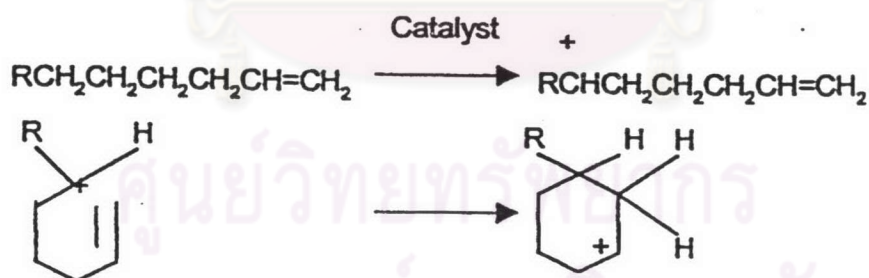


The propene may be protonated to an isopropyl carbonium ion:

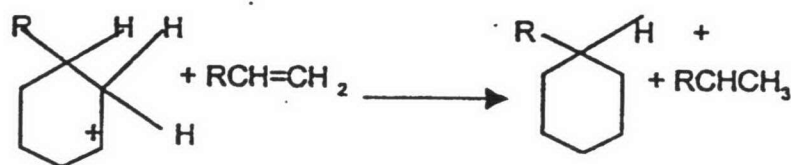


An isopropyl carbonium ion cannot experience a beta fission (no C-C bond beta to the carbon with the positive charge). It may either abstract a hydride ion from another hydrocarbon, yielding propane, or revert back to propene by eliminating a proton. This could explain the relatively higher yield of propane from catalytic cracking units than from thermal cracking units.

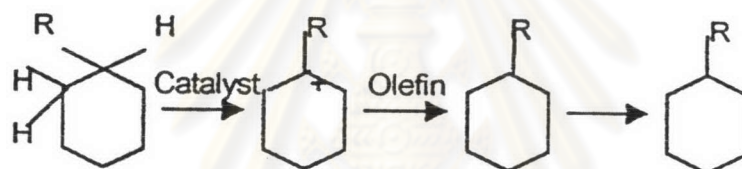
Aromatization of paraffins can occur through a dehydrocyclization reaction. Olefinic compounds formed by the beta scission can form a carbonium ion intermediate with the configuration conducive to cyclization. For example, if a carbonium ion such as that shown below is formed (by any of the methods mentioned earlier), cyclization is likely to occur.



Once cyclization has occurred, the formed carbonium ion can lose a proton, and a cyclohexene derivative is obtained. This reaction is aided by the presence of an olefin in the vicinity ($\text{R}-\text{CH}=\text{CH}_2$).



The next step is the abstraction of a hydride ion by a Lewis acid site from the catalyst surface to form the more stable allylic carbonium ion. This is again followed by a proton elimination to form a cyclohexadiene intermediate. The same sequence is followed until the ring is completely aromatized.



During the cracking process, fragmentation of complex polynuclear cyclic compounds may occur, leading to formation of simple cycloparaffins. These compounds can be a source of C_6 , C_7 , and C_8 aromatics through isomerization and hydrogen transfer reactions.

Coke formed on the catalyst surface is thought to be due to polycondensation of aromatic nuclei. The reaction can also occur through a carbonium ion intermediate of the benzene ring. The polynuclear aromatic structure has a high C/H ratio.

2.4 Hydrocracking Processing [26]

Hydrocracking is essentially catalytic cracking in the presence of hydrogen. It is one of the most versatile petroleum refining schemes adapted to process low value stocks.

Generally, the feedstocks are not suitable for catalytic cracking because of their high metal, sulfur, nitrogen, and asphaltene. The process can also use feeds with high aromatic content.

Products from hydrocracking process lack olefinic hydrocarbons. The product state ranges from light hydrocarbon gases to gasolines to residues. Depending on the operation variables, the process could be adapted for maximizing gasoline, jet fuel, or diesel production.

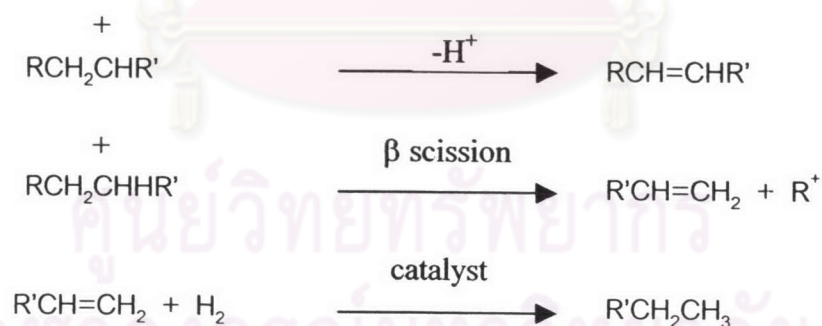
Table 2.5 Analysis of products from hydrocracking process [26].

Yields: Typical from various feeds: Feed	Naphtha	LCCO	VGO	VGO
Catalyst stages	1	2	2	2
Gravity, °API	72.5	24.6	25.8	21.6
Aniline pt, °F	145	92	180	180
ASTM 10% EP, °F	154/290	478/632	740/1,050	740/1,100
Sulfur, wt%	0.005	0.6	1.0	2.5
Nitrogen, ppm	0.1	500	1,000	900
Yields, vol.%				
Propane	55	3.4	-	-
Iso-Butane	29	9.1	3.0	2.5
n-Butane	19	4.5	3.0	2.5
Light naphtha	23	30.0	11.9	7.0
Heavy naphtha	-	78.7	14.2	7.0
Kerosine	-	-	86.8	48.0
Lt. Naphtha ROC cl	85	76	77	76
Hv. Naphtha ROC cl	-	65	61	61
Kerosine freeze pt, °F	-	-	-65	-75
Diesel pour pt, °F	-	-	-	-10

The dual-function catalysts used in hydrocracking provide high surface area cracking sites and hydrogenation-dehydrogenation sites. Amorphous silica-alumina, zeolites, or mixture of them promote carbonium ion a high iso/normal ratios. The hydrogenation-dehydrogenation activity, on the other hand, is provided by catalysts such as cobalt, molybdenum, tungsten, vanadium, palladium, or rare earth elements. As with catalytic cracking, the main reactions occur by carbonium ion and beta scission, yielding two fragments that could be hydrogenated on the catalyst surface. The main hydrocracking reaction could be illustrated by the first step formation of a carbonium ion over the catalyst surface:



The carbonium ion may rearrange, eliminate a proton to produce an olefin, or crack at a beta position to yield to an olefin and a new carbonium ion. Under an atmosphere of hydrogen and in the presence of a catalyst with hydrogenation-dehydrogenation activity, the olefins are hydrogenated to paraffinic compounds. This reaction sequence could be represented as follows:



As can be anticipated, most products from hydrocracking are saturated. For this reason, gasoline from hydrocracking units have lower octane ratings than those produced by catalytic cracking units; they have a lower aromatic content due to high hydrogenation

activity, products from hydrocracking units are suitable for jet fuel use. Hydrocracking also produces light hydrocarbon gases (LPG) suitable as petrochemical feedstock.

Other reactions that occur during hydrocracking are the fragmentation followed by hydrogenation (hydrogenolysis) of the complex asphaltenes and heterocyclic compounds normally present in the feeds.

Hydrocracking reaction conditions vary widely, depending on the feed and the required products. Temperature and pressure range from 400 to 480 °C and 35 to 170 atmospheres, respectively. Space velocities in the range of 0.5 to 2.0 hr⁻¹ are applied.

2.5 Metal Catalysts [27, 28]

Metal catalysts are of particular interest for reactions involving hydrogen, such as hydrogenation, hydrogenolysis, hydrocracking and catalytic reforming. The use of iron for ammonia synthesis and for the Fischer-Tropsch reaction, and nickel for steam reforming and methanation. In many of these applications the metal is highly dispersed on a support, in aggregates so small that many or most of the atoms present are on the surface. A central question here is the extent to which the rate of a reaction per atom of exposed metal (turn number) and, more importantly, the relation rates of alloys; by kinks, steps and other crystal imperfections; and by the blockage of some of the sites by deliberately added poisons or by accumulation of carbonaceous deposits. There is also a possible role of the support in influencing the properties of the metal.

Metals may also be useful for oxidation reactions. Examples are the use of supported silver for oxidation of ethylene to ethylene oxide; platinum-rhodium wire gauze for the partial oxidation of ammonia to nitric oxide or for conversion of a mixture of methane, ammonia and air to hydrogen cyanide and bulk silver for the partial oxidation of methanol to

formaldehyde. In oxidation reactions with metals, which characteristically involve relatively high temperature, questions arise of crystal growth, migration and the loss of active material by volatilization associated with chemisorbed oxygen and formation of metal oxides.

The metallic function, in the case of hydrocracking, must ensure the appropriate performance of at least three types of reactions. The selection of metal (groups of metals) and the selection of the promoters used are based on extended, in-depth studies.

Early studies under Raseev led to the following conclusions: NiMo and NiW are the most appropriate as metal couples among the base metals. Among the noble metals, Pt and Pd are preferred.

Catalysts made of NiMo and NiW are used in plants with a single stage of hydrocracking. They are always used in the first of systems with two stages.

More details concerning the formulation of hydrocracking catalysts and their manufacture, activation, characterization and testing, as deactivation and reactivation in operation, are given in the excellent monograph of Scherzer and Guia [35]

2.6 Zeolite [29]

2.6.1 History of Zeolites

2.6.1.1 Previous history

The history of zeolites began in 1756 when the Swedish mineralogist Cronstedt discovered zeolite material stilbite. He recognized zeolite as a new class of materials consisting of hydrated aluminosilicates of alkali and alkaline earths. Because the crystals

exhibite swelling and boiling when heated in a blowpipe fame, Cronstedt called the mineral a "zeolite" derived from two Greek words, "zeo" and "lithos" meaning "to boil" and "a stone". In 1840 Damour observed that crystals of zeolites could be reversibly dehydrated with no apparent change in their transparency or morphology. Schafhautle reported the hydrothermal sythesis of quartz in 1845 by heating a "gel" silica with water in an autoclave. Way and Thompson (1850) clarified the nature of ion exchange in soils. Eichhore in 1858 showed the reversibility of ion exchange on zeolite materials. St. Clarife Deville reported the first hydrothermal synthesis of a zeolite, in 1865. In 1866 Friedel developed the idea that structure of dehydrated zeolites consists of open spongy frameworks after observing that vorious liquids such as alcohol, benzene, and chloroform were occluded by dehydrated zeolites. Grandjean in 1909 observed that dehydrated chabazite adsorbs ammonia, air, hydrogen and other molecules, and in 1925 Weigel and Steinhoff reported the first molecular sieve effect. They noted that dehydrated chabazite crystals rapidly adsorbed water, methyl alcohol, ethyl alcohol, and formic acid but essentially excluded acetone, ether or benzene. In 1927 Leonard described the first used of x-ray diffraction for identification in mineral synthesis. The first structures of zeolites were determined in 1930 by Taylor and pauling. In 1932 McBain established the term "moleculor sieve" to define porous solid materials that act as sieves on a molecular acale.

Thus, by the mid-1930's the literature described the ion exchange, adsorption, molecular sieve and structural properties of zeolite minerals as well as a number of reported synthesis of zeolites. The latter early synthetic work remains unsubstantiated because of incomplete characterization and the difficulty of experimental reproducibility.

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Barer began his pioneering work in zeolite adsorption and synthesis in the mid-1930's to 1940's. He presented the first classification of the then known zeolites based on molecular size consideration in 1945 and in 1948 reported the first defined synthesis of zeolite including the synthetic analogue of the zeolite mineral merdenite.

2.6.1.2 Industrial history

2.6.1.2.1 Synthetic zeolites

Barrer's in the mid-late 1940's inspired the Linde Division of Union Carbide Corporation to initiate zeolite synthesis in search of new approaches for separation and purification of air. Between 1954 R.M. Milton and coworker D.W. Breck discovered a number of commercially significant zeolites; type A, X and Y. In 1954 Union Carbide commercialized synthetic zeolites as a new class of industrial material for separation and purification. The earliest applications were the drying of refrigerant gas and natural gas. In 1955 T.B. Reed and D.W. Breck reported the structure of synthesis zeolite A. In 1959 Union Carbide marketed the "ISOSIV" process for normal-isoparaffin separation, representing the first major bulk separation process using true molecular sieving selectivity. Also in 1959 a zeolite Y-based catalyst was marketed by Carbide as an isomerization catalyst.

In 1962 Mobil Oil introduced the use of synthetic zeolite X as a cracking catalyst. In 1969 Grace described the first modification chemistry based on steaming zeolite Y to form an "ultrastable" Y. In 1967-1969 Mobil Oil reported the synthesis of the high silica zeolites beta and ZSM-5. In 1974 Henkel introduced zeolite A in detergents as a replacement for the environmentally suspect phosphates. By 1977 industry-wide 22,000 tons of zeolite Y were in use in catalytic cracking. In 1977 Union Carbide introduced zeolite for ion-exchange separations.

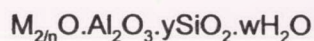
2.6.1.2.2 Natural zeolites

For 200 years following their discovery by Cronsted, zeolite mineral (or natural zeolite) were considered to occur typically as minor constituent in cavities in basaltic and volcanic rock. Such occurrences precluded their being obtained in mineable quantities for commercial use. From 1950 to 1962 major geologic discoveries revealed the widespread occurrence of a number of natural zeolite in sedimentary deposits throughout the Western United States. The discoveries resulted from the use of x-ray diffraction to examine very fine-grained (1-5 μm) sedimentary rock. Some zeolites occur in large near monomineralic deposits for mining. Those that have been commercialized for adsorbent applications include chabazite, erionite, mordenite and clinoptilolite.

2.6.2 Structure of Zeolite

Zeolites are crystalline aluminosilicates of group IA and IIA elements such as sodium, potassium, magnesium, and calcium.

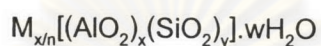
Chemically, they are represented by the empirical formula:



Where y is 2 to 10, n is the cation valence, and w represents the water contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline inorganic polymer based on an infinitely extending three-dimensional, four-connected framework of AlO_4 and SiO_4 tetrahedra (Figure 2.3) linked to each other by the sharing of oxygen ions. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by a cation. The framework structures contain channels or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange. The water may be removed reversibly, generally by the application of heat,

which leaves intact a crystalline host structure permeated by the micropores and voids which may amount to 50% of the crystals by volume.

The structure formula of zeolite is based on the crystallographic unit cell, the smallest unit of structure, represented by:



Where n is the valence of cation M , w is the number of water molecules per unit cell, x and y are total number of tetrahedra per unit cell, and y/x is 10 to 100.

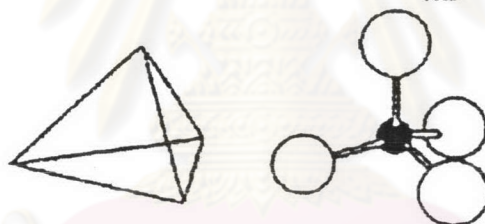


Figure 2.4 SiO_4 or AlO_4 tetrahedral [29].

In most zeolite structures the primary structural units, the AlO_4 or SiO_4 tetrahedral, are assembled into secondary building units (SBU). The final structure framework consists of assemblages of secondary units.

A secondary building unit consists of selected geometric groupings of those tetrahedra, which can be used to describe all of known zeolite structures. These secondary building unit consist of 4(A4R), 4(S6R) and 8(S8R)-member single ring, 4-4(D4R), 6-6(D6R), 8-8(D8R)-member double ring, and 4-1, 5-1, 4-4-1 branch ring. The topologies units are

show in Figure 2.4. Also listed are the symbols used to describe them. Most zeolite framework can be generated from several different SBU's. Description of know zeolite structures based on their 5-1 building units. Offertile, zeolite L, cancrinite, and erionite are generated using only single 6-member ring. Some zeolite structure can be described by several unit.

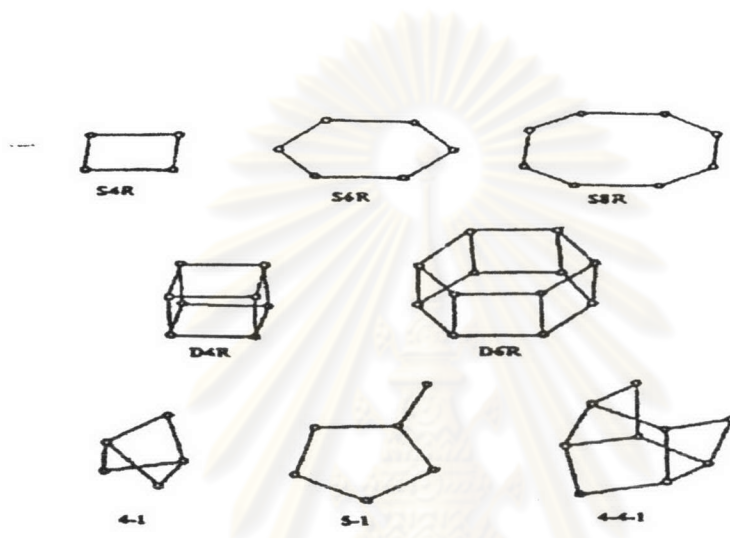


Figure 2.5 Secondary building units (SBU's) found in the zeolite structures [29].

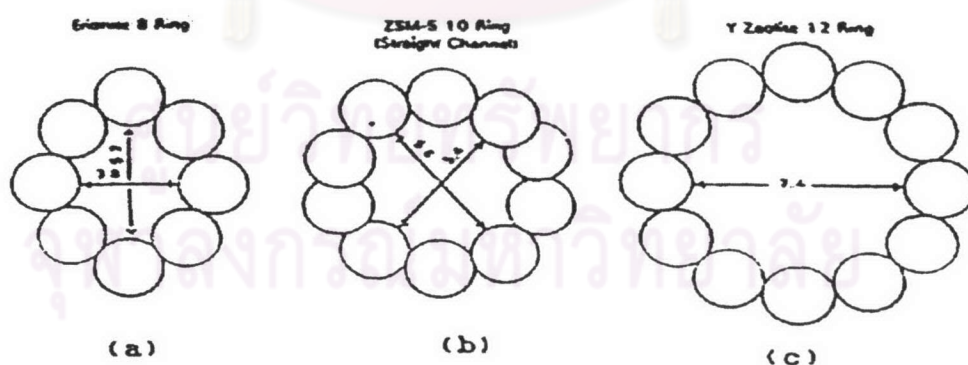


Figure 2.6 Typical zeolite pore geometries [29].

Table 2.6 Zeolites and their secondary building units. The nomenclature used is consistent that presented in Figure 2.5 [29].

Zeolite	Secondary Building Unite								
	6	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Bikitaite								×	
Li-A(BW)	×	×	×						
Analcime	×	×							
Yugawaralite	×		×						
Episitbite								×	
ZSM-5								×	
ZSM-11								×	
Ferrierite								×	
Dachiardite								×	
Brewsterdite	×								
Laumonite		×							
Mordenite								×	
Sodalite	×	×							
Henulanite									×
Stibite									×
Natrolite							×		
Thomsonite							×		
Edgtonite							×		
Cancrinite		×							
Zeolite L		×							
Mazzite	×								
Mertinoite	×		×			×			
Philisite	×		×						
Losod		×							
Erionite	×	×							
Paulingite	×								
Offretite		×							
TMA-E (AB)	×	×							
Gismondine	×		×						
Levyne		×							
ZK-5	×	×	×		×				
Chabazite	×	×			×				
Mazzite	×	×	×		×				
Rho	×	×	×			×			
Type A	×	×	×						
Faujasite	×	×			×				

The catalytically most significant are those having pore opening characterized by 8-,10-, 12- ring of oxygen atoms. Some typical pore geometries are show in Figure 2.5.

2.5.2.1 Small pore zeolites

Structures of some small pore zeolite are illustrated in Figure 2.7. The erionite structure, Figure 2.7(a), is hexagonal containing "supercage" supported by column of cancrinite units linked through double 6 rings. Access to, and between, the supercages are gained through 8 rings.

In the chabazite framework, Figure 2.7(b), the double rings layer sequence is ABCABC, and the 6 ring units are linked together titled 4 ring units. The framework contains large ellipsoidal cavities, Figure 2.7(c), each entered through six 8 ring units, these cavities are joined via their 8 ring units, forming a 3 dimensional channel system.

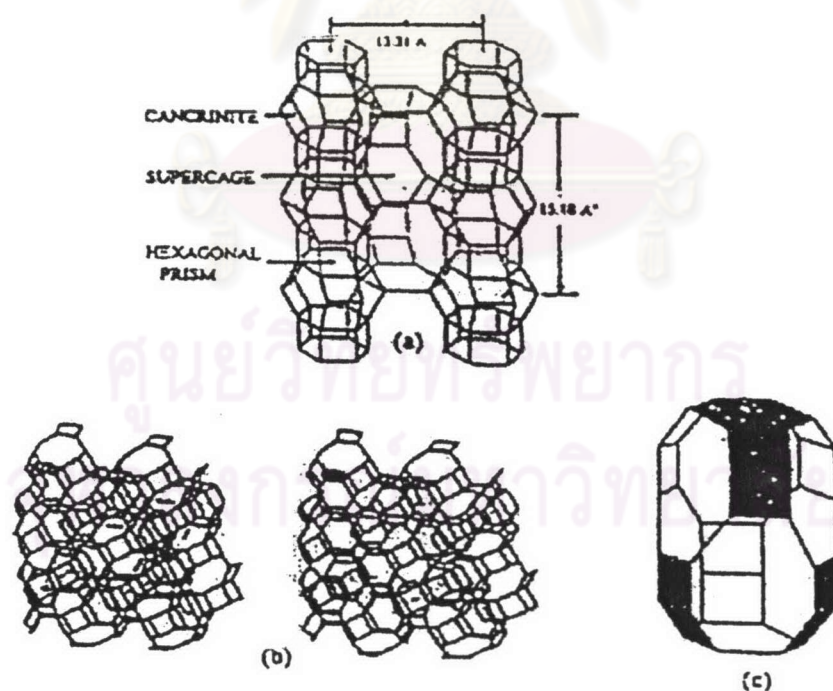


Figure 2.7 Small pore zeolite

(b) Chabazite framework

(a) Erionite framework

(c) Chabazite cavity [29].

2.5.2.2 Medium pore zeolites

The channel system of zeolite ZSM-5, represented in Figure 2.8, shows a unique pore structure that consists of two intersecting channel systems: one straight ($5.5 \times 5.6 \text{ \AA}$) and other sinusoidal ($5.1 \times 5.4 \text{ \AA}$) and perpendicular to the former. Both channel systems have ten-membered ring elliptical openings.

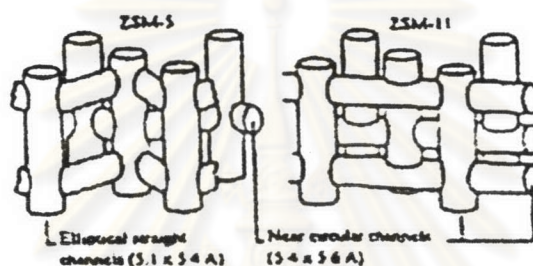


Figure 2.8 ZSM-5 and ZSM-11 channel systems [29].

2.5.2.3 Large pore zeolites

Mordenite, Figure 2.9(a), is characterized by one dimensional system of parallel elliptical channels, defined by 12 oxygen ring.

The faujasite structure, Figure 2.9(b), is built up of truncated octahedra interconnected via double 6 ring units. Faujasite contains extremely large supercages ($\sim 13 \text{ \AA}$ diameter) entered through 12 oxygen ring.

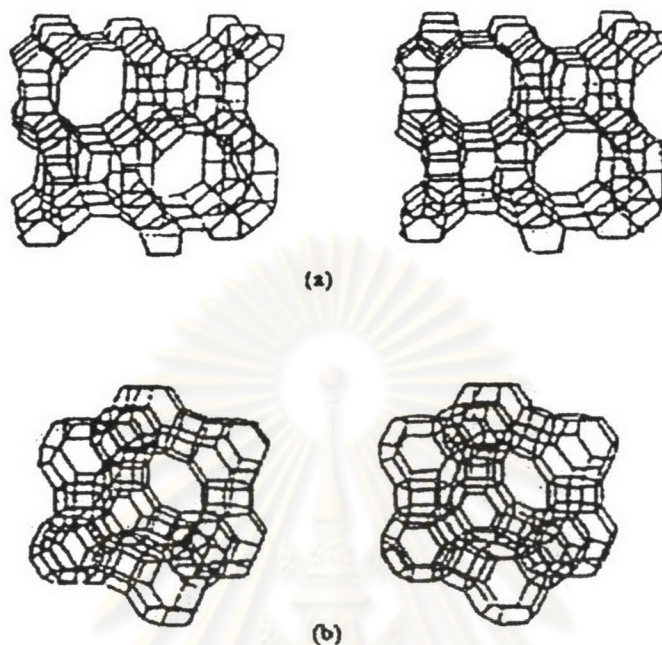


Figure 2.9 Large zeolite

(a) Mordenite framework

(b) Faujasite framework [29].

2.6.3 X and Y Zeolite Structures

X zeolite, Y zeolite and faujasite have topologically similar structures. They differ in their characteristic silica-to-alumina ratios and consequently differ in their crystal-lattice parameter, with a variation of about 2 percent over the range of permissible Si/Al ratios. They also differ in properties as cation composition, cation location, cation exchangeability, thermal stability, adsorptive and catalytic character.

In the X and Y zeolites and faujasite, the silica and alumina tetrahedra are joined together to form a cuboctahedron, as shown in Figure 2.10. This unit is referred to as a sodalite unit or truncated octahedron, contains 24 silica and alumina tetrahedra. The sodalite unit is the secondary building block of a number of zeolites, including sodalite, zeolite A, zeolite X, zeolite Y and faujasite. Molecules can penetrate into this unit through the six-membered oxygen ring, which has a free diameter of 2.6 \AA , the unit contains spherical void volume with

6.6 \AA , free diameter. Since the pore diameter is so small, only very small molecules, e.g., water, helium, hydrogen, or ions can enter the sodalite cage.

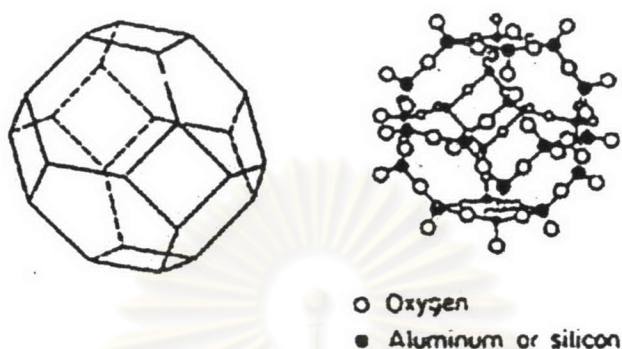


Figure 2.10 Sodalite cage structure. A formal representation of a truncated octahedron is shown on the left, and individual atoms are indicated on the right; the lines in the structure on the left represent oxygen anions, and the points of intersection represent silicon or aluminium ions [29].

The unit cell of the faujasite-type zeolite is cubic with a unit-cell dimension of 25 \AA , and it contains 192 silica and alumina tetrahedral. The unit cell dimension varies with Si/Al ratio. Each sodalite unit in the structure is connected to four other sodalite units by six bridge oxygen ions connecting the hexagonal faces of two units, as shown in Figure 2.9. The truncated octahedra are stacked like carbon atom in a diamond. The oxygen bridging unit is referred to as a hexagonal prism, and it may be considered another secondary unit. This structure results in a supercage (sorption cavity) surrounded by 10 sodalite unit which is sufficient large for an inscribed sphere with a diameter of 12 \AA . The opening into this large cavity is bounded by 6 sodalite unites, resulting in a 12 member oxygen ring with a 7.4 \AA free diameter. Each cavity is connected to four other cavities, which in turn are themselves connected to three additional cavities to form a highly porous framework structure.

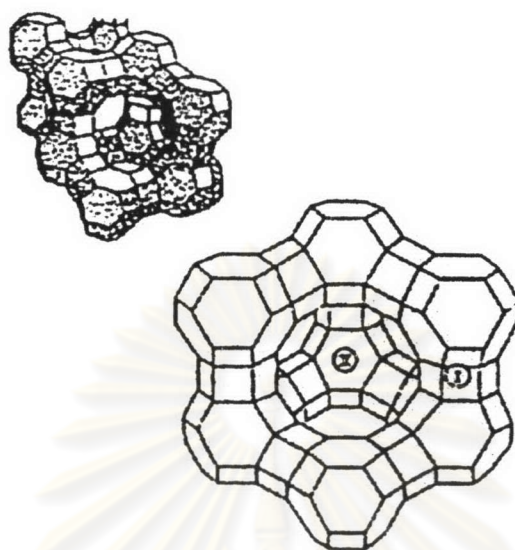


Figure 2.11 Perspective views of the fuajosite structure. The silicon or aluminium ions are located at the corner and the oxygen ions near the edges. Type I and II sites are indicated; the supercage is in the center [29].

This framework structure is the most open of any zeolite and is about 51 percent void volume, including the sodalite cage; the supercage volume represents 45 percent of the unit cell volume. The main pore structure is three-dimensional and large enough to admit large molecules, e.g., naphthalene and fluorinated hydrocarbon. It is within the pore structure that the locus of catalytic activity resides for many reactions. A secondary pore structure involving the sodalite unit exists but its apertures are too small to admit most molecules of interest in catalysis.

2.6.4 Zeolites as Catalysts

The first use of zeolite as catalysts occurred in 1959 when zeolite Y was used as an isomerization catalyst by Union Carbide. More important was the first use of zeolite X as a cracking catalyst in 1962, based upon earlier work by Plank Rosinski. They noted that

relatively small amounts of zeolites could be incorporated into the then-standard silica/alumina or silica/clay catalysts. The use of zeolite in this way as promoters for petroleum cracking greatly improved their performance.

2.6.4.1 Potential versatility of zeolites as catalysts

Vaughan has graphically described zeolites as “molecules boxes” which have variable dimensions suited to the encouragement of molecular rearrangements inside their confined geometry. The conditions inside the “box”, and of box itself, can be controlled in a variety of ways based upon the unique properties of zeolite frameworks as summarized in Table 2.7.

Table 2.7 Correlation between zeolite properties and catalytic functionality [29].

Property	Catalytic Functionality
Crystal voidage and channels	Extensive internal surface to encourage catalytic processes.
Variable pore size	Creates both reactant and product selectivity via molecules sieving.
Ion exchange	Cations (i) control pore size, (ii) create high potential energy field within voidage (active site) and (iii) enable distribution of catalytically active metals on the zeolite substrate.
Salt occlusion	Controls pore size, provide another method of metal incorporation and can improve thermal stability and poisoning resistance.
Framework modification	Varies lattice change (by synthesis or modification) to enhance Active site production and thermal stability.

2.6.4.1.1 Crystal voidage and channels

Although some heterogeneous reaction will take place at the external crystal surface, most practical zeolite catalysis takes place inside the framework. Here zeolites have the advantage of a very large internal surface, about 20 times larger than their external surface for the more open framework (e.g. zeolite X and Y). This internal capacity provides the

appropriate surfaces at which catalytic transformation can take place. In the faujasite zeolite is typically in the series of large cavities easily available via three-dimensional open-pore networks.

Further flexibility which is useful for planned catalytic uses arise in the more recently produces zeolites with subtle different cavity and channel systems. ZSM-5, for instance, has a three-dimensional system linked via intersections rather than cavities and mordenite catalysis seems to take place only in the largest channels.

2.6.4.1.2 Variable pore sizes

Given that catalytic reaction takes place largely within zeolite framework, access to this environment is patently controlled by oxygen windows. This is diffusion limited process, this is the effect of product molecules after transformations have taken place. This means that zeolites have very special practical advantages over the more traditional catalysts, in that admit only certain reactant molecules and this can be potentially tailored to produce a selected product. This selectivity is known as "shapes-selective catalysis" and controlled by configurational diffusion" this phrase was coined by Weiss to express a diffusion regime in which useful catalytic reactions are promoted by virtue of a matching of size, shapes and orientation of the reactant product molecules to the geometry of zeolitic framework.

2.6.4.1.3 Ion exchange

Perhaps more relevant is the way in which ion exchange can be employed to place cations into very specific framework sites so as to create small volumes of high electrostatic field. These fields are "active sites" to which an organic reactant molecule can be attracted thus promoting the bond distortion and rupture essential to molecular rearrangements.

Another feature of ion exchange is that it provides a route for the introduction of metal cations with a view to their subsequent reduction to metal particles. These exist in the

Framework substitution also can be created by the introduction of the atoms other than Si and Al into tetrahedral sites via synthesis or modification. The ZSM-5 can accept B and Ge into tetrahedral sites by simple salt treatment as mentioned earlier, although a similar reaction in other frameworks is by no means as facile.

2.6.5 Zeolite Active sites

2.6.5.1 Acid sites

Classical Bronsted and Lewis acid models of acidity are used to classify the active sites on zeolites. Bronsted acidity is proton donor activity; a tridiagonally co-ordinated alumina atom is an electron deficient and can accept an electron pair, therefore as a Lewis acid.

In general, the increase in Si/Al ratio will increase acidic strength and thermal stability of zeolite. Since the number of acidic OH groups depend on the number of aluminum zeolite's framework, decrease in Al content is expect to reduce catalytic activity of zeolite. If the effect of increase in the acidic centers, increase Al content, shall result in enhancement of catalytic activity.

Based on electrostatic consideration, the charge density at a cation site increase with increasing Si/Al. It was conceived that these phenomena are related to reduction of electrostatic interaction between framework sites, and possibly to difference in the order of aluminum in zeolite crystal-the location of Al in crystal structure.

Recently it has been reported the mean charge on proton was shifted regularly towards higher values as the Al content decrease. Simultaneously the total number of acidic hydroxyls, governed by the Al atoms, was decreased. This evidence emphasized that the

entire acid strength distribution (weak, medium, strong) was shifted towards stronger values. That is the weaker acid sites become stronger with the decrease in Al content.

An important factor in thermal and hydrothermal stability has been described to the lower density of hydroxyl groups which is parallel to the Al content.

A longer distance between hydroxyl groups decreases the probability of dehydrogenation that generates defects on structure of zeolites.

2.6.5.2 Generation of acid centers

Protonic acid centers of zeolite are generated in various ways. Figure 2.12 depicts the thermal decomposition of ammonium exchange zeolites yielding the hydrogen form.

The Bronsted acidity due to water ionization on polyvalent cations, described below, is depicted in Figure 2.13.



The exchange of monovalent ions by polyvalent cations could improve the catalytic property. Those highly charged cations create very acidic centers by hydrolysis phenomena.

The Bronsted acid sites are also generated by the reduction of transition metal cations. The concentration of OH groups of zeolite containing transition metals was noted to increase by reduction with hydrogen at 250-450 °C to increase with the rise of the reduction temperature.



The formation of Lewis acidity from Bronsted sites is depicted in Figure 2.14. The dehydration reactions decrease the number of protons and increase that of Lewis sites.

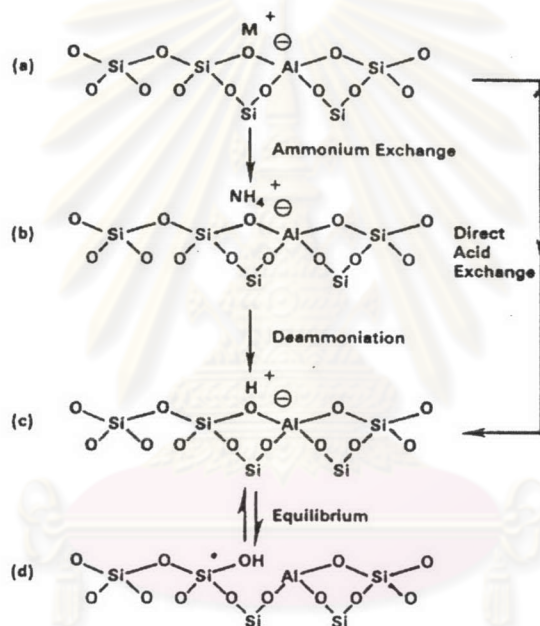


Figure 2.12 Diagram of the surface of a zeolite framework

(a) In the as-synthesized form M^+ is either an organic cation or an alkali metal cation.

(b) Ammonium in exchange produces the NH_4^+ exchanged form.

(c) Thermal treatment is used to remove ammonia, producing the H^+ , the acid form.

(d) The acid form in (c) is in equilibrium with the form shown in (d), where there is a silanol group adjacent to a tricoordinate aluminum [29].

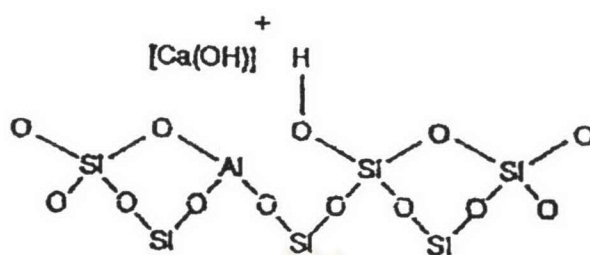


Figure 2.13 Water molecules coordinated to polyvalent cation are dissociated by heat treatment yielding Bronsted acidity [29].

Bronsted (OH) and Lewis (-Al-) sites can be presented simultaneously in the structure of zeolite at high temperature. Dehydroxylation is thought to occur in ZSM-5 zeolite above 500 °C and calcination at 800-900 °C produces irreversible dehydroxylation which causes defect in crystal structure of zeolite.

Dealumination is believed to occur during dehydroxylation which may result from the steam generation within the sample. The dealumination is indicated by an increase in the surface concentration of aluminum on the crystal. The dealumination process is expressed in Figure 2.15. The extent of dealumination monotonously increases with the partial pressure of steam.

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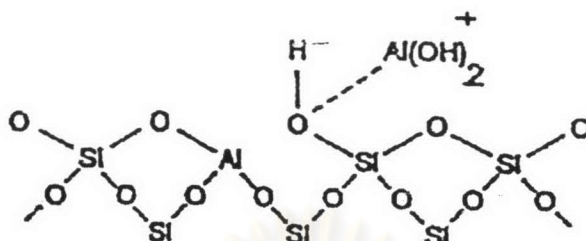


Figure 2.16 The enhancement of acid strength of OH group by their interaction with dislodge aluminium species [29].

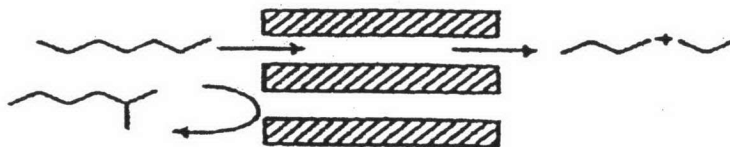
2.6.5.3 Basic sites

In certain instances reactions have been shown to be catalyzed at basic (cation) sites in zeolites without any influence from acid sites. The best characterized example of this is that of K-Y which splits n-hexane isomers at 500 °C. The potassium cations have been shown to control the unimolecular cracking (β -scission). Free radical mechanism also contributes to surface catalytic reactions in these studies.

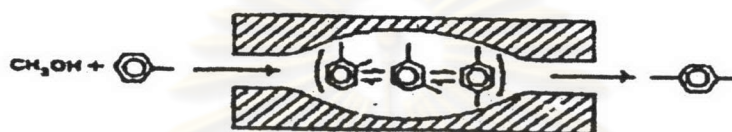
2.6.6 Shape-Selectivity Catalysis

Many reactions involving carbonium ion intermediates are catalyzed by acidic zeolites. With respect to a chemical standpoint the reaction mechanisms are not fundamentally different with zeolites or with any other acidic oxides. What zeolite adds is shape selectivity effect. The shape selectivity characteristics of zeolites influence their catalytic phenomena by three modes: reactant shape selectivity, product shape selectivity and transition state shape selectivity. These types of selectivity are depicted in Figure 2.17.

a) Reactant selectivity



b) Product selectivity



c) Transition state selectivity

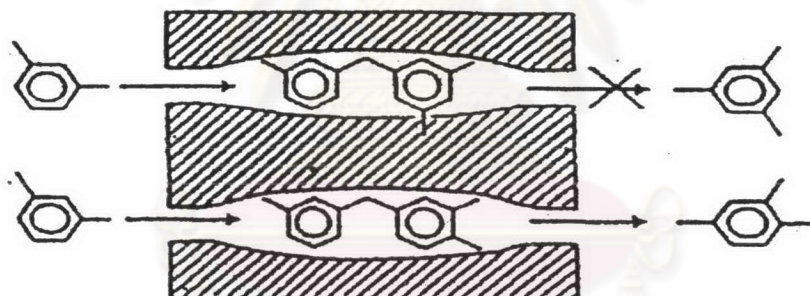


Figure 2.17 Diagram depicting the three types of selectivity [29].

Reactant or change selectivity results from the limited diffusibility of some of the reactants, which cannot effectively enter and diffuse inside crystal pore structures of the zeolites.

Product shape selectivity occurs as slowly diffusing product molecules cannot escape by monitoring changes in product distribution as a function of varying contact time.

Restricted transition state shape selectivity is a kinetic effect arising from local environment around the active site, the rate constant for a reaction mechanism is reduced if the space required for formation of necessary transition state is restricted.

Table 2.8 Kinetic diameters of various molecules based on the Lennard-Jones relationship [29].

	Kinetic Diameter (Angstroms)
He	2.60
H ₂	2.89
O ₂	3.46
N ₂	3.64
NO	3.17
CO	3.76
CO ₂	3.30
H ₂ O	2.65
NH ₃	2.60
CH ₄	3.80
C ₂ H ₂	3.30
C ₂ H ₄	3.90
C ₃ H ₈	4.30
n-C ₄ H ₁₀	4.30
Cyclopropane	4.23
i-C ₄ H ₁₀	5.00
n-C ₅ H ₁₂	4.90
SF ₆	5.50
Neopentane	6.20
(C ₄ H ₉) ₃ N	10.20
Benzene	5.85
Cyclohexane	6.00
m-xylene	7.10
p-xylene	6.75
1,3,5 trimethylbenzene	8.50
1,3,5 triethylbenzene	9.20
1,3 diethylenebenzene	7.40
1-methylnapthalene	7.90
(C ₄ H ₉) ₃ N	8.10

The critical diameter (as opposed to the length) of the molecules and the pore channel diameter of zeolites are important in predicting shape selective effects. However, molecules are deformable and can pass through openings which are smaller than their critical diameters. Hence, not only size but also the dynamics and structure of molecules must be taken into account.

Table 2.8 presents values of selected critical molecular diameters and Table 2.9 presents values of the effective pore size of various zeolites. Correlation between pore size (s) and kinetic diameter of some molecules are depicted in Figure 2.18.

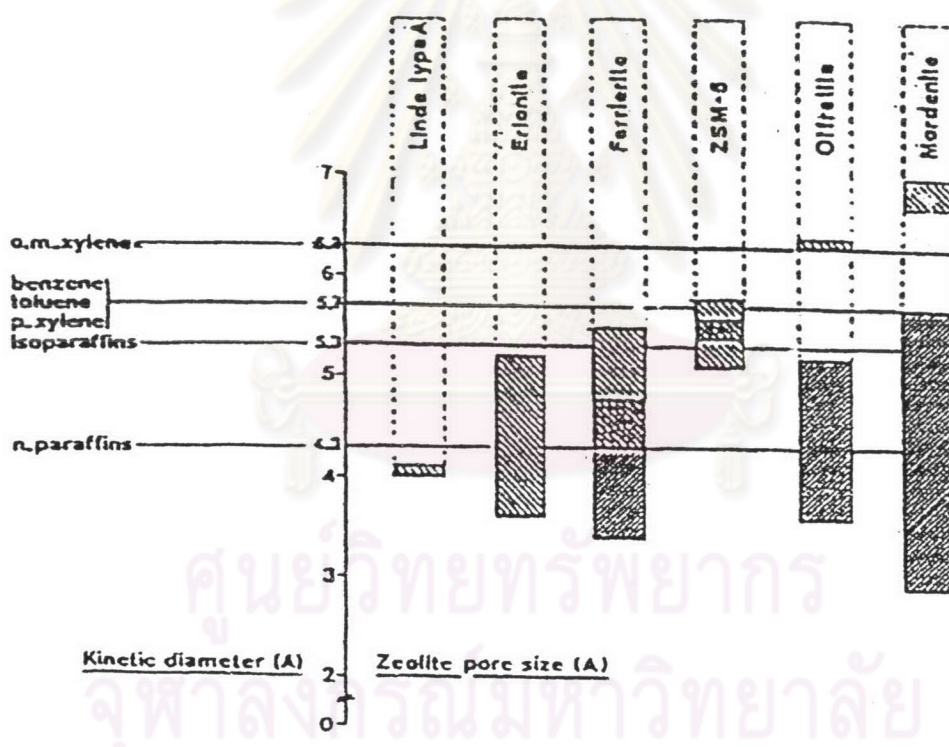


Figure 2.18 Correlation between pore size(s) of various zeolites and kinetic diameters of some molecules [29].

Table 2.9 Shape of the pore mouth opening of known zeolite structures. The dimensions are based on two parameters, The T atom forming the channel opening (8, 10, 12 ring) and crystallographic free diameters of the channels. The channels are parallel to the crystallographic axis shown in brackets (e.g. $\langle 100 \rangle$) [29].

STRUCTURE	4-MEMBER RING	10- MEMBER RING	12- MEMBER RING
Bikitaite	2.3x4.9[001]		
Brewsterite	2.3x5.0[100]		
	2.7x4.1[001]		
Cancrinite			6.2[001]
Chabazite	3.6x3.7[001]		
Dachiardite	3.6x4.8[001]	3.7x6.7[010]	
TMA-E	3.7x4.8[001]		
Edingtonite	3.5x3.9[110]		
Epistibite	3.7x4.4[001]	3.2x5.3[100]	
Erionite	3.6x5.2[001]		
Faujasite			7.4 $\langle 111 \rangle$
Ferrierite	3.4x4.8[010]	4.3x5.5[001]	
Gismondine	3.1x4.4[100]		
	2.8x4.9[010]		
Gmelinite	3.6x3.9[001]		7.0[001]
Heulandite	4.0x5.5[100]	4.4x7.2[001]	
	4.1x4.7[001]		
ZK-5	3.9 $\langle 100 \rangle$		
Laumontite		4.0x5.6[100]	
Levyne	3.3x5.3[001]		
Type A	4.1 $\langle 100 \rangle$		
Type L			7.1[001]
Mazzite			7.4[001]
ZSM-11		5.1x5.5[100]	
Merlinoite	3.1x3.5[100]		
	3.5x3.5[010]		
	3.4x5.1[001]		
	3.3x3.3[001]		
ZSM-5		5.4x5.6[101]	
		5.1x5.5[100]	
Mordenite	2.9x5.7[010]		6.7x7.0[001]
Natrolite	2.6x3.9 $\langle 101 \rangle$		
Offretite	3.6x5.2[001]		6.4[001]
Paulingite	3.9 $\langle 100 \rangle$		
Phillipsite	4.2x4.4[100]		
	2.8x4.8[010]		
	3.3[001]		
Rho	3.9x5.1 $\langle 100 \rangle$		
Stibite	2.7x5.7[101]	4.1x6.2[100]	
Thomsonite	2.6x3.9[101]		
	2.6x3.9[010]		
Yugawaralite	3.1x3.5[100]		
	3.2x3.3[001]		

2.6.7 Synthesis of HZSM-5 zeolite

1. Prepare a saturated solution of NaOH in hot water.
2. Dissolve alumina (ALCOA) in the basic solution if necessary heat up a little.
3. Add this solution onto SiO₂ (colloidal Ludox) in a high shear blender.
4. Add the organic template:
 - TPA (tetrapropylammonium bromide)
 - TEA (tetraethylammonium bromide)
5. Transfer to autoclave with Teflon-lined walls. Place in oven at about 120-175 °C.

Leave for 1-3 days.

6. Calcine at 600 °C to remove organics.
7. Reflux in HCl solution to remove Na ion.
8. Zeolite HZSM-5 should result.

2.7 Literature review

Lumberton J.L., Touzeyidio M., Guisnet M. [30], studied the reaction of catalytic hydroprocess simulated coal tars in activity of sulphided Ni-Mo/Al₂O₃ catalyst for the Hydroconversion of Model Compounds. The conversion of tars from coal pyrolysis into light aromatics, such as BTX (benzene-toluene-xylenes) and naphthalene, requires the hydrocracking of heavy polyaromatics in the presence of nitrogen and oxygen containing compounds. The hydroconversion of phenanthrene, which occurs through bifunctional catalysis, was chosen as a model reaction. It was carried out over a sulphided Ni-Mo/Al₂O₃ catalyst in the presence of carbazole and 1-naphthol. Carbazole poisons slightly through coking both the hydrogenating and the acid sites of the catalyst. 1-naphthol has a more significant deactivating effect: the hydrogenating sites of the catalyst are poisoned by the water eliminated from 1-naphthol and the acid sites by coke generated by 1-naphthol. Lastly, the hydrogenating activity of the catalyst is not substantially affected in the presence of

carbazole and 1-naphthol, but its cracking activity is much reduced, making it impossible for the catalyst to achieve the hydrocracking of phenanthrene into light aromatics.

Sriwanichanichapoom S. [19], studied the catalytic hydrotreatment of used lubricating oil by catalysts. The Co-Mo/Al₂O₃ catalyst can produce the product oils which had the best ASTM color, acidity, and viscosity index. Ni-Mo/Al₂O₃ catalyst produced the product oils which had the lowest sulfur content while NiW/Al₂O₃ catalyst produced the product oils which had the best viscosity and flash point.

Meusinger J., Corma A. [31], studied the activity of hydrogen simulated for kinetics on zeolite and cracking mechanism of n-heptane on zeolite HZSM-5 with high pressure hydrogen by tubular reactor at temperature 543°K, hydrogen gas pressure 2.4 mPa, spent spray stream 0.5-6.2 min, on condition simulated by HZSM-5, 10 min of reaction found that cracking ratio of n-heptane no effect by minor pressure of n-heptane during 0.2-0.47 mPa but effected with increased pressure of hydrogen gas that more forming structure of Carbon atom C₂-C₄.

Longstaff D.C., Hanson F.V. [32], studied the hydrogenation of acid catalyst in kerosene hydrocracking process on HZSM-5 in condition of hydrogen gas 4.1-8.7 mPa, temperature 373-390°C found that when we increased pressure of hydrogen gas in kerosene hydrocracking process become high portion of methane and C₂ but olefin and aromatics compound was reduced. Properties of catalyst was denatured at pressure 1.4 mPa, temperature 370°C, 16 hours.

Sharratt P.N., Lin Y.H., Garforth A.A., Dwyer J. [33], studied the decomposition by heat of HDPE bead on catalyst zeolite HZSM-5 (Si/Al = 17.5) with fluidized bed reactor was found at temperature 360°C, 15 minutes become ratio of C₃-C₅ 90% w/w

Sato Y. [34], studied how to improve heavy fraction of distillation oil from liquid Wandoan coal by catalyst Co-Mo and Ni-Mo on site of alumina. Found that temperature 390°C by product is amount of toluene and xylene, if temperature higher than by product is amount of n-paraffins.

Uemichi Y., Nakamura J., Itoh T., Sugioka M. [35], studied to restructure of used PE bead on catalyst HZSM-5 and silica-alumina on ratio 9:1 at temperature 375°C, W/F (mass of catalyst/ mass flow rate of polyethylene) = 7 in 2 step of series system found that received gasoline 58.8 w/w, octane number = 94, for conclusion this method can improve quality of gasoline.

Sato Y. [36], studied the pyrolytic coprocessing of used plastics and used lubricating oil to be fuel oil by method statistical pentagonal experimental design in small reactor capacity 40 mL. Found that LDPE and HDPE take oil quality more than 99% at temperature 460°C, 30 min, PP was taken same quantity as PE at temperature 430°C, 30 minutes, PS was take more quantity than 95% at temperature 426°C. On the same condition ABS take less quantity than PS. And PET take 75% oil at temperature 460°C, 30 minutes.

Pongphuntharak U. [26], studied to restructure of LDPE bead and coal by Ni-Mo/Al₂O₃ in small reactor found that at temperature 420°C, hydrogen gas pressure 60 kg/cm², reaction time 60 minutes, ratio of plastic per coal = 15:1 take high quantity of oil = 68.1 and component of product is 44.3% naphtha, 9.6% kerosene, 6.3% light paraffin, 3.2% heavy paraffin, and 4.7% w/w of long chain carbon.

Trisupakitti S. [29], studied to restructure of PE to gasoline by catalyst HZSM-5, found at temperature 450°C, hydrogen gas pressure 30 kg/cm² and reaction time is 60 minutes, received by product 20-45% of naphtha, 8-16% of kerosene, 9-16% of paraffin and 3-14% w/w of long chain carbon.

Ferdous D., Dalal A.K., Adjaye J. [37], was compared of hydrodenitrogenation reaction of basic nitrogen compound and nonbasis nitrogen compound by trickle bed reactor and selected catalyst NiMo/Al₂O₃ at temperature 355-400 °C, hydrogen pressure 1120-1420 psi. The results is basic nitrogen compound (acridine) can reformed HDN for eradicate 98-99% w/w of nitrogen gas from heavy oil. That's better than eradicate nonbasic nitrogen compound. (92-95% w/w carbazolec and 94-97% w/w 9-ethylcarbazole)



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