

CHAPTER II

THEORY

2.1 Catalysis [29]

Catalysis is an essential chemical phenomenon. It involves substance that increases the rate at which chemical reaction approaches equilibrium, without being consumed in the process called catalyst. In catalysis process, the catalyst is chemically unchanged at the end of the reaction. When the reaction has finished, the same mass of catalyst as the beginning will be obtained. The ability of a substance to act as a catalyst depends on its chemical nature. It provides an alternative route for the reaction that has lower activation energy (E_a). The energy profile with and without catalyst were shown in Figure 2.1.

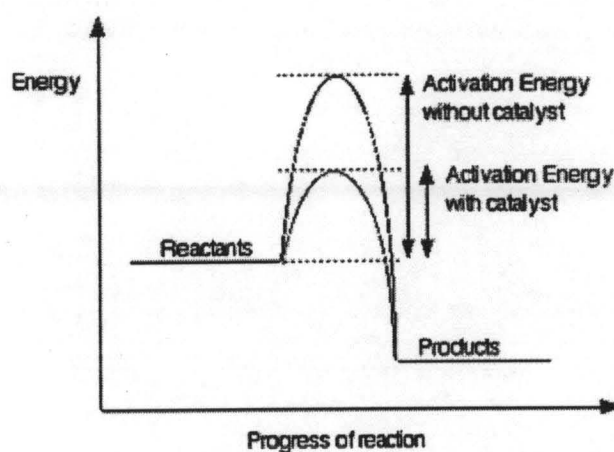


Figure 2.1 The potential energy profile of the reaction with and without catalyst.

Industrial catalysts comprise wide variety of materials that was manufactured by a variety of methods. Many catalysts or porous structure were studied. The commercially useful catalyst particle size is determined by the process in which to be used, fixed beds and fluidized beds. In fluidized beds reactors, usually present in the catalyst powder supplied. The particles present generally range from about 20-300 μm in diameter. For fixed beds particles generally range from about 0.0625-0.5 inches in

diameter. In general, 60% of commercially produced chemical products involve catalyst at some stage in the process of their manufacture.

2.1.1 Types of catalysts

Catalysts can be divided into two main types, heterogeneous and homogeneous catalysts. Biocatalyst is often seen as a separate group. In nature enzymes are catalyst in metabolic pathway whereas in biocatalysts enzymes are used as catalyst in organic chemistry.

2.1.1.1 Homogeneous catalysts

The homogeneous catalysts are in the same phase as the reactants, the catalyst is a molecule which facilitates the reaction. The reactants coordinate to the catalyst (or *vice versa*) and then transformed to product (s), which released from the catalyst. Typically, everything will be presence as gas or contained in a single liquid phase. In addition, the catalysis of organic reactions by metal complexes in solution has grown rapidly in both scientific and industrial importance.

2.1.1.2 Heterogeneous catalysts

Heterogeneous catalyst is presented in different phases from the reactants e.g. a solid catalyst in a liquid reaction mixture. A number of phase combinations can occur in heterogeneous catalyst was shown in Table 2.1.

Table 2.1 Phase combinations for heterogeneous catalyst [29]

Catalyst	Reactant	Example
Liquid	Gas	Polymerization of alkenes catalyzed by H_3PO_4
Solid	Liquid	Decomposition of H_2O_2 catalyzed by gold
Solid	Gas	NH_3 synthesis catalyzed by iron
Solid	Liquid + Gas	Hydrogenation of nitrobenzene catalyzed by Palladium

A simple model heterogeneous catalysis involves the catalyst providing a surface on which the reactants temporarily become adsorbed. Bonds in the reactants

become weakened sufficiently for new bonds to be created. The bonds between the products and the catalyst are weaker, so the products are released.

The mechanism of heterogeneous catalysis comprises five steps between compounds adsorbed on the surface of solid catalyst [30].

- (1) Diffusion of the reacting substances over the catalyst particle.
- (2) Adsorption of the reacting substances on the catalyst.
- (3) Interaction of the reacting substances on the surface of catalyst.
- (4) Desorption of the reaction products from the catalyst particle.
- (5) Diffusion of the reaction products into the surrounding medium.

Furthermore, catalyst particles have internal pores that are accessible to the reactant molecules, so that diffusion proceeds in two steps, external and internal surface.

2.2 Porous materials

Porous materials have found wide applications in many technological fields such as adsorption and environmental technology including catalysis because of their high surface area, large pore volume, and uniformity in pore size. The design and processing of novel porous materials, driven by the rapidly growing demands of emerging applications such as separation, purification, immobilization of biological molecules, drug delivery and gas storage, etc. Porous materials can be classified based on the IUPAC pore diameter into three groups that was shown in table 2.2.

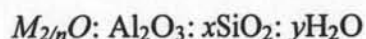
Table 2.2 IUPAC classification of porous materials [31]

Porous material	Pore diameter (nm)
Microporous	up to 2
Mesoporous	2-50
Macroporous	50 to up

2.3 Zeolites (molecular sieves) [32-33]

Zeolite is one of porous materials that play the diversified role such as catalysis, adsorption and ion-exchange, etc. They are highly crystalline hydrated

aluminosilicates which upon dehydration develop in the ideal crystal a uniform pore structure. They have minimum channel diameters in the range of 3-10 Å depend upon the type of zeolite and the nature of the cations present. The structure consists of three-dimension framework of SiO_4^{4-} and AlO_4^{5-} tetrahedral, each of which contains a silicon or aluminium atom in the center. The oxygen atoms are shared between adjoining tetrahedral. Zeolite has the general formula as



Which M represents a metal cation generally from group I and II of valence n . x and y was varied with the type of zeolite. They have quite large cages joined by smaller opening then, they have a very high internal surface area in the form of pores of fixed geometry.

2.3.1 Acid sites in zeolites

Zeolite acts as the acid catalyst due to the present of acid site. Brønsted acidity is at the proton donor site, and electron deficient atom that can accept an electron pair behaves a Lewis acid site. Both types of acid site of zeolite were shown in Figure 2.2.

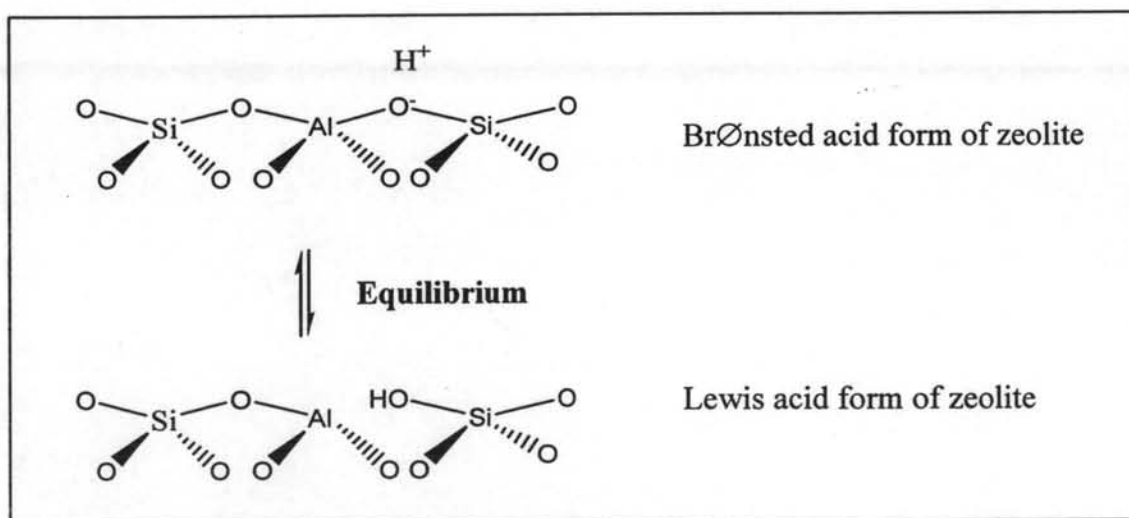


Figure 2.2 Brønsted and Lewis acid sites of zeolites.

2.3.2 Shape selectivity

Shape selective plays a very important role by either reactant shape selectivity, product shape selectivity, or transition-state shape selectivity. Reactant

shape selectivity results from the limited diffusion of some reactants, which cannot effectively enter and diffuse inside the crystal. In the product shape selectivity, it can be described in the same way. Restricted transition-state shape selectivity is a kinetic effect arising from the local environment around the active site. The rate constant for a certain mechanism is reduced if the necessary transition state is too bulky to form readily.

2.4 Titanosilicate materials

Microporous titanosilicate is one of zeolite-type materials. They are considered as possible new catalysts or molecular sieves and ion exchangers. They have been interested since the discovery of important catalytic properties of ZSM-5 structure titanium silicalite-1 (TS-1) in oxidation reactions in 1983. Titanosilicate compound was represented by the following compositional formula $x\text{TiO}_2(1-x)\text{SiO}_2$, where x is from 0.0001-0.2. In this group, octahedral and tetrahedral atoms are exclusively corner-linked. The UND-1 is a titanosilicate compound that built up from SiO_4 six-membered ring and isolated TiO_6 octahedral. The ion-exchange behavior of AM-2 ($\text{K}_2\text{TiSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$) was also studied and showed that selectivity for extra-framework cations [34]. Other examples of titanosilicate compounds were TSP used as photocatalyst [35] and EMS-3 that has high exchange capacity due to the divalent anionic charge on the Ti nuclei [36]. The structures of UND-1, AM-2 and TSP are shown in Figure 2.3.

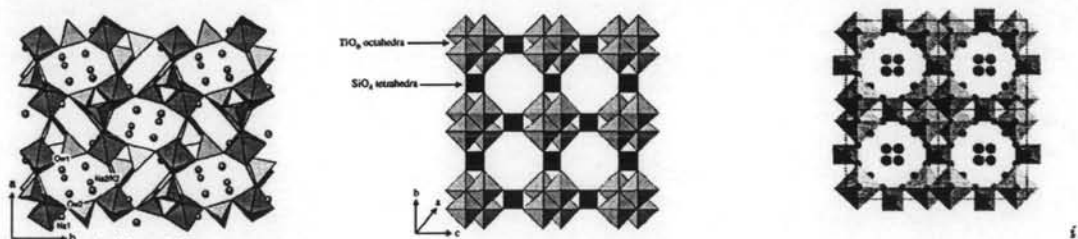


Figure 2.3 Structures of some titanosilicate compounds.

2.5 ETS-10 (Engelhard titanosilicate -10)

ETS-10 is one of microporous titanosilicate family that first discovered by Engelhard in 1989. It is the microporous zeolite-type materials contained 12-member ring with the dimension $4.9 \text{ \AA} \times 7.6 \text{ \AA}$. ETS-10 comprises corner-sharing SiO_4

tetrahedral and TiO_6 octahedral linked through oxygen atom. The presence of tetravalent Ti atom in an octahedron generates two negative charges that leads to an ion-exchange capacity almost as high as zeolite Y, which are balanced by exchangeable Na^+ and K^+ cations. The size and shape of ETS-10 crystals can be controlled by adjusting the synthesis conditions, including pH, temperature, and initial gel compositions [37].

2.5.1 Structures of ETS-10

The titanosilicate ETS-10 has a mixed tetrahedral-octahedral framework. Its structure consists of stacked sheets and different stacking sequences can be found. ETS-10 ideally has basic anhydrous formula of $[\text{M}_{2/n}\text{Si}_5\text{TiO}_{13}]$ where M represents the cation with a charge of plus n . A tetragonal body centered unit cell with $a = 7.481$ and $c = 27.407$ was derived from the single crystal data measured with CCD detector [38]. The TiO_6 octahedral share *trans* vertices to form TiO_5 infinite chains. These chains are each connected two folded chains of SiO_4 tetrahedral to form $[\text{TiSi}_4\text{O}_{13}]$ columns. The column are packed into layers parallel to the (001) plane with the columns in neighboring layers perpendicular to each other. The connection between Ti and Si atom to form framework structure was shown in Figures 2.4 and 2.5.

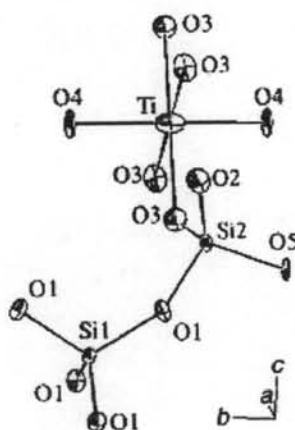


Figure 2.4 Coordination environments of the Ti and Si atoms of ETS-10 [38].

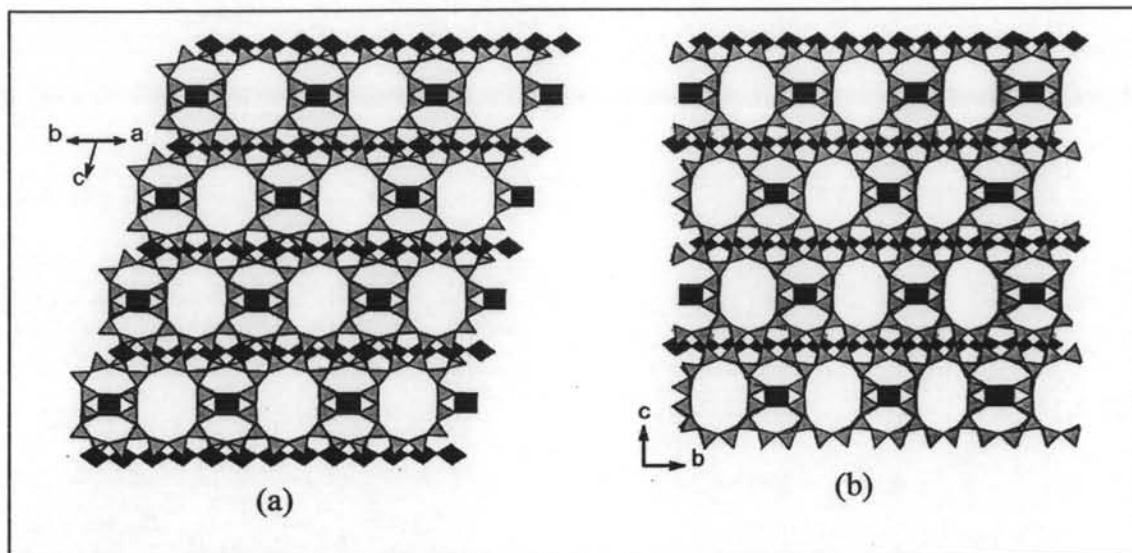


Figure 2.5 Titanosilicate ETS-10 projections: (a) down $[110]$ direction for polymorph B and (b) down $[100]$ direction for polymorph A, Dark TiO_6 octahedral, light grey SiO_4 tetrahedral [39].

ETS-10 is highly disordered, being composed of a random intergrowth of two end-member polymorphs exemplified by broad powder X-ray diffraction reflections. Two hypothetical polymorphs of ETS-10 were ABCDABCD stacking (polymorph A) and ABAB stacking (polymorph B) that shown in Figure 2.5.

The structure of ETS-10 is built of strips of five-membered silicon-oxygen rings and two orthogonal sets of titanium-oxygen chains, which differ from each other in their surrounding. The three representative clusters describing ETS-10 were shown in Figure 2.6 [40].

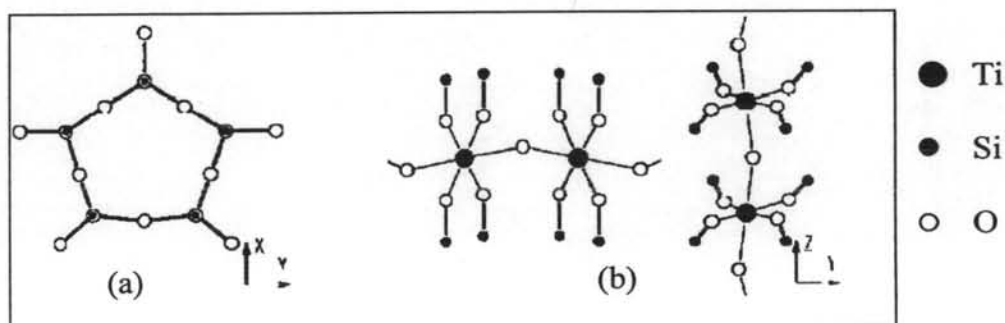


Figure 2.6 Main clusters in ETS-10, a: five-membered ring of SiO_4 tetrahedral; b: two types of dimer of TiO_6 octahedral.

From NMR investigation, Na^+ ions reside in the both 12- and 7-member ring channels in NaETS-10. They are very mobile and weakly bond to framework as counter ions and can be exchanged reversibly without damaging the framework structure. In addition, only extra framework positions which corresponded to general sites in the space group. Two chemical environments of extra-framework sodium cations were measured by solid-state NMR. [41-42].

2.5.2 Properties and application of ETS-10

The ETS-10 structure contains two minus charge per Ti atom. It has the possibility as ion-exchanger and basic catalyst. ETS-10 was used in a number of chemical processes, which mainly exploit the strong basic character of the alkali form for catalyzing such processes as hexane reforming [43], Aldol-type condensation [44] and alcohol dehydrogenation [15]. However, an acid form of ETS-10 obtained by thermolysis of an ammonium-exchanged sample (HETS-10) was shown to be active in the acid-catalyzed in isomerization of but-1-ene [45].

In addition to its unique adsorption or ion exchange property, one of the most striking features of ETS-10 is that the TiO_6 octahedral form linear chains confined atomic $-\text{O}-\text{Ti}-\text{O}-\text{Ti}-\text{O}-$ wires display peculiar optical and electronic properties [46-48]. The well defined mono-atomic $-\text{O}-\text{Ti}-\text{O}-$ chains with band gap energy of 4.03 eV of ETS-10 makes it a promising candidate for photocatalytic applications. Substitution for titanium atom with other elements such as Ag, Co, and Cu can lead to significantly higher photocatalytic activity. The photo-degradation is expected to occur similar to that on TiO_2 .

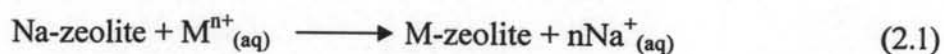
Because of large pore containing structure, ETS-10 has projected as one of the best candidate to replace conventional zeolite to removal of heavy metals in waste water [13].

Two principal methods to create and enhance basicity in zeolite have been proposed and investigated. First one is modification of intrinsic basicity, i.e. the Lewis basicity of the framework oxygen, by either using different framework cation, or exchange of cation that balance the charge of framework. Another method is using of the zeolite as a support for basic species, i.e. the occlusion of metal (alkali) clusters, or small metal hydroxide and/or oxide particles.

2.6 Modification of catalysts

2.6.1 Ion-exchange

The efficiency way of modifying the acidity and basicity of catalyst is ion-exchange. Ion exchange is often an essential procedure in the preparation and/or manufacture of zeolites for use either as sorbents or catalysts. Metal ion and cationic complexes can occupy framework cationic sites of zeolite as shown in equation 2.1.



The interaction is stronger than that on the case of physisorption. This method provides stronger coulombic interaction between species and zeolite anionic framework. These exchange reactions obey the same kinetic laws as the reaction of heterogeneous catalysis. They take place in two consecutive stages, the diffusion of solute to be exchanged at the surface and the ionic exchange itself. When the support is a porous solid, as are most catalyst supports, the diffusion limitations can be extragranular or intragranular.

2.6.2 Impregnation [49-50]

Supported metal catalysts may be prepared by three distinct methods (i) deposition, (ii) co-precipitation and (iii) impregnation. All of these, the last mentioned is the most important. It consists of soaking the carrier with a solution of a suitable metal salt, followed by evaporation to dryness. The supported salt is then either reduced or, in certain case, calcined in air to convert the salt to the oxide which is then reduced to the metal. The main functions of carrier are to provide a structural framework for the catalytic component and increase the surface area per unit weight of metal. Other desirable effects may include such factors as increased stability due to small crystallites of metal being sufficiently separated to prevent sintering and a greater resistance to poisoning. The choice of carrier depends to a large extent upon the purpose for which the catalyst is required.

2.6.2.1 Catalyst supports

The most ubiquitous carrier is alumina. It is inert to most reacting systems, structurally stable to relatively high temperatures and is available in

a variety of form with surface area ranging from less than 1 m²/g up to about 300 m²/g. Silica gel, either in the form of granules or powder, is also a useful carrier and is available with surface area up to about 800 m²/g. Porous carbon is thermally stable to temperature of 1000°C, They have the highest known surface areas of any material up to 1300 m²/g. These “activated” carbons are commonly used as catalyst carriers for organic reactions.

2.6.2.2 Interaction between catalyst and support

Two types of impregnating can be considered, depending on interaction exists between support and the precursors. Impregnation with no interaction was prepared by putting precursor solution in contact with the support, so that by the effect of capillary forces the solution is introduced into the pores of support and distributed there. Theoretically the solute concentration is the same at all points in the pore volume. Wetting process can be done according two methods, depending on the total amount of solution (excess of solution and repeated application of solution). The procedure is followed by drying that cause the precursor to crystallize in the pore and calcining to fix the chemical structure of precursors prior to final activation.

Impregnation with interaction occurs when the solute to be deposited establishes a bond with the surface at the time of wetting. Such interaction results in a near-atomic dispersion of the active species precursors. The interaction can be an ion exchange, an adsorption, or a chemical reaction.

2.7 Characterization of materials

2.7.1 Powder X-ray Diffraction (XRD)

Many different experimental techniques have been utilized to characterize the microporous materials. Often several techniques are used in combination, in order to provide unambiguous structural information. XRD technique provides direct information of the pore architecture of the materials.

Different features of a powder diffraction pattern can be exploited in the characterization of a material (Table 2.3). Powder diffraction data is most commonly used as fingerprint in the identification of a material,

but the other information that can be gleaned from a diffraction pattern should be concerned. The diffraction experiment should be adapted to optimize that feature which provides the information desired.

The main components of XRD instrument are an X-ray source, a specimen holder and a detector, and almost all are capable of recording a respectable powder diffraction pattern.

Table 2.3 Information from powder x-ray diffraction pattern [51]

Feature	Information
Peak positions (2θ values)	Unit cell dimensions
Non-indexable lines	Presence of a crystalline impurity
Systematically absent reflections	Symmetry
Background	Presence (or absence) of amorphous material
Width of peaks	Crystallite (domain) size, stress/strain and stacking faults
Peak intensities	Crystal structure

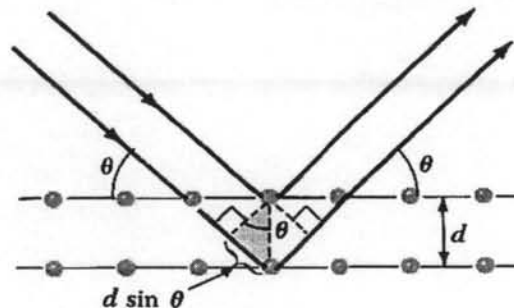


Figure 2.7 Diffraction of X-rays by a crystal.

Figure 2.7 shows a monochromatic beam of X-ray incident on the surface of crystal at angle θ . The scattered intensity can be measured as a function of scattering angle 2θ .

$$n\lambda = 2d \sin\theta \quad (2.2)$$

From the Bragg equation (2.2), d is the distance between equivalent atomic planes, θ is the angle between the incident beam and these planes, n is an integer and λ is the wavelength of X-ray source. Then from XRD results, it is able to determine the interplanar spacing of the sample.

2.7.2 Nitrogen adsorption-desorption technique

A great deal of very useful information is derived from measurement of the physical adsorption of gases on porous solids. The monolayer capacity of nonporous solid, measured by chemisorption, or by physisorption well above the boiling point of the adsorbing gas, can be easily translated into a surface area. The most common adsorbate is probably N_2 at 77 K. Adsorption amount depends on gas pressure, adsorption temperature, and properties of adsorptive gas and adsorbent solid. In nitrogen adsorption isotherm measurement, temperature is constant and gas is limited, thus the isotherm changes according to the property of solid. The surface area of a solid includes both the external surface and the internal surface of the pores. Several forms of isotherm besides the langmuir type have been shown in Figure 2.8. According to the IUPAC definition, microporous materials exhibit a Type I adsorption-desorption isotherm. Nonporous or macroporous exhibit types II, III, and VI and mesoporous exhibits types IV and V.

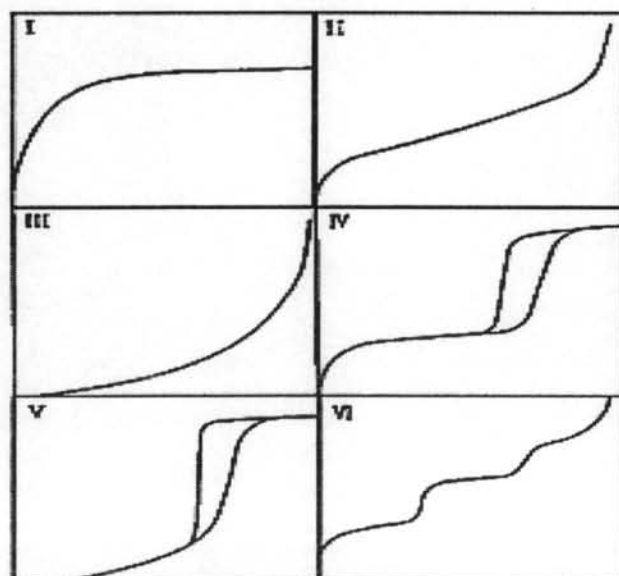


Figure 2.8 The IUPAC classification of adsorption isotherm.

Adsorption isotherms are described as shown in Table 2.4 based on the strength of the interaction between the sample surface and gas adsorbate.

Table 2.4 Features of adsorption isotherms [52]

Type	Features	
	Interaction between sample surface and gas adsorbate	Porosity
I	Relatively strong	Micropores
II	Relatively strong	Nonporous
III	Weak	Nonporous
IV	Relatively strong	Mesopore
V	Weak	Micropores or Mesopore
VI	Relatively strong Sample surface has an even distribution of energy	Nonporous

The t-plot method was invented by Lippens and de Boer. Standard isotherm shows the relationship between relative pressure and thickness of adsorption layer. Specific surface area, a_s (m^2/g) can be calculated from the equation 2.3 with the slope of t-plot, s [53].

$$a_s = \frac{s \times 0.354}{22414} \times L \times \sigma = 1.541 \times s \quad (2.3)$$

Where L is Avogadro constant and σ is cross sectional area of adsorptive. There are 3 different types of t-plot isotherm. If t-plot is a linear curve the original point, and thus the adsorbent is considered to be non-porous material. If t-plot has 2 slopes, the one is a sharp slope passing the original point and the other is more gradual slope, it means that the adsorbent has homogenized sized micropores. And the last isotherm that draws a sharp strength line but become smoother curve from some point, it is considered to have mesopores.

MP method measures distribution from the curvature of t-plot. v_p is an integrated value of pore volume (v_1), which can be obtained from equation 2.4.

$$v_1 = (a_1 - a_2) \times (t_1 + t_2) / 2 \times 10^{-3} \quad (2.4)$$

Although d_{peak} is the peak position it is not suitable for MP method analysis when d_{peak} is below 0.71 nm, due to the same reason for the fact that average pore diameter is not accurate unless 2 or more adsorption layers are formed in pores.

2.7.3 Diffuse Reflectance-ultraviolet spectroscopy (DR-UV)

UV-Vis analysis is commonly associated with liquid. However, the state of the art DR-UV cell allows solid to be analyzed. In generally, DR-UV was used to study of various metal-containing species, coupled with different epoxides in an attempt to obtain information on the effects of temperature and time on their reaction. Theories of diffuse reflectance are compared and applied to experimental results. Expressions are obtained for the Kubelka-Munk constants and the remission function in terms of fundamental optical parameters. The depth of penetration of light into a sample is calculated using the modified particle model theory. It is concluded that most powdered samples of only 1-mm thickness can be regarded as infinitely thick for diffuse reflectance purposes. The Kubelka-Munk equation is expressed as follows:

$$f(R) = \frac{(1 - R^2)}{2R} = \frac{k}{s} \quad (2.5)$$

Where R is the absolute reflectance of the sampled layer, k is the molar absorption coefficient and s is the scattering coefficient.

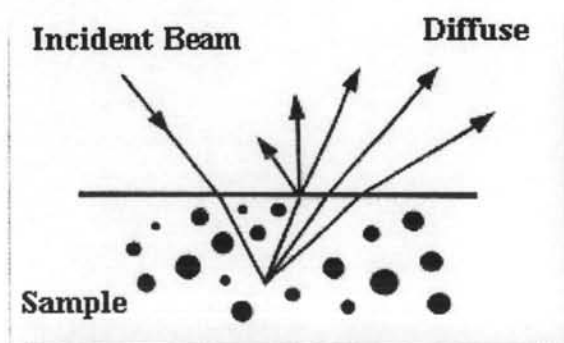


Figure 2.9 Diffuse reflectance beam in the medium system.

2.8 Diesel Oil [54]

Nowadays, the diesel engine is inherently more efficient than its gasoline counterpart. Increasing attention world wide is being paid to chemistry of diesel fuels. This heightened interest is related to both the thermal efficiency and the environmental aspects.

2.8.1 Properties of diesel fuels

The first property is Cetane Number (CN). It is a measurement of ignition quality or ignition delay, and is related to the time required for a liquid fuel to ignite after injection into a compression ignition engine. Two standards, cetane (n-hexadecane) and 1-methylnaphtalene (1-MN) are assigned CN values of 100 and 0, respectively. Heating value is defined as the amount of heat released per unit mass of fuel from its complete combustion. This property is also referred to as calorific value or energy content. Typical heating values for diesel fuels are in the range of 134,000 Btu/gal to 148,000 Btu/gal.

Density is the mass per unit volume of diesel fuel at a given temperature. It has an importance in diesel engine performance, since fuel injection operates on a volume metering system. In the case of viscosity, it is a measure of the internal fluid friction, which tends to oppose any dynamic change in the fluid motion. It is an important property of diesel fuel because of its relevance to the performance of the fuel injection equipment, particularly at low temperatures when the increase in the fluidity of fuel.

Low temperature characteristics of diesel fuel including cloud point that is the temperature at which wax is first precipitated. Usually it is in the range between 10 and -20°C . Whereas pour point is the temperature at which the amount of wax precipitated out of the solution is sufficient to gel the fuel that is generally $5-11^{\circ}\text{C}$ below cloud point. Another important property is sulfur content. It is expressed as weight percentage of sulfur in the fuel. Upon combustion, sulfur is converted to SO_x (SO_2 and SO_3) which poison the catalytic converter and also contributes to acid rain. The maximum value depends on each country.

2.8.2 Composition of diesel fuels

Diesel fuels consist mainly of saturated (paraffins and naphthenes) and aromatic hydrocarbons. Saturated compounds generally are long-chain alkanes with carbon numbers in the range of C_{10} - C_{20} that correspond to boiling point 174°C to 344°C , respectively. Alkylated cycloalkanes are also present in diesel fuels. Decahydronaphthalenes and perhydrophenanthrenes are typical examples of cycloalkanes in diesel fuels. Aromatic components in diesel fuels include alkylated benzene, indanes, naphthalenes, phenanthrenes and pyrenes.

2.8.3 Diesel fuel additives

Additives are chemicals introduced in very small proportions to fuel to improve performance, enhance its desirable characteristics and to reduce the undesirable ones. The first additive is stabilizers. Most stabilizers are antioxidants that act as radical scavengers. Typical stabilizers are alkylated phenols such as 2,6-di-tert-butyl-4-methyl phenol and secondary amines. The second is cold flow improver, it includes ethylene vinyl acetate, polyolefin ester, and polyamides. These types of additives function as wax-anti-settling agents because they can modify the shape of wax crystals, which otherwise are platelets tending to gel together. Another is cetane improvers. They are reactive compounds that can generate free radical and favor auto-ignition. These include mainly alkyl nitrates, nitroso compounds and some peroxides. It is possible to obtain cetane number improvements between 3 and 6 numbers.

Combustion improvers are mainly organic compounds of metal such as barium, calcium, lithium and platinum. Direct combustion improvers function by reacting with water to produce hydroxyl radicals, which enhances combustion of soot.

2.8.4 Alternative diesel fuels

They are developed for securing the supply of future transportation fuels and for cleaner fuel utilization. Alternative fuels for diesel engines include synthetic middle distillates from natural gas, liquefied petroleum gas (LPG), compressed natural gas (CNG), dimethyl ether (DME), biodiesel, and other.

2.9 Natural palm oil [55]

Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. It is the second-most widely produced edible oil, after soybean oil. There are two species of oil palm, the better known one is originating from Guinea, Africa and was first illustrated by Nicholas Jacquin in 1763. Each fruit contains a single seed (the palm kernel) surrounded by a soft oily pulp. Oil is extracted from both the pulp of the fruit (palm oil, edible oil) and the kernel (palm kernel oil, used mainly for soap manufacture). For every 100 kilograms of fruit bunches, typically extract 22 kilograms of palm oil and 1.6 kilograms of palm kernel oil. Palm oil itself is reddish and contains a high amount of carotenoids. It is used as cooking oil, to make margarine and is a component of many processed foods. Both of palm oil and palm kernel oil are high in saturated fatty acids. Saturated fat also found in coconut oil, beef fat, and milk fat is alleged to correlate with an increased incidence of atherosclerosis and coronary heart disease. The oil palm gives its name to the 16 carbon saturated fatty acid palmitic acid found in palm oil; monounsaturated oleic acid is also a constituent of palm oil while palm kernel oil contains mainly lauric acid. Palm oil is the largest natural source of tocotrienol, part of the Vitamin E family. Palm oil and palm kernel oil are one of the few vegetable oils relatively high in saturated fat.

2.9.1 Palm oil components

(a) Major components

Triglycerides form the major component and bulk of the glyceridic material present in palm oil and palm kernel oil with small amount of monoglycerides and diglycerides which are mainly compositions of the extraction process. Triglycerides are esters formed from one glycerol and three fatty acids with hydrogen in all the hydroxyl groups in the glycerol molecule replaced by fatty acid chains via the acid (carboxylic) ends as shown in Figure 2.10.

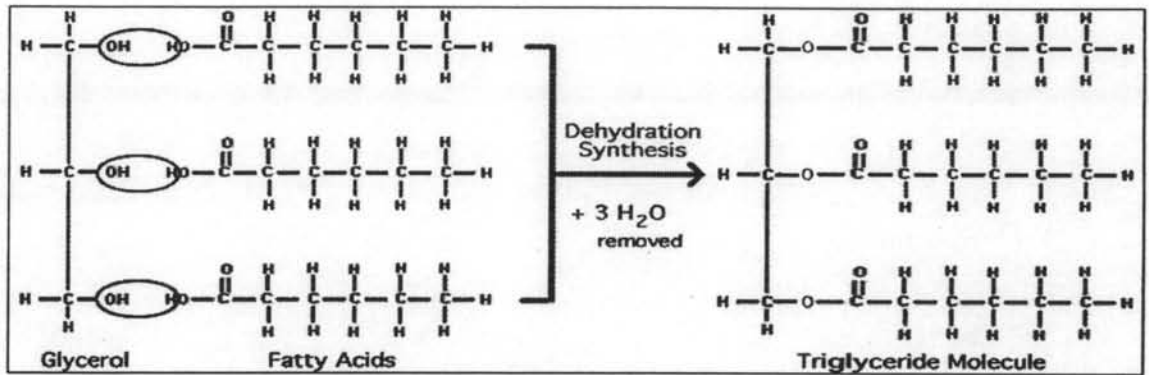


Figure 2.10 Triglycerides formation diagram.

Most fats and oils contain mixed triglycerides, two or even three different fatty acid groups are presented in the molecule. The detailed structure of triglycerides present in palm oil is important because they define some of the physical characteristics of the oil. The melting point of triglycerides is depending on the structures and position of the component acids present. The presence of partial glycerides 1,2-diglycerides, 1,3-diglycerides and trace amount of monoglycerides also affect the crystallization behaviour of the oil.

(b) Minor components

The carotenoids, tocopherols, sterols, phosphatides, triterpenic and aliphatic alcohol form the minor constituents of palm oil. Though the total present in palm oil is less than 1%, nevertheless they play a significant role in the stability and refinability of the oil, in addition to increasing the nutritive value of oil. Crude palm oil contains between 500 to 700 ppm of carotenoids mainly in the forms of α - and β -carotenes, the precursor of Vitamin A. The presence of these carotenoids appears to offer some oxidative protection to the oil by itself being oxidized first prior to the triglycerides. Moreover, crude palm oil also contained tocopherols and tocotrienols in the range of 600 to 1000 ppm and at slightly lower levels in refined palm oil. The combined effects of the properties of carotenoids, tocopherols, tocotrienols and 50% unsaturation of acids confer on palm oil a higher oxidative stability as compared to a lot of vegetable oils.

2.9.2 Physical and Chemical properties of palm oil

(a) Physical properties of palm oil

The apparent density is an important parameter from the commercial point of view since it is used for volume to weight conversions. It can also be used as a purity indicator for palm oil. The solid fat content of oil is a measure (in percentage) of the amount of solid fat present in the oil at any one temperature. It is measured by means of wide-line nuclear magnetic resonance spectroscopy. The solid present in the oil at any one temperature is due to the process of crystallization occurring in the oil as consequence of its chemical properties. The physical properties of palm oil are summarized in Table 2.5 and inherent chemical properties of palm oil are shown in Table 2.6.

Table 2.5 Major physical properties of palm oil

Property	Mean (of 215 samples)	Range
Apparent Density @ 50°C (g/ml)	0.889	0.888-0.889
Refractive Index @ 50°C	1.455	1.455-1.456
Solid Fat Content		
10°C	49.6	40.0-55.2
15°C	34.7	27.2-39.7
20°C	22.5	14.7-27.9
25°C	13.5	6.5-18.5
30°C	9.2	4.5-14.1
35°C	6.6	1.8-11.7
40°C	4	0.0-7.5
45°C	0.7	0.0-4.5
Slip melting point (°C)	34.2	31.1-37.6

(b) Inherent chemical properties of palm oil**Table 2.6** Inherent chemical properties of palm oil

Chemical characteristics	Mean	Range
Saponification value (mg KOH/g oil)	195.7	190.1-201.7
Unsaponifiable matter (%)	0.51	0.15-0.99
Iodine value (Wijs)	52.9	50.6-55.1

2.9.3 Fatty acids composition of palm oil

The fatty acids of palm oil could be of the same type or different. The property of a triglyceride will depend on the different fatty acids that combine to form the triglyceride. The fatty acids themselves are different depending on their chain length and degree of saturation. The short chain fatty acids are of lower melting point and are more soluble in water. Whereas, the longer chain fatty acids have higher melting points. The melting point is also dependent on degree of non-saturation. Unsaturated acids will have a lower melting point compared to saturated fatty acids of similar chain length. The two most predominant fatty acids in palm oil are C16:0 (saturated) palmitic acid and C18:1 (unsaturated) oleic acid. Typical fatty acid composition of palm oil is given in Table 2.7.

Table 2.7 Typical fatty acid composition of palm oil

C. No.: DB	Fatty acid	%Weight
C12:0	Lauric acid	0.2
C14:0	Myristic acid	1.1
C16:0	Palmitic acid	44.0
C18:0	Stearic acid	4.5
C18:1	Oleic acid	39.2
C18:2	Linoleic acid	10.1
C18:3	Linolenic acid	0.4
C20:0	Arachidic acid	0.4

C: carbon, DB: double bond

2.10 The production of biodiesel [56]

2.10.1 Direct use and blending

In 1980, Bartholomew addressed the concept of using food for fuel. It was not practical to substitute 100% vegetable oil for diesel fuel. But a blend of 20% vegetable oil and 80% diesel fuel was successful. Mixture of degummed soybean oil and No. 2 diesel fuel in the ratio of 1:2 and 1:1 were tested for engine performance, the results indicated that 1:2 blend should be suitable as a fuel for agricultural. Two problems associated with the use of vegetable oil as fuels were oil deterioration and incomplete combustion.

2.10.2 Thermal cracking (pyrolysis)

To solve the problem of high viscosity of vegetable oils, the pyrolysis was chosen to produce the biodiesel. The pyrolysed material can be vegetable oils, animal fat, natural fatty acids and methyl ester of fatty acids. A large scale of thermal cracking of tung oil calcium soaps was reported. Tung oil was first saponified with lime and then thermally cracked to yield a crude oil, which was refined to produce diesel fuel. Soybean oil was thermally decomposed and distilled in air and nitrogen sparged with a standard ASTM distillation apparatus. Moreover, Rapeseed oil was pyrolysed to produce a mixture of methyl esters in the tubular reactor between 500 and 850°C in nitrogen. The mechanism of thermal decomposition of triglycerides was shown in Figure 2.11.

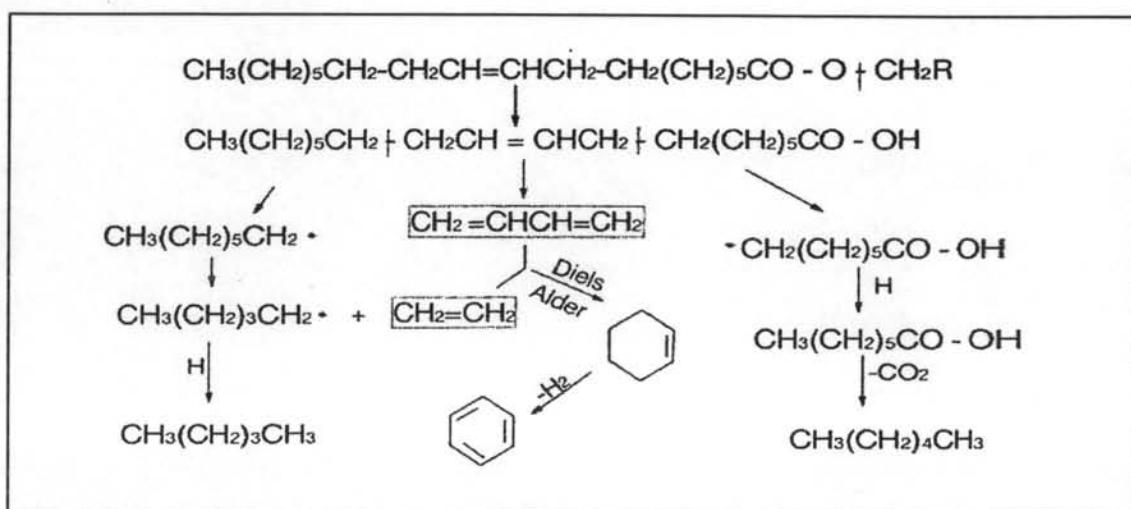


Figure 2.11 The mechanism of thermal decomposition of triglycerides.

2.10.3 Transesterification (Alcoholysis) [56]

Transesterification or alcoholysis is the displacement of alcohol from ester by another in a process similar to hydrolysis, except than alcohol is used instead of water. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used in shifting the equilibrium to the product side. The reaction can be catalyzed by alkali, acid or enzyme such as NaOH, KOH, H₂SO₄ and lipase, respectively. The transesterification reaction diagram of triglycerides is presented in the Figure 2.12.

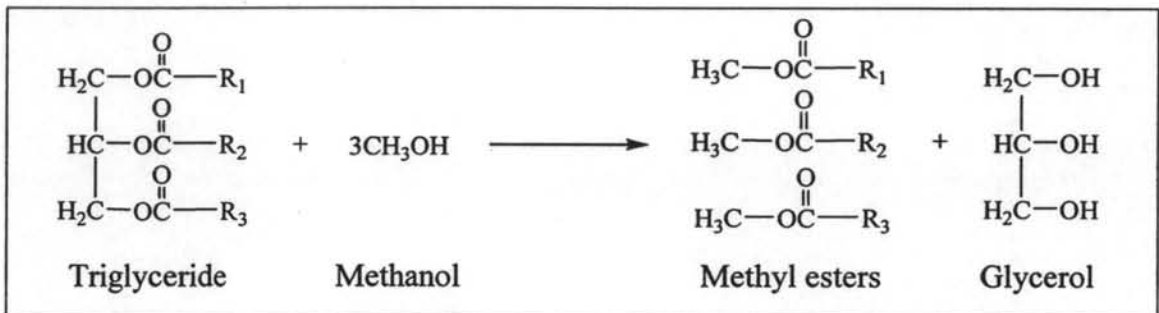


Figure 2.12 Typical transesterification diagram of triglycerides.

2.10.3.1 Transesterification kinetics and mechanism [57]

Transesterification of triglycerides (TGs) with alcohol proceeds via three consecutive and reversible reactions where the FFA ligands combine with alcohol to produce a fatty acid alkyl ester, diglyceride and monoglyceride intermediates, and finally glycerol by-product. The stoichiometric reaction requires 1 moles of TG and 3 mole of methanol to produce 3 mole of linear ester and 1 mole of glycerol. In presence of excess alcohol, the forward reaction is pseudo-first order and the reverse reaction is found to be second-order. It was observed that transesterification is faster when catalyzed by alkali. The mechanism of acid and alkali-catalyzed transesterification is described in Figures 2.13 and 2.14, respectively.

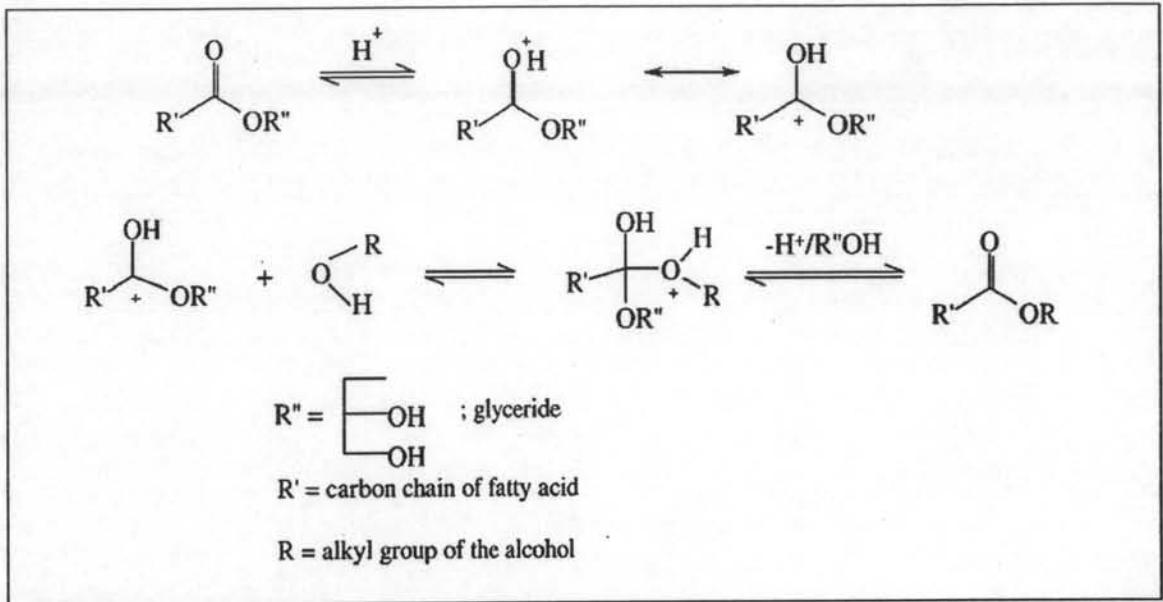


Figure 2.13 Mechanism of acid catalyzed transesterification reaction.

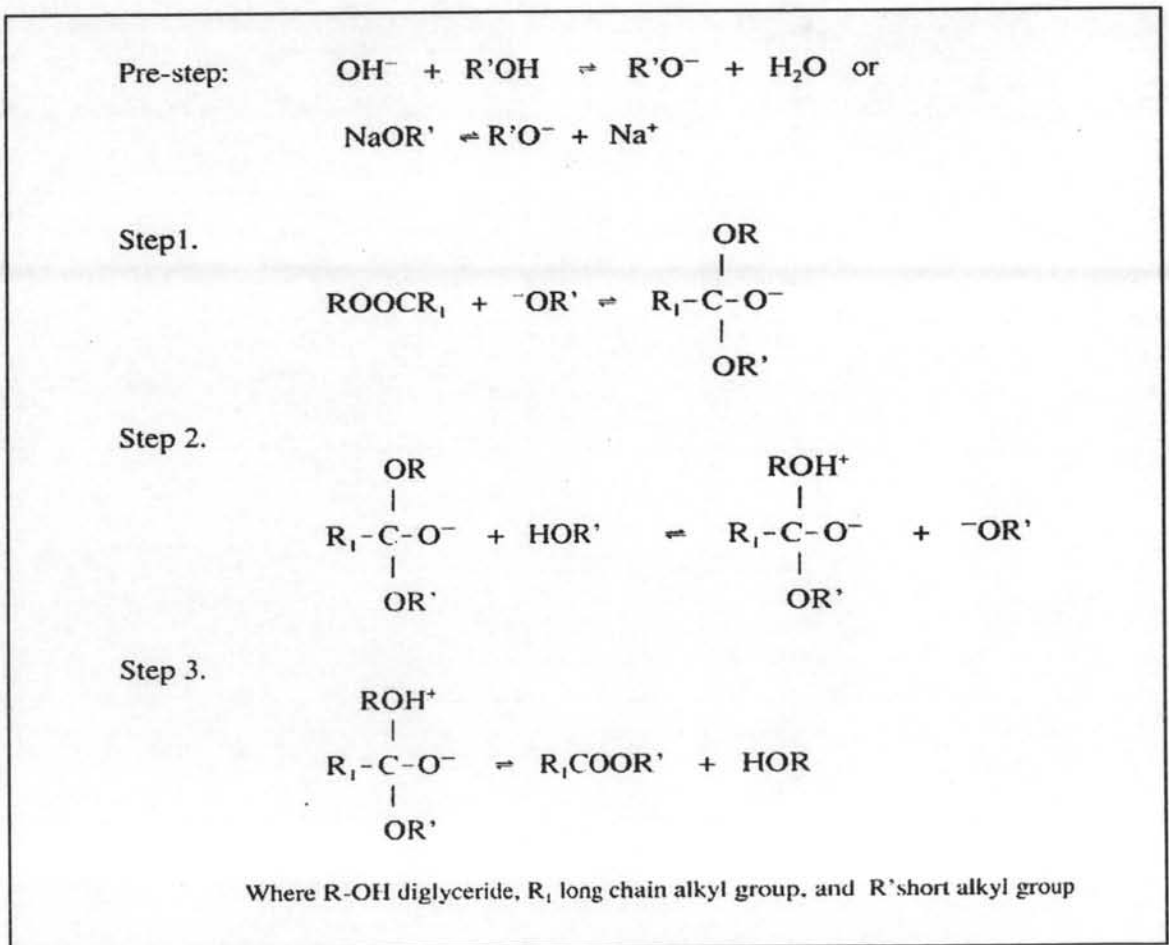


Figure 2.14 Mechanism of base catalyzed transesterification reaction.

2.10.3.2 Transesterification parameters [56, 58]

The most relevant variables that influence the transesterification reactions are the following

(a) Moisture and free fatty acid

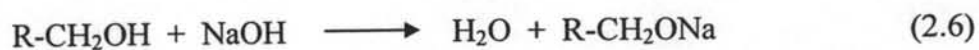
The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency.

(b) Molar ratio of alcohol to oil

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The molar ratio is associated with the type of catalyst used. Methanol present in amounts of above 1.75 equivalents tended to prevent the gravity separation of glycerol, thus adding more cost to the process. Higher molar ratios result in greater ester conversion in a shorter time.

(c) Catalyst type and concentration

Catalysts in transesterification reaction are classified as alkali, acid, or enzyme. Alkali-catalyzed reaction is more efficient and less corrosive than acid-catalyzed. Alkali catalysts include sodium hydroxide (NaOH), sodium methoxide (NaOMe), potassium hydroxide (KOH), and sodium hydride (NaH). Methoxide compound was more effective than hydroxide compound because of the assumption that a small molecule of water was produced upon mixing NaOH and MeOH.



In the case of acid catalyst, it is suitable if the glycerides contain high free fatty acid content and more water. The acids could be sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), hydrochloric acid (HCl) or organic sulfuric acid. This type of catalyst gives high yield of esters but the reaction is very slow, requiring almost always more than one day in finishing.

Lipase is enzymes that can be used as catalyst for transesterification and esterification reactions. It has many advantages such as possibility to regeneration and reuse and high thermal stability, but it also has some disadvantages include lose some activity, support enzymes is not uniform and more expensive.

(d) Reaction time

The conversion rate increases with reaction time. The di- and monoglycerides increased at the beginning and then decreased. At the end, the amount of monoglycerides was higher than that of diglycerides.

(e) Reaction temperature

Transesterification can occur at different temperature, depending on the oil used and catalyst types. Temperature clearly influenced the reaction rate and yield of esters.