

CHAPTER II

THEORY AND LITERATURE REVIEW

Castor oil is also known as Ricinus oil, oil of Palmas Christi, tangantangan oil and Nealoid, which derived from the bean of the castor plant. Its exceptional chemical and physical characteristics which relate to its uniquely high content of an unsaturated hydroxy fatty acid, *cis*-9,12-hydroxy octadecenoic acid, commonly known as ricinoleic acid [3]. Methyl ricinoleate is a methyl ester of ricinoleic acid that can be prepared by the transesterification of castor oil with methanol under acid and basic conditions.

2.1 Fatty acids composition of castor oil

The composition of fatty acid in castor oil derived from analysis of the methyl ester of castor oil fatty acid with gas chromatographic method is given in Table 2.4 [4].

The structure of the glycerides of castor oil has been ascertained with approximately 68 % tri-ricinolein, 28 % di-ricinolein, 3 % mono-ricinolein and 1 % ricinoleic acid [5]. The fatty acid compositions of castor oil were shown in Table 2.1.

Table 2.1 Fatty acid compositions of castor oil [4]

Fatty Acid	Percentage
Palmitic acid	0.9 to 1.2
Stearic acid	0.7 to 1.2
Oleic acid	1.1 To 3.3
Linoleic acid	1.2 To 3.7
Linolenic acid	0.2
Ricinoleic acid	89.0 to 89.4
Dihydroxy stearic acid	1.3 to 1.4

2.2 Characteristic of methyl ricinoleate [6-8]

Castor oil is a material with a diversity of uses shared by no other natural fat. It is unique not only in carrying overwhelmingly a single fatty acid but in that this acid is very special one. Ricinoleic acid has an 18-carbon backbone, with a hydroxyl group on the 12-carbon atom and a *cis* double bond between carbon 9 and 10 whose structure is shown in Figure 2.1.

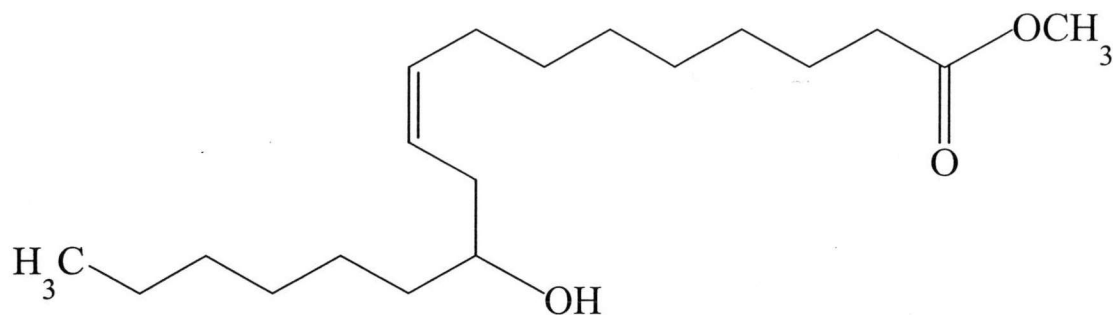
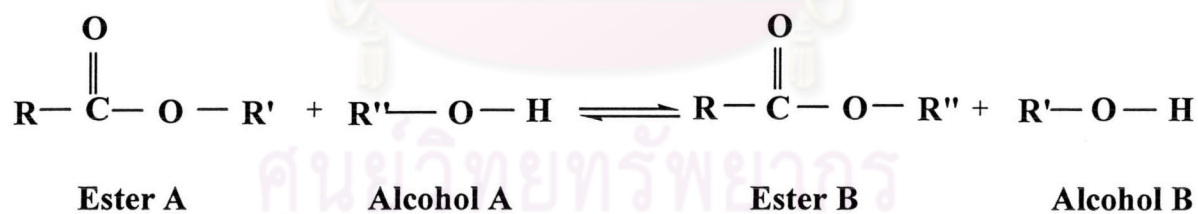


Figure 2.1 Structure of methyl ricinoate

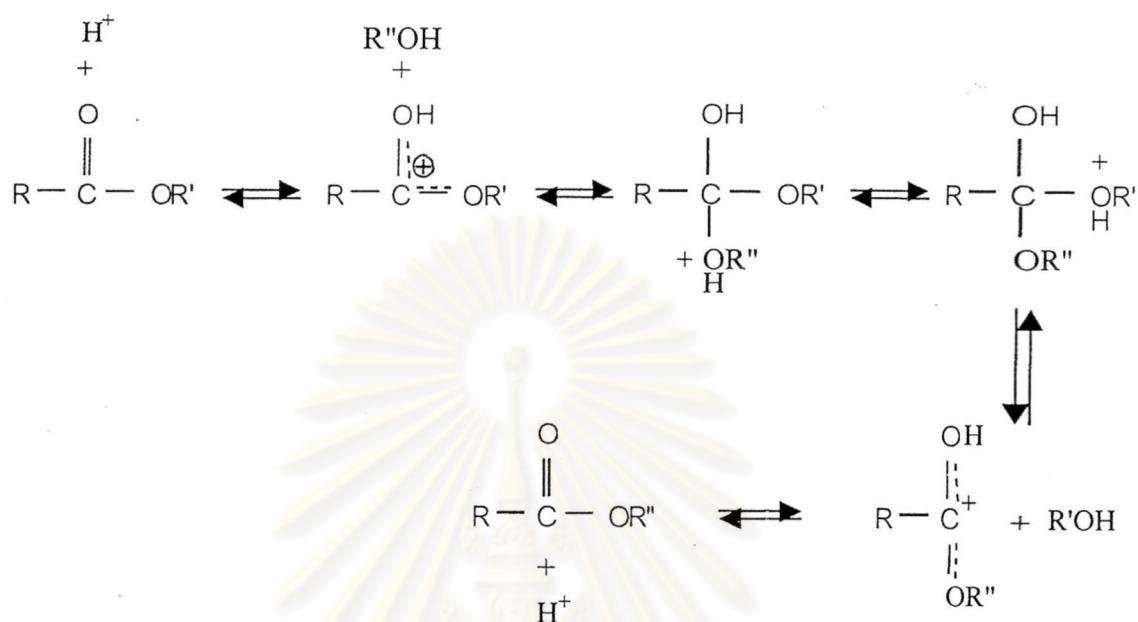
Methyl ricinoate is the methyl ester of ricinoic acid that can be prepared by transesterification of castor oil, which is catalyzed by acid (H_2SO_4 or dry HCl) or base (usually alkoxide ion) catalyst (Scheme I).

Scheme I

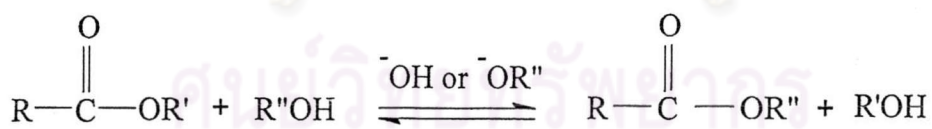


The mechanisms are shown in Scheme II for acid catalyst and in Scheme III for basic catalyst.

Scheme II. The mechanisms of transesterification of castor oil using acid catalyst.



Scheme III. The mechanisms of transesterification of castor oil using basic catalyst.



Transesterification is an equilibrium reaction. To shift the equilibrium to the right, it is necessary to use a large excess of alcohol whose ester we wish to make, or else to remove one of the products from the reaction mixture. The second approach is the better one when feasible, since in this way the reaction can be driven to completion.

Table 2.2 Characteristics of methyl ricinoleate

Properties	Value
Specific gravity (25 °C)	0.925
Refractive index n_D^{20}	1.4628
Saponification value	173 to 178
Iodine value	83 to 85
Hydroxyl value	minimum 160
Viscosity (Stokees @ 25 °C)	0.3 poise
Boiling point	245 °C

2.3 Chemical reaction of methyl ricinoleate

The chemical reaction of fats and fatty acids are important because they are employed in the manufacture of commercial products. Fats and fatty acids are organic chemicals and thus are subject to the numerous reactions available to the synthetic organic chemist. Because of the hydroxyl groups, double bond and ester linkages in methyl ricinoleate provide similarly reaction sites for the preparation of many useful derivatives as castor oil used. Chemical reactions commercially used to create important castor oil derivatives are shown in Table 2.3 [9].

Table 2.3 Chemical reactions of methyl ricinoleate

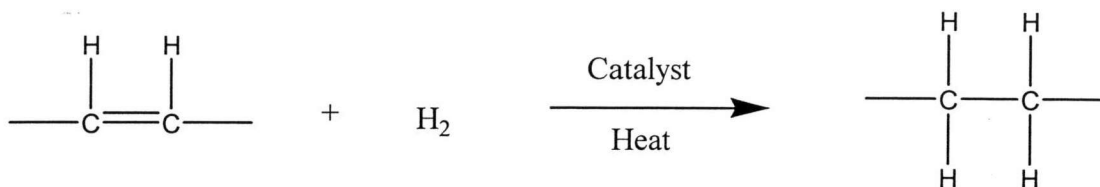
Part of structure	Nature of reaction	Type of products
Ester linkage	<ol style="list-style-type: none"> 1. Hydrolysis 2. Esterification 3. Alcoholysis 4. Reduction 5. Saponification 6. Halogenation 7. Amidation 	<p>Fatty acids , glycerol</p> <p>Esters</p> <p>Mono and diglycerides, monoglycols, etc.</p> <p>Alcohols</p> <p>Soluble soaps</p> <p>Insoluble soaps</p> <p>Fatty acid halogens</p> <p>Amine salts</p> <p>Amides</p>
Double bond	<ol style="list-style-type: none"> 1. Oxidative Polymerization 2. Hydrogenation 3. Epoxydation 4. Halogenation 5. Addition reaction 6. Sulfonation 	<p>Polymerized oils</p> <p>Hydroxystearates</p> <p>Epoxidized oils</p> <p>Halogenated oils</p> <p>Polymerized oils</p> <p>Sulfonated oils</p>

Part of structure	Nature of reaction	Type of products
Hydroxyl group	<ol style="list-style-type: none"> 1. Dehydration 2. Caustic fusion 3. Pyrolysis 4. Halogenation 5. Alkoxylation 6. Esterification 4. Amination 5. Sulfation 9. Urethane reaction 	Dehydrate castor oils Sebacic acid Copryl alcohol Undecylenic acid Heptaldehyde Halogenated castor oils Alkoxyated castor oils Alkyl castor oils 12-amino oleate Sulfated castor oil (Turkey red oil) Polymers

2.4 Hydrogenation [10-13]

Hydrogenation of the ethylenic linkages in glyceride oils to produce products, which improved properties, is one of the major processes in the fat and oil industry. There are two reasons to hydrogenate oil. First, since the number of double bond is reduced, the opportunity for oxidation is decreased, and thus the flavor stability is increased. Second, the physical characteristics are changed such as the melting point is raised. The reaction consists of the direct addition of hydrogen at double bond in the fatty acid chain, according to the following Scheme IV.

Scheme IV



The reaction requires a catalyst, which employed in commercial hydrogenation invariably consists basically of nickel. The greatest amount of hydrogenation is carried out with catalysts composed of the metal or metals in a finely divided form, prepared by special methods and often supported on a highly porous, inert, refractory material, such as diatomaceous earth.

In the hydrogenation process, gaseous hydrogen, liquid oil, and the solid catalyst must be brought together at a suitable temperature. In ordinary practice it may be assumed that the hydrogen is first caused to dissolve in the oil, and the hydrogen-laden oil is then brought into contact with the catalyst by mechanical mean. The rate at which hydrogenation proceeds under the conditions outlined above depends upon the temperature, the nature of oil, the activity of catalyst, the concentration of catalyst, and the rate at which hydrogen and unsaturated oil molecules are supplied together to the active catalyst surface.

When the vegetable oils are hydrogenated, at least three different types of reduction can occur. The first type is the reduction of carbon-carbon double bonds in the fatty acid chains which results in the reduction of the iodine value (I.V.). In all cases, isomerization accompanies the type of hydrogenation being considered, therefore, any discussion of the mechanism must explain both. During reduction of the I.V., the color and odor of the triglycerides are improved, indicating that at least

some of trace quantity materials are being hydrogenated. These materials contain carbonyl, quinone-type, and etc. structures. The mechanism for this second type of hydrogenation is not well understood, partly because of the large and probably variable number of trace materials present in the oil or fat. The third type of hydrogenation that is possible for oils or fats involves the production of fatty alcohols and glycerin (This type of reduction is sometimes called hydrogenolysis).

2.5 Catalyst and catalysis [14-17]

2.5.1 Definition of catalyst

A catalyst, according to the classical definition of Ostwald, is a substance that alters the rate of a chemical reaction without affecting the energy factor of the reaction or being consumed in the reaction. Properly speaking, therefore, a catalyst cannot initiate but can only accelerate a reaction. In numerous instances, however, including the hydrogenation of fats and oils, the reaction rate is so imperceptibly slow in the absence of a catalyst that the latter must be considered an essential element of the reacting system.

The fact that a catalyst cannot initiate a reaction does not mean that its introduction into a reacting system may not influence the composition of the reaction products or that different catalysts may not yield different products. In many cases, reaction follows a number of alternative courses. Hence, the composition of the final products will depend on the relative rate of the various alternative reactions. Where a number accelerate some of them to a far greater extent than others.

Catalysts increase the reaction rate through their influence on the activation energy. A catalyst breaks the reaction up into two successive steps: the combination of catalyst and reactants to form an unstable intermediate compound, and the

breakdown of this compound to yield a new product and the free catalyst. This has the effect of permitting the energy barrier to be surmounted in two small steps, rather than one large one (Figure 2.2). In other words, two reactions with relatively low activation energies are substituted for a single reaction with high activation energy.

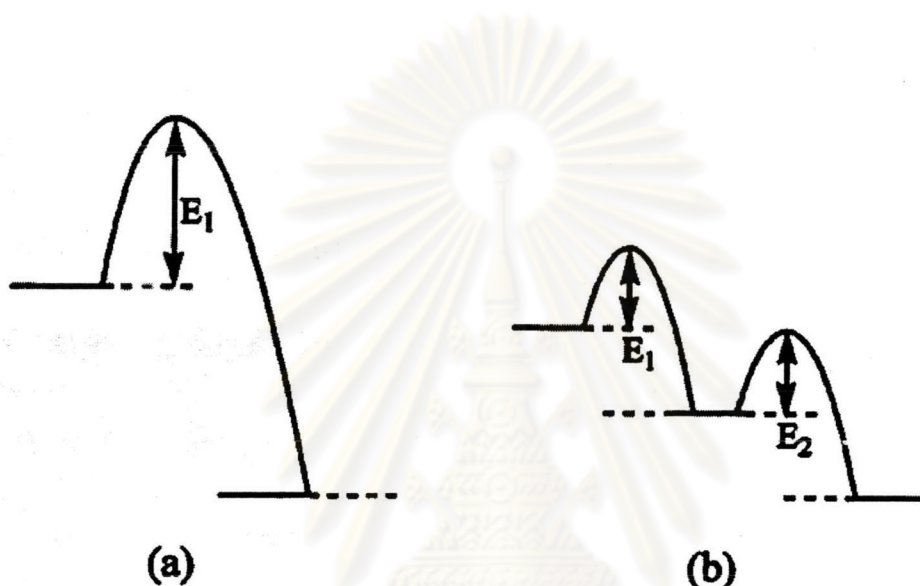


Figure 2.2 Graphical representation of the activation energy factor in (a) uncatalyzed and (b) catalyzed reaction

2.5.2 Classification of catalysts

The numerous catalysts known today can be classified according to various criteria: structure, composition, area of application, or state of aggregation. Here the catalysts shall be classified according to the state of aggregation in which they act. There are two large groups: heterogeneous catalysts (solid-state catalysts) and homogeneous catalysts. There are also intermediate forms such as homogeneous

catalysts attached to solids (supported catalysts), also known as immobilized catalyst. The well-known biocatalysts (enzymes) also belong to this class.

In supported catalysts the catalytically active substance is applied to a support material that has a large surface area and is usually porous. By far the important catalysts are the heterogeneous catalysts.

Whereas for heterogeneous catalysis, phase boundaries are always present between the catalyst and the reactant, in homogeneous catalysis, catalyst, starting material, and products are present in the same phase. Homogeneous catalysts have a higher degree of dispersion than heterogeneous catalysts since in theory each individual atom can be catalytically active. In heterogeneous catalysts only the surface atoms are active.

2.5.3 Catalytic activity

The activity of a catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. The rate may be expressed in any of several ways. The performance of an industrial reactor is frequently given in terms of a space-time yield (STY), which is the quantity of product formed per unit time per unit volume of reactor.

2.5.4 Heterogeneous catalysis

The type of catalysis that operates the fat hydrogenation is the heterogeneous catalysis. By definition, a heterogeneous system is one in which catalyst and the reactant exist in different physical states. Heterogeneous catalysis is to be somewhat sharply distinguished from homogeneous catalysis, in which the catalyst and the reactants comprise a single phase. In homogeneous catalysis the catalyst functions in

the form of individual molecules, which uniformly distributed through the reaction system. Thus the question of catalyst structure or of surface phenomena does not enter. On the other hand, in heterogeneous catalysis it is the question surface, which performs the catalytic function; hence the nature of the surface is of extreme importance. A catalyst operating in a homogeneous system is defined simply in terms of its chemical constitution and its concentration in the system. With all other factors controlled, the effect of a homogeneous catalyst of definite composition is exactly predictable upon the basis of its concentration. If the catalyst is the solid, however, its behavior will depend on not only both the nature and extent of its surface. The fact that the submicroscopic character of its surface determines the characteristics of a solid catalyst renders the study and control of such catalysts very difficult. Apparently similar catalysts may differ enormously in their activity and specific action.

In the catalytic heterogeneous reaction, Figure 2.3, there is a reaction occurring between fluid and porous solid catalysis. In order for the reaction to occur, the reactants in the fluid must first be transported to the outer surface of solid, and they must diffuse through the pores of the solid to the catalytic active site. At least one of the reactant species must usually be chemisorbed onto the surface of the solid. Subsequently, the reaction occurs among chemisorbed species between a chemisorbed species and another species that is either physically adsorbed or that collides with the chemisorbed species directly from the liquid phase. After the reaction, products are desorbed and diffused out through the pores *via* various steps, which respond in a different way to experimental variable such as pressure, temperature. For bulk-fluid velocity, and the chemical and physical structures of the catalyst, it is convenient to classify them as follows:

1. External mass transfer of reactants from the bulk fluid to the external surface of the catalyst particle.
2. Internal diffusion of reactants to active sites within the particle.
3. Adsorption of reactants on active sites.
4. Surface reaction.
5. Desorption of products.
6. Internal diffusion of products to surface of particle.
7. External mass transfer of products to bulk fluid.

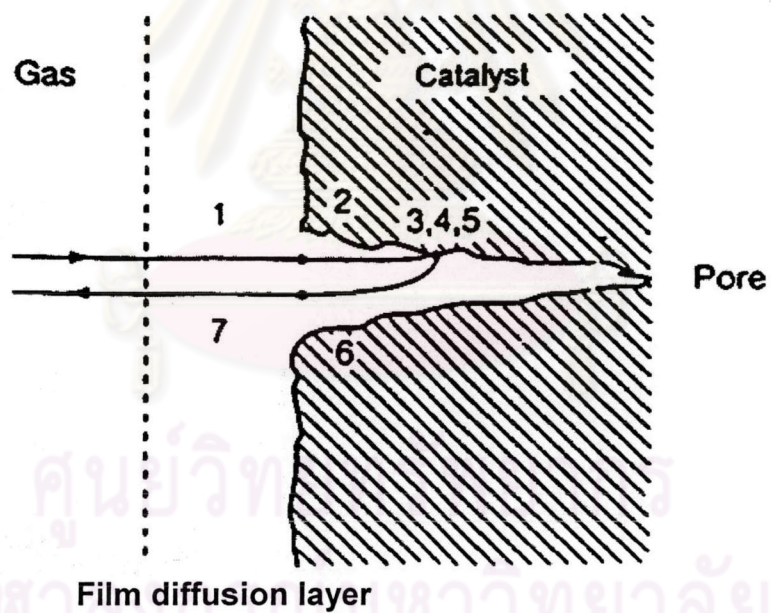


Figure 2.3 Individual steps of a heterogeneously catalyzed gas-phase reaction.

2.5.5 Preparation of heterogeneous catalysts [14,18]

Preparation of the catalyst is a very important step in the study of heterogeneous catalysts. Heterogeneous catalysts are necessary to keep the properties of high reactivity, stability, and prevention of side reactions. These properties depend on the preparation technique. In the past, preparation of catalyst was an art. Properties of the catalyst may not be the same in each batch of preparation even if the same technique is used. It is according to the difficulty in the control of the reaction condition. Testing instruments of catalyst give reproducibility of reaction.

There are many catalyst preparation techniques used in industry. Each catalyst has some selectivity on the preparation method. The most popular technique is impregnation.

Impregnation is the most popular and the easiest technique. A support, such as alumina, was added into metal salt solution such as nitrate salt. After dispersion of the metal salt in order to equilibrium, heating is applied to convert metal salt on the surface of support to metal oxide.

Impregnation can be done by two techniques.

1. Wet Impregnation

The support was added into an excess amount of metal salt solution. The amount of metal salt can be calculated from the different amount of metal salt in solution before and after the impregnation process. This process is too complicated and inconvenient to carry out in the laboratory.

2. Dry Impregnation

This is the most convenient technique for laboratory scale work. In this technique, it is necessary to prepare the solution, which the amount of metal salt is equal to the surface of support.

Dry impregnated catalysts became commercially available for use in the hydrogenation reaction. Their combination of performance characteristics (i.e., good activity, excellent selectivity, and superior filterability compared with impregnation catalysts) made them attractive to edible oil hydrogenators. They currently constitute essentially 100% of commercial catalysts consumed worldwide in the edible oil industry. In this experiment, dry impregnation was used for preparing catalysts because this method is a convenient technique and easy to work in laboratory.

These catalysts are generally used today because they have proven to be highly selectivity, easy to regenerate, and resistant to poison.

2.5.6 Supported catalysts [19]

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

The main function of the catalyst support is to increase the surface area of the active component. Catalytic activity generally increases with increasing catalyst surface area, but a linear relationship cannot be expected since the reaction rate is

often strongly dependent on the structure of the catalyst surface. However, in many reactions, the selectivity decreases when the catalytic surface is enlarged. The choice of the appropriate catalyst support for a particular active component is important because in many reactions the support can significantly influence the reaction rate and the course of the reaction. The nature of the reaction system largely determines the type of catalyst support. Typical catalyst supports are porous solids such as alumina oxides, silica gel, MgO, TiO₂, ZrO₂, aluminosilicates, zeolites, activated carbon, and ceramics.

The term alumina is used to describe various hydrated and anhydrous aluminum oxides. Most commercially available aluminas are prepared from the mineral bauxite (a mixture of hydrated aluminas and several non-alumina impurities) and are available at > 99% purity. Thermally stable high-surface-area forms of alumina can be prepared, with acidic or basic surfaces. These may be used as acid or base catalysts or supports for other catalytic materials.

Alumina (Al₂O₃), the acidic component in a dual function catalyst, exists in several distinct forms: the gamma form or the alpha form, depending on the method of preparation and subsequent treatment. Activated aluminas are amphoteric, containing either acidic or basic sites of various strength. As shown in Figure 2.4, if γ -alumina is heated above 800 K, the residual water is driven off to generate a catalytically inactive form known as α -alumina. Activated alumina is often used as supports, where they provide a large surface area on which catalysts (metal) can be highly dispersed.

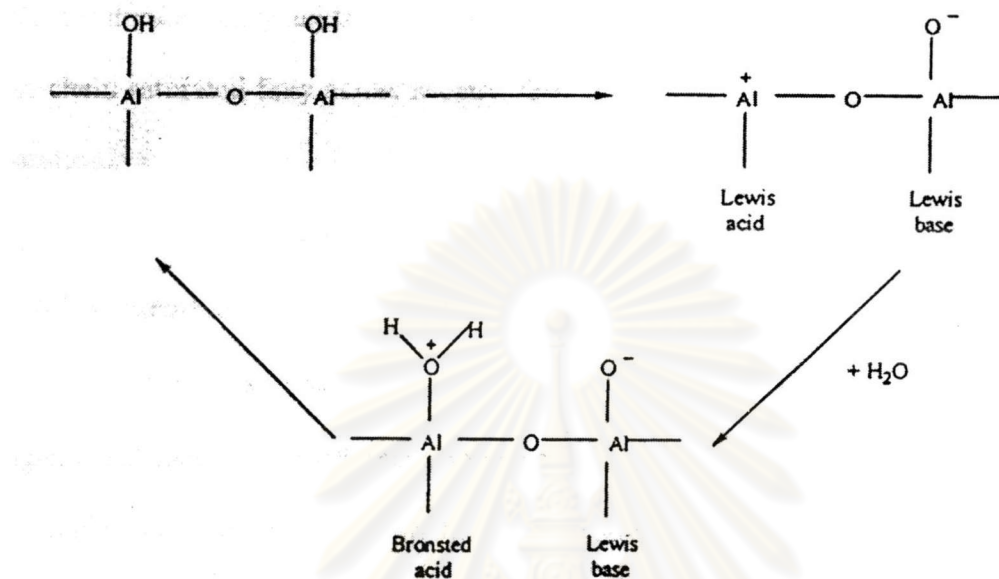


Figure 2.4 Acidic and basic sites on alumina

2.6 Reactors [20]

There are two main types of reactor used for carrying out continuous reactions in the liquid phase, tubular reactor, and stirred flow reactor (Figure 2.5)

จุฬาลงกรณ์มหาวิทยาลัย

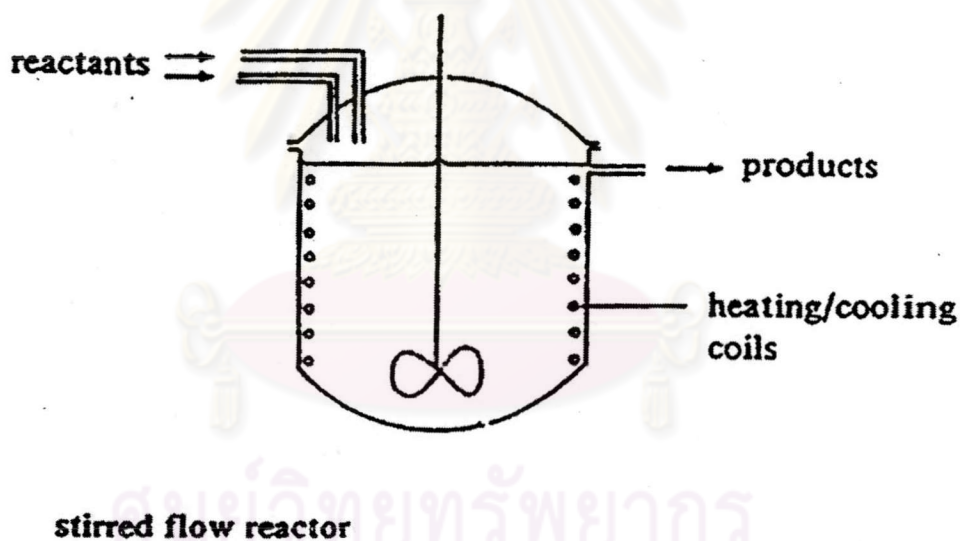
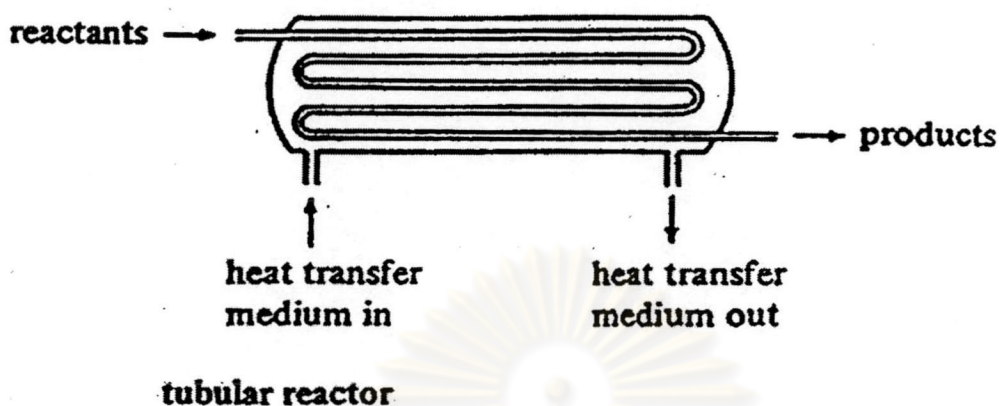


Figure 2.5 Reactors for continuous processing in the liquid phase

Tubular reactors consist, as the name implies, of a tube, or tubes, through which the reactions mixtures flows. Usually, provision is made for the addition or removal of heat transfer medium circulating round the tubes.

Stirred flow reactors consist of a vessel with an agitator and provision for continuously adding reactants and removing products. Heat transfer may be provided for by a variety of means, e.g. by a jacket, or by coils immersed in the reaction mix turns.

2.7 Literature reviews

The product from the hydrogenation of methyl ricinoleate is methyl 12-hydroxystearate. Only a few articles on this reaction appear in the literature. Most of the researches in this area were concentrated on the hydrogenation of castor oil.

Daopiset, S[21] studied the hydrogenation of methyl ricinoleate under varying reaction condition using nickel catalyst. The suitable operating condition was found to be; temperature 150 °C, hydrogen pressure 150 psig, agitation speed 800 rpm, hydrogenation time 2 hours and concentration of catalyst 0.07 % w/w (catalyst /oil). The resulting methyl ester wax had an iodine value of 2.72, a hydroxyl value of 163.12, an acid value of 1.47, and melting point 48.5 °C.

Vangmanerat, B[22] studied hydrogenation of castor oil under various reaction conditions using nickel catalyst. The optimum condition was found to be; temperature 140 °C, hydrogen pressure 150 psig, concentration of catalyst 0.2 % w/w (catalyst /oil), agitation 800 rpm, and hydrogenation period 2 hours. The resulting castor wax had an iodine value of 4.68, a hydroxyl value of 139.11, an acid value of 0.99, and melting point at 84 °C.

Paquot and Richet [23] found that the preferred conditions for total hydrogenation of castor oil without dehydroxylation were hydrogen pressure at 100-150 psig and 100-110 °C or at 50 psig and 150 °C. However, at 230-240 °C the dehydroxylation occurred. Gupta and Aggarwal [24] found that in the process of hydrogenation of castor oil with 2 % Ruffert nickel catalyst, at low temperature (150-160 °C) and high pressure (200 lb/sq.in.) the reduction of the OH group was retarded, but at high temperature (250 °C) and low pressure (70-75 lb/sq.in.) almost complete dehydroxylation occurred.

Srivasan *et al*[25] studied the hydrogenation of castor oil and methyl ricinoleate at atmospheric pressure using Raney catalyst and 20 % dry-reduced nickel catalyst, which was prepared by precipitating NiCO₃ in the presence of "Hyflo-super-cell" (Celite), in amounts of 0.1 and 1.0 % at temperature from 80-240 °C. They found that products with low hydroxyl value were obtained at higher temperature, whereas at low temperature simple hydrogenation of ricinoleic acid molecule took place. They obtained products rich in hydroxyl group by hydrogenation of castor oil in the presence of a solvent (ethyl alcohol), at room temperature and hydrogen pressure 40 psig.

Van Loon [26] using 3 % reduced nickel from nickel keiselguhr catalyst, and found that at 5-120 atm. of hydrogen pressure and temperature below 200 °C, all the unsaturation of castor oil and only 15-20 % of the hydroxyl groups were removed. Above 200 °C, the rate of hydroxyl reduction was increased.

Hladik and Zajic [27] studied the hydrogenation of castor oil at atmospheric pressure and low temperature (120-180 °C) in the presence of nickel catalysts and found that the optimal hydrogenation was achieved with 0.5 % nickel catalyst at 150 °C.

Kaczanowski and Jakabowski [28] investigated the hydrogenation of the castor oil at 1.2 atm., 150 °C, and using nickel catalyst. After a 5-hour passage of H₂ at a rate of 2 l/min, the product had iodine value 14.1 saponification value 184.8, acid value 2.28, hydroxyl value 13.3 and melting point 79.8 °C.

Hector [29] studied process for the catalytic hydrogenation of castor oil using nickel on alumina support catalysts under 50-100 atmospheres and temperature between 150-180 °C. The optimum temperature and pressure were 175 °C and 100 atmospheres respectively. The iodine value of products was lowered from 84 to less than 4 and the hydroxyl value had remained unchanged 5.2.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย