CHAPTER III

THEORETICAL CONSIDERATIONS

As this study concerns field of catalysis this chapter is devoted to the basic theories on catalysis. This is shown in part 3.1 and 3.2 of this chapter. The catalyst selected to be studied is a Raney nickel, which has long been known and commercially used in hydrogenation processes. It was widely used because of ease of preparation. Details of this nickel catalyst are presented in part 3.3.

In experiment, the palladium will be incorporated into Raney nickel catalyst to study its effect on activity and selectivity. Palladium, in this case, is thought to be a promoter, the concept of which will be presented in part 3.4.

Castor oil, derived from the beans of the castor plant passing through hydraulic presses or expellers (continuous mechanical screw-presses) followed by solvent extraction, is used for testing activity and selectivity of catal-ysts in hydrogenation reaction. It has unique characteristic of containing on its molecule one double bond, a hydroxyl group, which distinguishes it from other vegetable oils. The chemistry of castor oil will be described in part 3.5. In part 3.6, the theory of hydrogenation of castor oil is presented.

3.1 Theory of Catalysis.

3.1.1 Definition. [29]

Basically, 'catalyst' is considered as chemical compound capable of directing and accelerating thermodynamically feasible reaction while remaining unaltered at the end of the reaction, whose thermodynamic equilibrium it consequently cannot change.

This implies that the position of equilibrium attained in the presence of a catalyst is the same as that ultimately arrived at when no catalyst is present. Another implication is that a catalyst can increase the rate only of a reaction that is already thermodynamically feasible; it cannot initiate a reaction that is thermodynamically impossible. Since the presence of the catalyst does not alter the equilibrium constant, the quotient of the rates for the forward and reverse reactions must also be unchanged.

Moreover, by increasing the velocity of a normally undetectable, slow reaction to values that can be observed or predominate, a catalyst can, for all practical purposes, actually initiate a heretofore unobserved reaction.

'Catalysis' is the phenomenon, essentially a chemical one, of a catalyst in action. The ability of a substance to act as a catalyst in a specified system depends on its chemical nature. For catalysis to occur, there must be a chemical interaction between catalyst and the reactant-product system, but this interaction must not change the chemical nature of the catalyst.

By increasing the velocity of a desired product relative to unwanted reactions, the formation of a desired product can be maximized compared with undesirable by-products. This is one of the most important features of catalysis.

In fact it is possible to divide catalytic system into two distinct categories:

a) When the catalyst is of the same phase as the reactants and no phase boundary exists, we speak of homogeneous catalysis.

b) When a phase boundary separates the catalyst from the reactants, we speak of heterogeneous catalysis.

Other than the difference due to the presence of the phase boundary between the catalyst and reactants, the functions of the two types of catalysis are also different. In homogeneous catalysis, the catalyst functions in the form of individual molecules, which are uniformly distributed throughout the reaction system. On the other hand, it is the catalyst surface, in heterogeneous catalysis, which performs the catalytic function; hence the nature of the surface is of extreme importance. With all other factors controlled, the effect of a homogeneous catalyst of definite composition can be exactly predicted upon the basis of its concentration. In contrast, for heterogeneous catalyst, its behaviour will depend not only upon its chemical composition, but also to a very large degree upon both the nature and extent of its surface.

Inasmuch as hydrogenation of castor oil is classified as heterogeneous catalysis, according to that mentioned above, some

insights into the mechanism of heterogeneous catalysis will be necessitated. The description is shown in the following section.

3.1.2 Mechanisms of Heterogeneous Catalysis. [29]

The chemical reactions of heterogeneous catalysis occur between compounds adsorbed on the surface of the solid catalyst. The entire cycle comprises five consecutive steps, each of which can have more or less influence on the overall reaction rate, depending on its relation to the others. The steps are:

(1) Diffusion of the reaction substances over the catalyst particle.

(2) Adsorption of the reacting substances on the catalyst.

(3) Interacion of the reacting substances on the surface of the catalyst.

(4) Desorption of the reaction products from the catalyst particle.

(5) Diffusion of the reaction products into the surrounding medium.

Steps 1 and 5 correspond to the physical processes of mass transfer to and from the catalyst particle and into and out of its pores. Steps 2, 3 and 4 involve chemical phenomena that comprise the chemical transformation [29].

3.1.2.1 Steps 1 and 5: Diffusion of Reactants and Products.

Surface, and not mass, affects the activity of a solid catalyst; the specific activity of a unit weight of catalyst is a direct function of its intrinsic activity and of its specific surface, with the intrinsic activity measured as the activity per unit surface of catalyst (or active phase) and the specific surface measured as the surface per unit weight.

However, a high intrinsic activity and high specific surface are not in themselves enough; the reactants must be able to reach the active surface quickly and the products to quickly leave it, in order for the active surface to achieve its maximum potential. These movements of molecules through the fluid surrounding the solid catalyst are governed by the laws of diffusion.

The physical process of diffusion tends to equalize concentrations. Consequently, a rapid disappearance of reactants undergoing transformation on the catalyst surface brings about a concentration gradient. Diffusion acts to equalize that gradient through a flow of molecules toward the surface. Furthermore, catalyst particles have internal pores that are accessible to the reactant molecules, so that diffusion proceeds in two steps, external and internal:

External diffusion (D_E): Particles of catalyst can be thought of as surrounded by a stationary layer of mixed molecules of reactants, products and diluents; the molecules of a reactant must pass through this layer to reach the external surface of the particle. Since the stationary layer (or film) offers resistance to flow, a concentration gradient is set up

between the fluid and the surface of the particle; and according to Fick's law, the flow of reactant through the layer is proportional to this concentration gradient.

Internal diffusion (D_1): Assuming that an excess of reactant molecules reach the external surface of the catalyst particle, a second concentration develops between that surface and any point in the interior pores; and the internal diffusion is due to this gradient. However, the internal diffusion is more complex with respect to the important internal catalytic surface, following one or more of several possible mechanisms depending on the internal geometry of the catalyst particle. In addition to resistance to flow imposed by the medium in the catalyst pores, there is molecular (Knudsen) diffusion when the average diameter of the pores is of the same order of magnitude as the average free path of the molecules, as well as adsorbed-phase diffusion when gases condense inside the pores.

3.1.2.2 Step 2: Chemisorption of the reacting substances.

As the inward-diffusing reactants arrive in the neighborhood of the catalyst surface, they are chemisorbed, i.e., they react with the surface to give birth to new chemical species, which react with each other according to mechanisms that are energetically more favorable than the chemistry of the same reactions induced by heat alone (See Fig.3.1).

The diagram in Fig 3.1 illustrates the progressive absorptions of energies of activation (E) followed by associated releases of heats (ΔH) to achieve a final result without incurring the large energy of activation needed by a thermal

process. Starting from datum A, the reactants first absorb energy
of adsorption (E_a) from the environment in order to release heat of
adsorption (ΔH_a) and arrive at energy-level B. From level B, the
reactants absorb energy of chemical activation, then react and
desorb so as to release the net heats of reaction and desorption
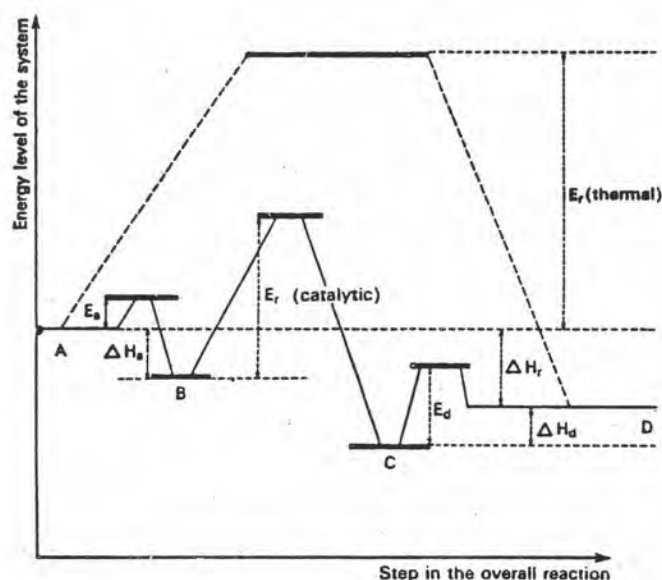$(\Delta H_r$ and $\Delta H_d)$ after absorbing an intermediate energy of desorption
(E_d).

Fig.3.1 Changes in the potential energy of an exothermic
catalytic reaction system [29].

This step is in itself a complex process
that takes place in two steps, physical adsorption and chemical
adsorption. First, the reactant molecule undergoes physical
adsorption, during which Van der Waal forces of attraction bind the
molecule to the surface of the catalyst. This physical adsorption
is characterized by both a very low heat of adsorption and
reversibility, so that merely heating or lowering the pressure will
cause the adsorbed molecules to be liberated. When the external
fluid is gaseous, an equilibrium between the gas phase and the
adsorbed phase is established immediately as the solid is put under

pressure; and elevating the pressure leads to the progressive formation of several layers of adsorbed molecules, until condensation occurs.

Physical adsorption exhibits little selectivity beyond the tendency of molecules with higher boiling points to adsorb more readily on the surfaces of all solids. Thus physical adsorption makes only one contribution to catalytic action: it reduces the energy of activation of the subsequent chemical adsorption [30].

By contrast, chemical adsorption, or chemisorption, exhibits the same characteristics as a true chemical reaction; it brings about the formation of covalent (or electrovalent) bonds of the same kind that hold together the atoms of a molecule. Like chemical reactions, chemisorption is subject to the conventional laws of thermodynamics and kinetics; it exhibits both reversibility at low temperatures as well as irreversibility at high temperatures and conditions when the chemisorbed molecules become dissociated and unable to be reconstituted in the original compound.

The nature of the molecules adsorbed from the surrounding field causes chemisorption to proceed in two different manners, summarily described as dissociative and associative. Saturated molecules tend to be adsorbed in the dissociative manner, with the molecules cleaving into radicals or ions that have free valences to attach to the free valences of the adsorbing surface. Unsaturated molecules tend to be adsorbed in the associative manner by opening the double bond and forming two new covalent bonds with the adsorbing surface.

In any event, chemisorption is limited to only one layer of molecules and, unlike physical adsorption, is specific, so that different molecules will not be adsorbed on the same surface to the same amount or in the same way. The stoichiometry of chemisorption is dependent on the adsorbing metal, the adsorbed molecule, and the percentage of the surface occupied by the adsorbed molecules.

3.1.2.3 Step 3 : Transformation of the Adsorbed Species.

The chemisorbed complex of atoms and radicals formed from the original molecules does not remain frozen in the bi-dimensional adsorbed layer; if the temperatures are high enough it in turn becomes active and acquires greater mobility over the solid surface; and the subsequent chemical reactions proceed from that.

However, it is not possible to identify the complicated mechanisms involved in the rearrangement of a surface complex for the interaction of adsorbed molecules. It is quite possible that the different planes of cleavage (100, 110 and 111) would lead to different surface complexes, as well as varying catalytic activity and specificity for differing reactions [29].

3.1.2.4 Step 4: Desorption of Products.

At this step there are only three observations:

(1) This step is the reverse of the adsorption process, and it therefore follows the same laws.

(2) The reaction products cannot be too strongly adsorbed on the catalyst surface, or they will prevent the reactants from reaching that surface and thus play the role of catalyst poisons.

(3) When the desired product is an intermediate product, it should be desorbed rapidly in order to avoid degradation.

Now, it can be clearly seen that heterogeneous catalysis is a complex one, and the important part of the catalyst is its structure. There are numerous theories devised to explain the phenomena on the surface. This will be described in the subsequent section.

3.2 Theory of Catalyst Surface.

Since heterogeneous catalysis is a surface phenomenon, an essential requirement in an active catalyst is a highly extended surface. With all other factors being equal, the smaller the individual catalyst particles, the more active the catalyst.

In spite of the obvious relationship of surface area to catalyst activity, it does not follow that the activity is determined solely by the magnitude of the surface area. The latter may be made very large without the catalyst necessarily being very active. In fact, metallic nickel dispersed to the colloidal state may be virtually devoid of catalytic activity. All evidence indicates that the activity of a hydrogenation catalyst is due to a certain degree and kind of heterogeneity in the catalyst surface. The development of this heterogeneity will not occur under all conditions but must be achieved by special methods of catalyst

preparation.

The various phenomena associated with heterogeneous catalysis are best explained on the basis of the "active spots" theory of Taylor [31]. This theory assumes that the metal atoms on the surface of the catalyst possess varying degree of unsaturation, according to the extent to which they are elevated above the general catalyst surface, or otherwise released from the mutually restraining influence of their neighboring atoms. The relatively few metal atoms that are thus highly unsaturated are the ones capable of entering into temporary combination with the hydrogen and the unsaturated oil, thereby furthering the hydrogenation reaction. Each unsaturated atom or concentration of unsaturated atoms constitutes an active spot or center. The catalytic activity of each unsaturated atom corresponds to the extent of its unsaturation (Fig. 3.2).
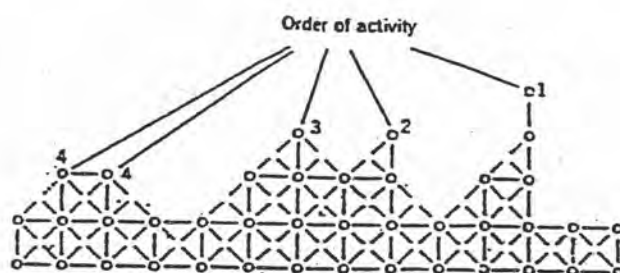

Fig.3.2. Schematic representation of a catalyst surface [32].

An alternative theory of catalyst structure envisions the active portions of a catalyst as areas where the normal crystal lattice of the metal is slightly expanded to fit more exactly the dimensional requirements for two-point adsorption on either side of a double bond. In the case of nickel, the normal interatomic

spacing of 2.47 Å is actually a little smaller than the theoretical optimum. Expansion may occur as metallic nickel is produced by the reduction of a nickel compound (an expansion of 0.16 Å has been reported in Raney nickel) or simply from reduced interatomic attraction in very small crystallites.

According to the active-spot theory, the most active nickel atoms, which are attached to the surface by the minimum of constraint, are but one step removed from a gaseous state. Armstrong and Hilditch [33] have considered it probable that such atoms are actually momentarily detached from the catalyst during the period of their catalytic function, and that the nickel that actually operates in a gaseous form. The subsequent migration and attachment of the nickel atom to the most exposed part of the catalyst surface is assumed to maintain a state of average similarity to the original catalyst.

There is considerable evidence that the hydrogenation of an ethylenic compound must be preceded by two-point adsorption of the carbon atoms on either side of the double bond. This requirement would impose certain dimensional limitations upon the space lattice of any catalytically active metal. Actually, the metals which are at all effective in hydrogenation of double bonds (nickel, cobalt, iron, copper, platinum and palladium) all have interatomic spacings close to that (2.73 Å) calculated as optimum for such two-point adsorption.

Twigg and Rideal [34] have correlated the catalytic activity of various metals with their interatomic distances. Using the distances 2.47 Å for Ni-Ni, 1.52 Å for C-C and 1.82 Å for C-Ni, they showed that for adsorption of the C-C group the valence angle for the bond would have to be 105°4' (Fig.3.3), which is considerably
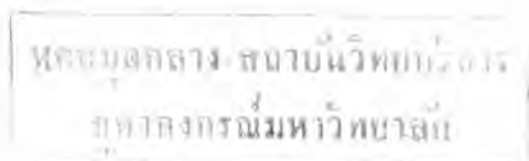
less than the tetrahedral angle 109°28'. For the valence angle of the bond to equal the tetrahedral angle the interatomic distance for the metal would have to be 2.73 Å. Significantly, the interatomic distances for platinum and palladium are 2.76 and 2.74 Å, respectively. They should fit the C-C group without appreciable strain and probably are very good catalyst for that reason.
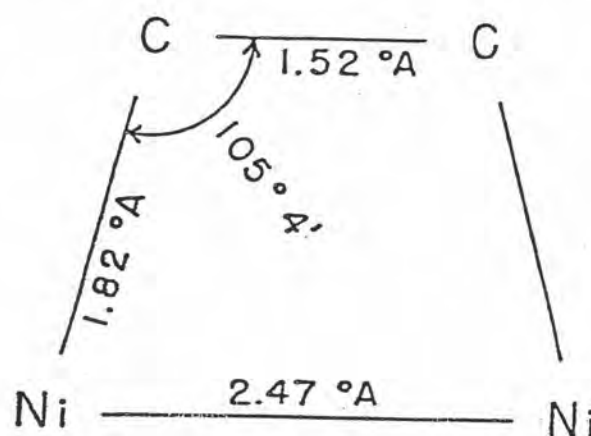
Fig.3.3. Interatomic distance and valence angle for C=C adsorbed on nickel surface [35].

In the next section, the catalyst used in this study, Raney nickel, is introduced. This catalyst is obtained from the leaching of Ni-Al alloy by NaOH solution. In this section, the preparation of Ni-Al alloy and in turn the conversion to Raney nickel catalyst are explained. Then the mechanism of the leaching is proposed.

3.3 Raney Nickel.

3.3.1 Preparation of the Ni-Al Alloy.

Alloys composed of nickel and aluminum were found by Raney [36] to yield nickel having catalytic activity when the other portion of the alloy was leached by selective reaction with

appropriate reagents. The elements magnesium and zinc can also be used. However, for all practical purposes nickel-aluminum alloys containing 42 to 50% of nickel are used. At these percentages it is believed that the nickel aluminum compounds in the alloy include Ni_3Al and $NiAl$, Ni_2Al_3 and $NiAl_3$, but not $NiAl_2$ or $NiAl_5$. The compositions $NiAl_3$ and Ni_2Al_3 are thought to be the ones which most readily yield an active catalyst. The NiAl reacts only slightly with the alkali employed to remove the aluminum from the alloy.

An alloy containing 42 to 50% of nickel is prepared by working nickel shot into molten aluminum heated to about 1,200 °C and protected from oxidation by a salt flux or an inert atmosphere. After solidification the alloy is usually reduced to a fine powder, which is easily accomplished because the alloy possesses little tensile or compressive strength and is friable.

3.3.2 Conversion of the Powdered Alloy into a Catalyst.

This is accomplished by digesting the alloy with alkali and removing the aluminum as a salt. Numerous procedures describing this conversion, which differ only in detail, have been published. Those described by Raney [37] and Bailey [38] are typical for plant-scale hydrogenations, while those described by Adkins and Billica [5] are good for laboratory use.

The leaching of aluminum from Raney Ni-Al alloy with aqueous alkali occurs according to the reaction [39]

$$Al + 3NaOH \longrightarrow Na_2AlO_3 + 3/2\ H_2$$

The chemical composition and physical properties of

the alloy are given in Table 3.1.

Table 3.1. Properties of Raney Alloy [39].

	Raney Ni-Al alloy
chemical composition	
Ni, wt%	50.0
Al, wt%	50.0
Solid-phase density, g/cm^3	4.10
particle density, g/cm^3	3.99
porosity	0.027
pore vol, cm^3/g	0.007

The preparation of Raney catalyst for plant use is
very simple. A 20 to 30% solution of NaOH in water is placed in an
open vessel equipped with an agitator and a steam jacket, the amount
of solution being such that the NaOH is considerably in excess of
that theoretically required to react with the aluminum in the amount
of alloy to be treated. The powdered alloy is added at a slow rate.
The reaction is vigorous, particularly at first, and the heat
liberated quickly brings the solution to the boiling point. Later
the heat is dissipated by generating steam, which is vented to the
atmosphere together with the hydrogen which is formed as a
by-product. Water is added to the reaction vessel to keep the
volume of the solution approximately constant. After all of the
powder has been added and the reaction has subsided somewhat, the
mixture is digested with an occasional addition of water for an
additional 2 or 3 hours at about 120°C. Then the steam is turned
off, the agitation is discontinued, and the nickel in the form of a
sludge is allowed to settle. Most of the solution, which contains

sodium aluminate and the unreacted NaOH is drawn off; and the sludge is washed repeatedly with cold water until all traces of alkali have been removed. Because the sludge is highly pyrophoric, it must be kept wet all times.

After washing is completed, the last wash is drawn off as cleanly as possible, and the residual sludge is covered with oil. Heat is then applied, and vacuum, if it is available, to dry the sludge and replace the protective water with oil. The catalyst is highly pyrophoric; hence it would become inactivated if dried without protection from the air.

3.3.3 The Leaching Mechanism.

The first model proposed is the shrinking core model of Levenspiel [40]. In the model, leaching first occurs on the external surface of the alloy particle, and as time progresses, the reaction interface migrates toward the center of the alloy particle.

Now it is evident that the leaching process cannot be depicted by simple shrinking core models because of the inherent complex nature of the process. This is due to the following reasons. It has been reported by Presnyakov et al. [41] that leaching occurs in various stages, involving the following phase transformation: $NiAl_3 \longrightarrow Ni_2Al_3 \longrightarrow NiAl \longrightarrow Ni_3Al \longrightarrow Ni$. Therefore, the reaction may not be restricted to the reaction interphase, but may occur throughout the alloy matrix consisting of different Ni-Al phases. Furthermore, there is an appreciable reduction in alloy particle size after leaching, which may be due to the removal of aluminum followed by recrystallization. It has also been reported by Freel et al. [42] and Ishikawa [43] that aluminum in $NiAl_3$ is more readily dissolved out by alkali than that in

Ni_2Al_3. Both these phases are present in Raney Ni-Al alloy containing 50 wt% Al.

According to Presnyakov et al. in the leaching process, alkali attack occurs first at the grain boundaries of $NiAl_3$. Alkali then spreads throughout the alloy volume by attacking the interlayers of the alloy, which are of capillary dimensions. This results in the development of cracks on the surface of $NiAl_3$ dendrites. These cracks later grow deeper and wider and also the branching of the cracks occurs simultaneously. This process is accompanied by the development of structural changes of the original alloy due to recrystallization of nickel, affecting adversely the leaching rate. This mechanism for the selective leaching of aluminum from the Raney alloy resembles closely the process of chain-type reactions occuring in solids. These solid-state reactions are typically of autocatalytic nature involving nucleation, chain-branching, and termination steps. The physical picture of this phenomenon is explained by the so-called strain theory [44].

In this study, the effects of palladium on the activity and selectivity of Raney nickel were studied. In this case, palladium was assumed to act as "promoter". So, in the next section is introduced the concept of promoter.

3.4 Promoters.

A 'promoter' is a metal or another substance that is deliberately added in a small amount to enhance the activity of a catalyst without being a catalyst for the reaction in question. It may also improve catalyst stability or selectivity for the desired reaction.

The term 'promoted catalyst' is applied to the catalyst containing 75 percent or more of the active phase.

The promotion of catalysts is much practiced in the field of catalysis, and the use of catalysts of two, three, four, or even more components is by no means unusal. In such complex systems the action of some of the components may more properly be called 'synergistic' than 'promotive', since usually more than one component will possess catalytic activity alone. Promotion in its proper sense is, however, very common.

A number of mechanisms have been proposed to explain the phenomenon of promotion. It has been supposed that the promoter acts as a secondary catalyst, accelerating the formation or decomposition of intermediate compounds; and assists in the adsorption of the reactants; or protects the catalyst from poisons.

Three functions of promoters have been identified.

(1) Textural promoter inhibit the growth of small particles of the active phase during use.

(2) Electronic or structure promoters may dissolve in the active phase and alter its electronic character.

(3) Poison-resistance promoters protect the active phase against poisoning by impurities in the reactants or generated by side reactions.

Promoters play a major role in the manufacture of fat hydrogenation catalysts, since catalysts of satisfactory selectivity can be prepared using them. With catalysts for the hydrogenation of

fats, it appears more reasonable to assume that the function of a promoter is simply structural and that it permits the development of larger numbers of active centers on the catalyst surface.

The hydrogenation of castor oil was carried out to examine the activities of the catalysts; Raney nickel and Raney nickel promoted with palladium. The chemistry of castor oil and the theory of hydrogenation are thus needed being mentioned.

3.5 The Chemistry of Castor Oil.

Castor oil is derived from the bean of the castor plant, Ricinus communis L., of the family Euphorbiaceae. The castor plant occurs in practically all tropical and subtropical countries, either wild or cultivated. Castor oil is also known as Ricinus oil, oil of Palma Christi, tangantangan oil and Neoloid.

Typical of most vegetable oils, the oil is a triglyceride of fatty acids. What is unique is that it contains 87-90% ricinoleic acid which is a fatty acid with 18 carbon atoms, one double bond in the ninth and tenth positions and one hydroxyl group adjacent to the twelfth carbon atom. It is also named a 12-hydroxy oleic acid whose structure is shown in Fig.3.4.

3.5.1 Fatty Acids Composition of Castor Oil.

The composition of fatty acids in castor oil derived from analysis of the methyl ester of castor oil fatty acid with gas chromatographic methods is given in Table 3.2 [35] below.

| 18 | 17 | 16 | 15 | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 |

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\displaystyle H}{C}=\overset{\displaystyle H}{C}-\cdots$$

$$18\!:\!1^{\underline{9\ cis}} \qquad OH^{12}$$
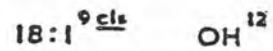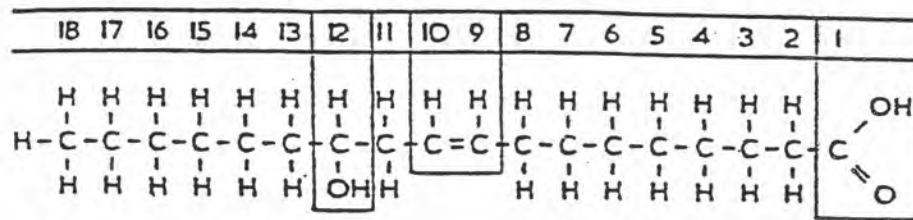
ricinoleic ocid

Fig.3.4. Structure of ricinoleic acid [35].

Table 3.2 Fatty Acids Composition of Castor Oil [35].

Fatty Acid	Percentage
Palmitic acid	0.9 to 1.2
Stearic acid	0.7 to 1.2
Oleic acid	3.2 to 3.3
Linoleic acid	3.4 to 3.7
Linolenic acid	0.2
Ricinoleic acid	89.0 to 89.4
Dihydroxy stearic acid	1.3 to 1.4

The structure of the glycerides of castor oil has been analyzed to be composed approximately of 68% tri-ricinolein, 28% di-ricinolein, 3% mono-ricinolein and 1% ricinoleic acid. These typical analytical values for castor oil may vary, according to the origin of the beans and to the analytic methods used.

3.5.2 Characteristics of Castor Oil.

No other known oil contains a similarly high content of hydroxy fatty acid. This characteristic composition of glycerides distinguishes castor oil from all other vegetable oils and is responsible for its remarkable physical and chemical properties. The non-drying castor oil has the highest viscosity (which changes only slightly at different temperatures) of all vegetable oils.

Castor oil also has the highest density of all oils. Unlike all other vegetable oils, it is miscible with alcohol in every concentration, but it has only limited miscibility with aliphatic petroleum solvents. Its remarkable heat resistance and ability to burn almost without residue give it the properties of a
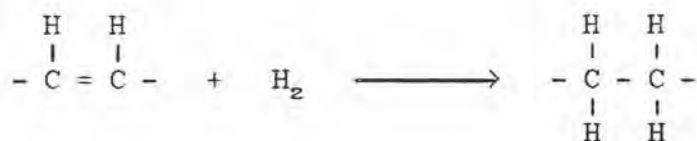
Table 3.3 Characteristics of Castor oil [35].

Density (20 °C)	0.955 to 0.968 g/ml
Refractive index n_D^{20}	1.476 to 1.479
Saponification value	175 to 187
Iodine value	82 to 88
Unsaponifiable matter	0.3 to 0.7%
Hydroxyl value	Minimum 160
Viscosity (20 °C)	9.5 to 11.0 poise
Miscibility	Complete in alcohol and glacial acetic acid; with hydrocarbons at normal temperatures in limited quantities

lubricant.   Refined castor oil is an almost colorless, slightly
yellowish oil with the following characteristics (see Table 3.3).

3.6 Theory of the Hydrogenation of Castor Oil.

Hydrogenation of the ethylenic linkages in glyceride oils to
produce products of improved properties is one of the major
processes in the fat and oil industry. There are two reasons to
hydrogenate oils.   First, since the number of double bonds is
reduced, the opportunity for oxidation is decreased, and thus the
flavour 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
bonds in the fatty acid chains, according to the following scheme

$$\begin{array}{ccc} \underset{\displaystyle -C=C-}{\overset{\displaystyle H \quad H}{\mid \quad \mid}} & + \quad H_2 \quad \longrightarrow & \underset{\displaystyle \overset{\displaystyle -C-C-}{\underset{H \quad H}{\mid \quad \mid}}}{\overset{\displaystyle H \quad H}{\mid \quad \mid}} \end{array}$$

In 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 be dissolved in the oil, and the
hydrogen-laden oil is then brought into contact with the catalyst by
mechanical means.   In the usual type of equipment, reaction is
brought about by agitating the oil and suspended catalyst in a
closed vessel under the atmosphere of hydrogen. Agitation of the
catalyst-oil mixture serves the double purposes of promoting
solution of hydrogen into the oil and continuously renewing the oil
at the catalyst surface. The solubility of hydrogen and other gases
in oil increased with increasing temperature, and of course, with
pressure.

The rate at which hydrogenation proceeds under the conditions outlined above depends upon the temperature, the nature of the oil, the activity of the catalyst, the concentration of the catalyst, and the rate at which hydrogen and unsaturated oil molecules are supplied together to the active catalyst surface.

Fully hydrogenated castor oil (castor wax) of high hydroxyl content has a number of desirable properties, viz. high melting point, low solubility in organic solvents, non-toxicity, oxidation stability, high dielectric constant, etc. Castor wax has the above desirable properties only when the ethylenic linkage of the ricinoleic acid part of triglyceride molecule is reduced without appreciable dehydroxylation taking place during the hydrogenation process. The simple double bond hydrogenation gives glyceride of 12-hydroxystearic acid.
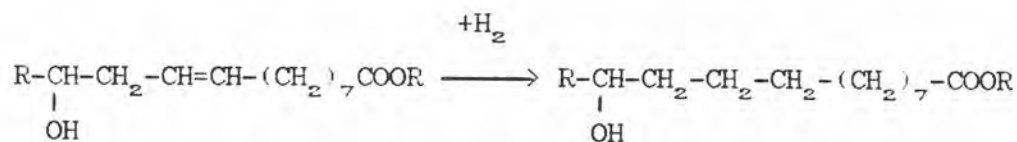
3.6.1 Nature of the Reactions.

The double bond and the hydroxyl group of ricinoleic acid are the two centers which are predominantly affected during hydrogenation. While saturation of the double bonds of the ricinoleic acid chain is undoubtedly the major reaction that occurs when castor oil is hydrogenated, it must be pointed out that a number of other reactions can occur even under comparatively mild conditions. These reactions include conjugated hydrogenation, dehydroxylation, isomerization, hydrolysis, estolide formation, etc [45, 46, 35].
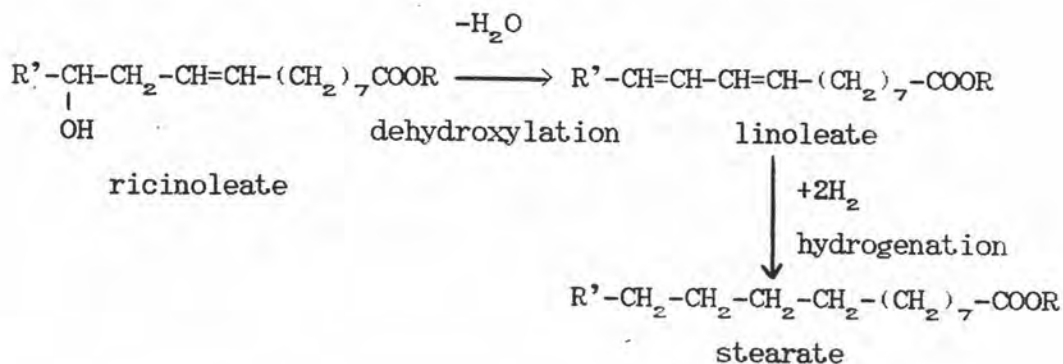
3.6.1.1 Hydrogenation.

The hydrogenation of the double bonds of the ricinoleic acid chain to give glycerides of 12-hydroxystearic acid

which can be commercially attained using nickel catalyst at about 150°C and 150 psig of hydrogen pressure. The hydrogenation reaction occurs according to the following reaction

$$R-\underset{\underset{OH}{|}}{CH}-CH_2-CH=CH-(CH_2)_7COOR \xrightarrow{+H_2} R-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-CH_2-(CH_2)_7-COOR$$

3.6.1.2 Dehydroxylation.

The dehydroxylation or dehydration of castor oil gives diene products. Castor oil is dehydrated by reacting the hydroxyl group of the ricinoleic acid with an adjacent hydrogen in the acid chain to form water molecule. The products are unsaturated fatty acids with two double bonds of the 9-12 and 9-11 linoleic acid types. The reaction is caused by high temperature during hydrogenation. Temperature above 150°C are avoided to minimize dehydroxylation. Finally, the diene products are hydrogenated to stearate by the following reactions.

$$R'-\underset{\underset{OH}{|}}{CH}-CH_2-CH=CH-(CH_2)_7COOR \xrightarrow[\text{dehydroxylation}]{-H_2O} R'-CH=CH-CH=CH-(CH_2)_7-COOR$$

ricinoleate

linoleate

$$\downarrow \begin{array}{l} +2H_2 \\ \text{hydrogenation} \end{array}$$

$$R'-CH_2-CH_2-CH_2-CH_2-(CH_2)_7-COOR$$

stearate

3.6.1.3 Isomerization.

The isomerization is the formation of isomeric unsaturated fatty acids with properties different from the
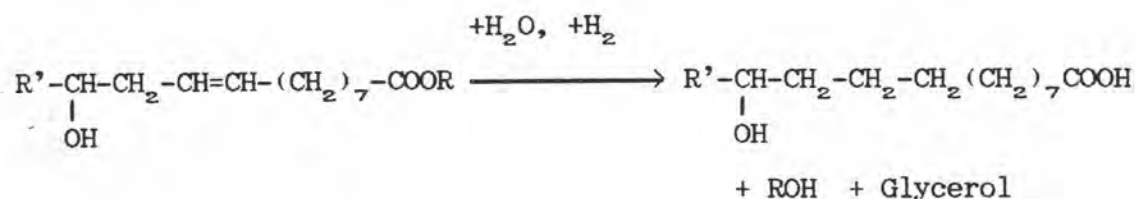
naturally occuring forms.   Such isomers may originate from:

(a) the addition of hydrogen at a double bond which is normally not saturated by natural process,

(b) the migration of double bonds,

(c) conversion of natural cis-forms to trans-forms.

In complete hydrogenation of castor oil, the isomerization reaction is negligible.

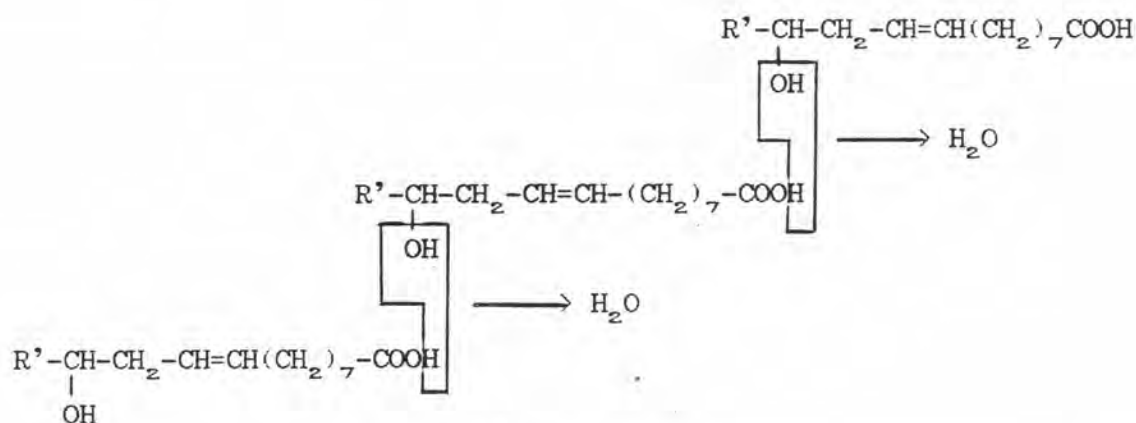### 3.6.1.4 Hydrolysis.

The hydrolysis of castor oil is due to molecule of triglyceride caused to be splitted into fatty acid and glyceride.   The reaction is occurred when there are water acid catalyst. During hydrogenation, water from the dehydroxylation and acidity of the catalyst cause the hydrolysis. Therefore, increasing the dehydroxylation will increase the hydrolysis. The extent to which hydrolysis undergoes is shown by the increase in acid value of the hydrogenated products. The reaction is the following.

$$R'\text{-CH-CH}_2\text{-CH=CH-(CH}_2)_7\text{-COOR} \xrightarrow{\text{+H}_2\text{O, +H}_2} R'\text{-CH-CH}_2\text{-CH}_2\text{-CH}_2\text{(CH}_2)_7\text{COOH}$$

with OH below the left CH and OH below the right CH

$$+ \text{ROH} + \text{Glycerol}$$

3.6.1.5 Estolide Formation.

The estolide formation is caused by

condensation reaction of the carboxyl end of ricinoleic acid in a triglyceride with the hydroxyl group of another. This occurs even at room temperature and can be hastended by heating. The structure of estolide trimer is shown in the following.

$$R'-CH-CH_2-CH=CH(CH_2)_7COOH$$
$$OH$$
$$\longrightarrow H_2O$$

$$R'-CH-CH_2-CH=CH-(CH_2)_7-COOH$$
$$OH$$
$$\longrightarrow H_2O$$

$$R'-CH-CH_2-CH=CH(CH_2)_7-COOH$$
$$OH$$

Note : $R' = CH_3-(CH_2)_5$

3.6.2 Characteristics of the Hydrogenation Reaction.

There are many characteristics, which are well understood, of the hydrogenation of castor oil that are the same as other hydrogenation of fatty materials. These are: the reaction is the addition of hydrogen to the ethylenic linkage of the unsaturated fatty acid chain; the reaction can take place only after there has been brought about effective contact of three different reactants --- hydrogen, an unsaturated fatty acid chain, and the active portion of a metallic catalyst. However, many other characteristics of the hydrogenation reaction will not be intelligible without careful consideration of the nature of this mechanism. This is because the three substances, respectively, are in gas, liquid and solid phases, thus, the mechanism by which the contact is achieved is rather involved.

3.6.2.1 Mechanism of Bringing Reactants together. [47]

It has been mentioned that the catalyst has a definite affinity or adsorptive power for both hydrogen and unsaturated fatty materials. Whether hydrogen is first adsorbed onto the surface of the catalyst, which then reacts with the oil, and subsequently desorbs the saturated fatty molecule; or adsorption of the fat occurs first; or adsorption of either occurs indifferently; is not at present known. It is certain, however, that the concentrations of hydrogen, of unsaturated molecules and of catalyst have major influences on the rate at which hydrogenation proceeds. Furthermore, in special cases any one of the three may become so small in relation to the others as to control the reaction rate.

Hydrogen pressure and degree of agitation are commonly listed among the factors influencing the rate and character of the reaction. There is no evidence, however, that these factors have other effects except the influences upon the concentration of hydrogen in the liquid phase. The manner in which they exert such effects may be appreciated from a consideration of the mechanic of gaseous diffusion [35].

In hydrogenation practice the concentration of dissolved hydrogen may vary within wide ranges. When an oil has a low iodine number and hence a low concentration of unsaturated fatty acids, or when very little catalyst is suspended in the oil, the concentration of dissolved hydrogen may obviously approach saturation if the agitaion is reasonably good. On the other hand, if agitation is relatively poor, the unsaturation of the oil relatively high, and the catalyst concentration likewise high, the

concentration of dissolved hydrogen will drop significantly. Such a condition is likely to occur particularly when a high concentration of catalyst is employed in laboratory hydrogenation. This may be recognized by failure of the reaction to be accelerated when the amount of catalyst is increased, and also by the rate of reaction remaining constant over a wide range of iodine numbers, rather than continuously decreasing as the degree of unsaturation falls. The hydrogenation rate depends, under these conditions, simply upon the rate at which hydrogen can be dissolved in the oil, and hence is independent, within limits of the concentration, of either of the other two substances.

Under most conditions the concentration of dissolved hydrogen will be intermediate between the two extremes cited above. Under fixed conditions, however, it will inevitably vary (increase) as the reaction proceeds, owing to progressive diminution in the concentration of double bonds in the unsaturated fat molecules.

The question of hydrogen concentration in the oil is important not only with respect to the reaction rate, but also in relation to the course of hydrogenation and, as a consequence, composition of the hydrogenated product. As implied above and being developed in subsequent section, there is evidence that agitation, pressure, catalyst concentration, and temperature are interrelated in their influences on the course of hydrogenation, and that the latter is possibly to be interpreted in terms of the concentration of hydrogen adsorbed on the catalyst.

3.6.2.2 Operating Variables in the Hydrogenation.

While hydrogenation occurs, the plant

operator has four variables under control which he can manipulate to change the selectivity to a marked extent. The variables are temperature, type and concentration of catalyst, hydrogen pressure, and agitation. These variables exert their influences, in a complex manner, upon the following six steps involved in hydrogenation:

(1) Solution of hydrogen in the oil,

(2) Adsorption of dissolved hydrogen on the catalyst,

(3) Prior, simultaneous, or latter adsorption of an unsaturated bond,

(4) Formation of a hydrogen-nickel-unsaturated bond complex,

(5) Decomposition of the complex, and

(6) Desorption of the saturated bond.

The choice of an operating temperature is usually limited to those between 80 and 200°C. Below this range the nickel catalyst employed posseses insufficient activity, and above this range there is detrimental effect to the oil and also the dehydroxlyation completely takes place. Also above 200°C the rate of reaction which at first increases with temperature begins to decrease. Between 135° and 175°C the rate of reaction of reaction is approximately doubled for an increase of 22°C. Increasing the temperature at which a hydrogenation is performed increases the dehydroxylation, hydrolysis and also estolide formation.

Agitation during hydrogenation may attain a number of effects. It will whip the hydrogen into the reaction mixture so that it can be dissolved and, thus, available for the reaction. The catalyst will be dispersed and suspended throughout the oil mixture so that it comes into intimate contact with the

hydrogen and the unsaturated carbon chains. And, also, the agitation will help dissipate the heat of the reaction and thus not permit any over heating or hot spots in the surface of catalyst. Increasing agitation speed not only decreases external diffusion resistance on the layer between the bulk of the fluid and the surface of the catalyst particle, but also decreases the dehydroxylation caused by hot spots or exothermic heat of reaction on catalyst surface and subsequently decrease the hydrolysis caused by H_2O from the dehydroxylation.

Increasing the amount of catalyst causes an increase in the reaction rate, but in such a manner that building up the catalyst concentration produces steadily diminishing returns. This, of course, is to be expected from the considerations mentioned previously. With a low concentration of catalyst the oil becomes substantially saturated with hydrogen and, if the unsaturation of oil high, the amount of catalyst becomes the factor limiting the rate of reaction. As the catalyst is increased, the role of limiting factor shifts gradually from catalyst concentration to hydrogen concentration, and eventually the latter is so low that the rate of reaction becomes, in effect, independent of the amount of catalyst. Generally, a catalyst concentration between 0.02 and 0.25% nickel is used in the hydrogenation of castor oil.

The hydrogen pressure exerted in the reaction vessel is generally between one atmosphere and 200 pounds per squared inch guage, within the range of which the reaction rate is roughly proportional to the pressure. Decreasing the pressure tends to increase in dehydroxylation. Below atmospheric pressure the reaction rate is generally too small.

3.6.2.3 <u>Heat of Reaction</u>

Hydrogenation is an exothermic reaction. Hydrogenation of castor oil yields sufficient heat of reaction to raise the temperature of the oil 1.6 to 1.7 °C for each unit decrease in iodine number. These figures were obtained in the range of 130°- 200 °C and were calculated to be equivalent to approximately 25 kcal/mole per double bond saturated. The heat of hydrogenation of fatty oils is thus not very different from that of other aliphatic compounds in the liquid phase (generally 27 - 28 kcal. per double bond per mole).