

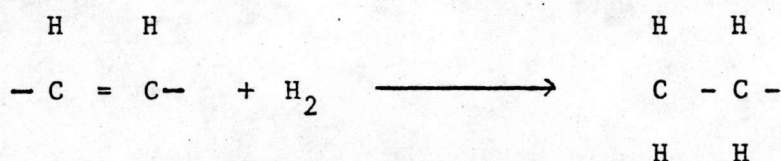
## CHAPTER 3



## THEORY

## 3.1 Introduction

Hydrogenation of the ethylenic linkages in glyceride oils to produce products of improved properties is one of the major process 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 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 bonds in the fatty acid chains, according to the following scheme



The reaction requires a catalyst, the catalyst employed in commercial hydrogenation invariably consists basically of nickel. The greatest amount of hydrogenation is carried out with powder 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 diatomeceous earth. The catalyst is suspended in the oil during hydrogenation, and at the conclusion is removed by filtration. Although catalysts decrease in activity

with repeated use, in most cases inactivation is slow, and a single charge of catalyst may be used a number of times.

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 means. In the usual type of equipment, reaction is brought about by agitation the suspension of catalyst and oil in a closed vessel in an atmosphere of hydrogen. Agitation of the catalyst-oil mixture serves the double purpose of promoting solution of hydrogenation in 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.

## 3.2 Theory of Catalysis

### 3.2.1 Definition of a Catalyst

A catalyst, according to the classical definition of Ostwald, is a substance which alters the rate of a chemical reaction without affecting the energy factors 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, reaction is so imperceptibly slow in the absence of a catalyst that the latter must be considered an essential element of the reaction system.

The fact that a catalyst cannot initiate reactions does not mean that the introduction of a catalyst 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 upon the relative rate of the various alternative reactions. Where a number of different reactions occur together, the addition of a catalyst to the system may 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 3.1). In other words, two reactions with relatively low activation energies are substituted for a single reaction with a high activation energy.

The alteration caused in the reaction rate is measured by the difference between the activation energy of the uncatalyzed reaction and that of the slower of the two steps of the catalyzed



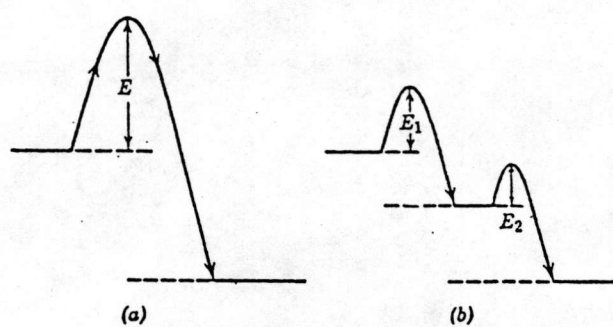


Figure 3.1 Graphical representation of the activation energy factor in (a) uncatalyzed and (b) catalyzed reactions



reaction. In view of the exponential relation,  $k = Ae^{-E_{act}/RT}$  where  $k$  is the rate of a chemical reaction,  $T$  is the absolute temperature,  $A$  is a factor related to the concentration of the reactants, and  $E_{act}$  represents the activation energy. It is readily apparent that the catalyzed reaction may proceed at a rate which very greatly exceeds that of the uncatalyzed reaction.

### 3.2.2 Heterogeneous Catalysis

The type of catalysis that operates in fat hydrogenation is heterogeneous catalysis. By definition, a heterogeneous system is one in which the catalyst and the reactants 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 are uniformly distributed throughout 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 catalyst 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 a solid, however, its behavior will depend not only upon its chemical composition, but also to a very large degree upon both the nature and extent of its surface. The fact that the characteristics of a solid catalyst are determined

so largely by the submicroscopic character of its surface 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, there is a reaction occurring between fluid and porous solid catalysts. In order for reaction to occur, the reactants in the fluid must first be transported to the outer surface of the solid, and then they must diffuse through the pores of the solid to catalytically active site. At least one of the reactant species must usually be chemisorbed onto the surface of the solid. Subsequently, reaction occurs among chemisorbed species or between a chemisorbed species and another species that is either physically adsorbed or that collides with the chemisorbed species directly from the fluid phase. After reaction, products are desorbed and diffuse out through the pores of the catalyst to the bulk fluid. Because the rates of these various steps respond in a different way to experimental variables such as pressure, temperature, bulk-fluid velocity, and chemical and physical structure 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

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6. Internal diffusion of products to surface of particle.
7. External mass transfer of products to bulk fluid.

### 3.2.3 Theory of Catalysts Structure (3)

Since heterogeneous catalysis is a surface phenomena, 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 will be.

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 method of catalyst preparation.

The various phenomena associated with heterogeneous catalysis are best explained on the basis of the "active spots" theory of Taylor. This theory assumes that the metal atoms on the surface of the catalyst possess varying degrees 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 which are thus highly unsaturated are the ones which are



capable of entering into temporary combination with the hydrogen and the unsaturated oil, in this way 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 (Figure 3.2).

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.

Hydrogenation catalysts are seldom prepared directly from massive nickel, but are made by first combining the nickel with other elements, as in nickel oxide, nickel hydroxide, nickel carbonate, nickel formate, nickel-aluminum alloy, etc., and then reducing the resulting compound to regain the nickel in metallic form. The efficacy of this procedure, in producing active nickel atoms relatively free from restraint by neighboring atoms, is evident from the schematic representation of catalyst reduction in Figure 3.3

According to the active-spot theory, the most active nickel atoms, which are attached to the surface by the minimum of constraint,

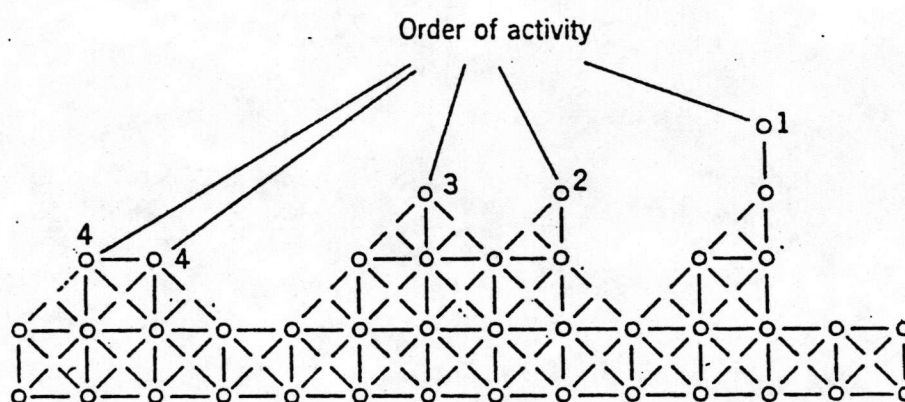


Figure 3.2 Schematic representation of a catalyst surface

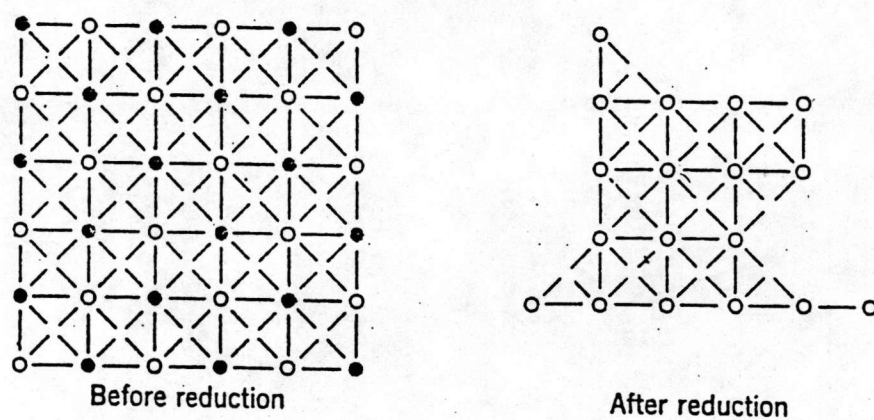


Figure 3.3 Schematic representation of effect of reduction on nickel catalyst.

(White circle = nickel atom; black circle = atom of oxygen, aluminum, etc.)



are but one step removed from a gaseous state. Armstrong and Hilditch 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 thus 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 absorption.

Twigg and Rideal (4) 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  $105^{\circ} 4'$  (Figure 3.4), which is considerably less than the tetrahedral angle  $109^{\circ} 28'$ . 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 catalysts for that reason.

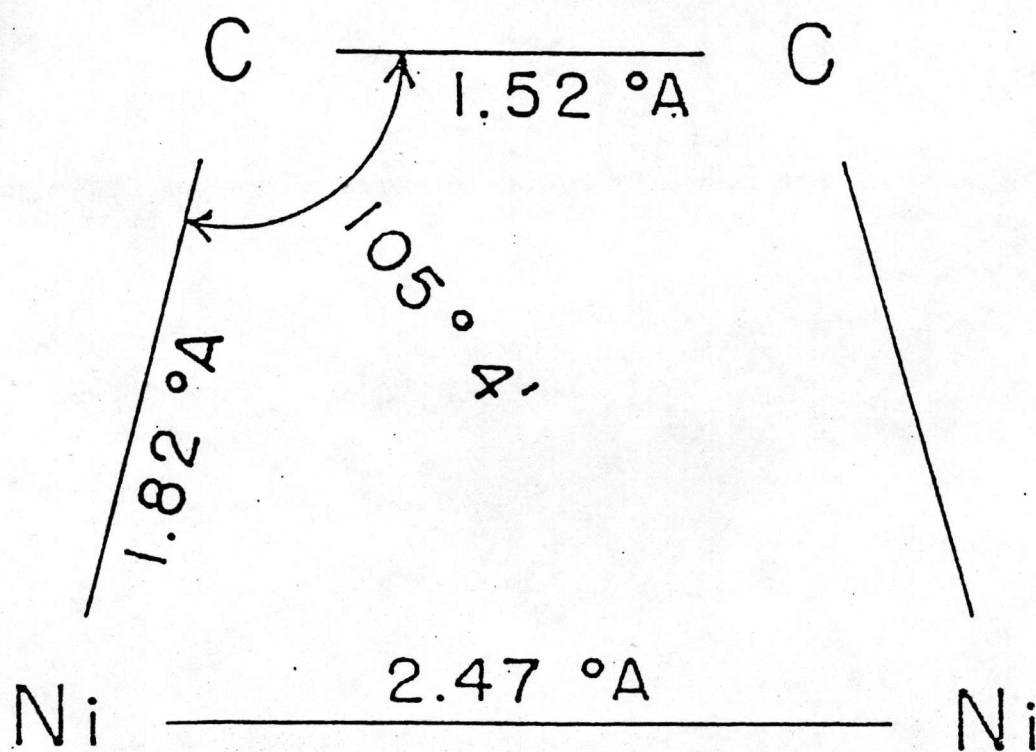


Figure 3.4 Interatomic distance and valence angle for C=C adsorbed on nickel surface.

For a number of other good reasons platinum and palladium are not used for the hydrogenation of fats and oils, except in the laboratory. A most important consideration is that they are much more expensive than nickel. Also, they are relatively unselective. Because all unsaturated bonds which are apparently hydrogenated with relatively equal facility, there is no marked preferential hydrogenation of the more unsaturated components of an oil. Finally, the noble metal catalysts are said to become poisoned easily. Therefore nickel catalyst has been widely used in industry for the hydrogenation of fats and oils.

### 3.3 Types of Catalysts and Methods of Preparation

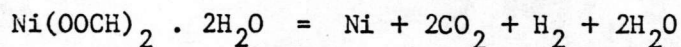
Catalysts which are used for hydrogenation can be classified in various ways. However, since there are only two metals, nickel and palladium, which have found any practical use in the hydrogenation of castor oil, they may be classified on the basis of the metal and also the method of reduction which is used to prepare the catalyst. Although palladium has not found wide use at the present in the hydrogenation, it would seem that some effort is being made to use this catalyst. As will be seen later, this catalyst does offer some interesting possibilities. Therefore practically all of the hydrogenation is now carried out with the aid of nickel catalysts. The commercially important preparations of nickel catalysts will be discussed the followings.

#### 3.3.1 Wet-reduction Method

The pyrolysis of a nickel salt is usually called the wet-reduction because it is carried out in a mixture of nickel



salt and oil and thus is in a liquid state during the reduction. In the preparation of wet-reduced catalysts it is essential that the nickel salt be reducible at a temperature below that at which thermal decomposition of the oil becomes pronounced. Various nickel salts have been proposed for the purpose, but the one which has found perhaps the greatest practical use is the formate, prepared by treating precipitated nickel hydroxide or nickel carbonate with formic acid. Nickel formate begins to decompose at about 150°C and rapidly decomposes above about 190°C by the following reaction :



A typical plant-scale preparation of catalyst from nickel formate has been described by Wurster (4). The reaction, according to him, is carried out in a vented vessel provided with electrical heating and an agitator. The ratio of oil to nickel formate in the charge is not critical; the use of 2 to 4 parts of oil to 1 of formate is common practice. Heating is then begun. When the temperature reaches 150°C, decomposition usually starts. It is at this point that the bubbling of a small amount of hydrogen gas through the mixture is begun. The hydrogen aids in stripping out the gaseous reaction products and aids in hydrogenating the oil carrier which is desirable. The temperature rises at a uniform rate until at a slower rate as decomposition becomes more rapid. At the end of the next one-half hour the temperature will have reached about 190°C. Then in the course of another one-half hour

the temperature will rise to 240°c, at which temperature the mixture is kept for an additional hour and a half to complete the reaction. The total time required is three to four hours. The length of time at a given temperature may vary somewhat according to the age of the nickel salt, freshly precipitated salt reducing more readily at low temperatures.

The catalyst-oil mixture is ready for immediate use, but if desired, the mixture can be cast into blocks or flaked on chilling rolls and then stored for future use. The highly hydrogenated fat protects the catalyst surfaces from oxidation and itself quite stable. Under ordinary conditions the mixture apparently keeps for years without any appreciable of catalytic activity.

Nickel formate catalysts generally have good activity and more uniform than the dry-reduced catalysts prepared by most methods. Since the catalyst is activated while in contact with oil, the some what trouble some operation of transferring the reduced catalyst to oil without access to air is avoid.

The chief disadvantage of wet-reduced catalysts is that they may contain nickel particles of colloidal or near-colloidal dimensions, which are very difficult to filter from the oil after hydrogenation is completed. The formation of colloidal nickel may be minimized by careful attention to the reduction temperature and time, but even under the best conditions wet-reduced catalysts are relatively difficult to filter cleanly from the oil. Oils hydrogenated with wet-reduced catalysts must usually be treated with bleaching earth or otherwise refined to ensure complete removal of the catalyst,

whereas good dry-reduced catalysts can in most cases be removed completely by simple filtration.

### 3.3.2 Dry - Reduction Method

To prepare a catalyst by this method, a nickel salt solution is absorbed on some type of carrier such as clay, alumina, or diatomaceous earth; then the material is dried and ground. The ground material is heated in a closed furnace in the presence of  $H_2$  to about  $500^\circ C$ . The supported nickel salt is reduced to black metallic nickel during the reduction. After the reduction is complete, the catalyst is quite pyrophoric so usually an inert gas is substituted for the hydrogen on the catalyst before the catalyst is exposed to the air. Thus the catalyst is stabilized and may be shipped without danger.

There are many types of process such as, precipitation method, electrolytic precipitation method, and impregnation method are commonly used for making dry-reduced catalyst. The detail of the methods were discussed in the followings.

#### 3.3.2.1 Precipitation

The precipitation involves in its initial stages the mixing of two or more solution or suspensions of material, causing precipitation; this is followed by filtration, washing, drying, calcining and reducing.

The salts of nickel which can be used in the production of precipitated catalysts are the chloride, nitrate



and sulfate. The latter is employed by far the most frequently, primarily because of its lower cost, and is one of the two main compounds used to prepare catalysts for the plant-scale hydrogenation of fats and oils. The other compound, as mentioned earlier, is nickel formate. The chloride and nitrate of nickel are used for precipitated catalysts when it is necessary to eliminate, insofar as possible, impurities which can poison the hydrogenation reaction. The nickel nitrate, in particular is desirable because on heating it decomposes into oxides of nitrogen and nickel oxide, NiO.

As precipitants for nickel salts, successful use has been made of sodium, potassium, and ammonium hydroxides, the corresponding carbonates and bicarbonates. Of these, sodium carbonate and sodium bicarbonate are the most generally suitable and are used predominantly. The use of ammonium hydroxide does have one advantage: Traces of ammonium salts which remain behind in the precipitated mass are easily volatilized during the reduction process.

A procedure essentially as described by Bailey (5) yields a good, active catalyst. According to this procedure 70 parts of chemically pure nickel sulfate hexahydrate is dissolved in 2500 parts of water. The solution is heated to boiling; and 15 parts of a fine grade of diatomaceous earth is added. A second solution is prepared consisting of 42 parts of chemically pure sodium bicarbonate and 650 parts of cold, distilled water. The second solution, which must be used while fresh, is added to the first solution at a uniform rate over a period of 1.2 to 1.5 hours while the latter is kept boiling and is being agitated vigorously with

a mechanical stirrer. The final solution containing the diatomaceous earth and nickel carbonates in suspension should be alkaline to phenolphthalein. At this point an additional 15 parts of diatomaceous earth is added, and boiling and agitation are continued for an additional 0.5 to 1.0 hour after which the mixture is filtered to remove the spent solution. The solid are resuspended in 2200 parts of distilled water, and the mixture is boiled for a short time and refiltered. The washing operation is repeated once or twice, care being taken not to prolong it unduly. Immediately after washing, the solid are dried at 105 to 110°C and pulverized to a fine powder which is the unreduced catalyst. After pulverization the solids are of high specific volume and fluffy in nature. Nickel content is approximately 25 %. Reduction is accomplished by heating in a stream of hydrogen for about 8 hours at 480 to 510°C.

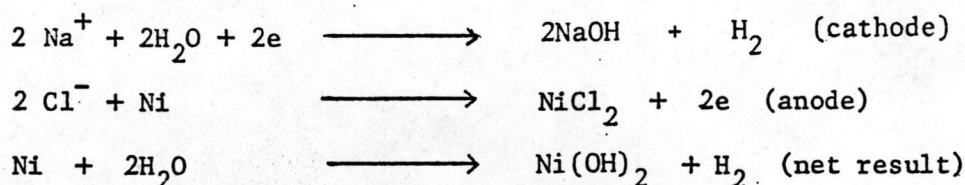
As is the reduction of all catalysts of this type, care must be exercised to remove entrapped air before the catalyst is heated in the presence of hydrogen; otherwise an explosion may result. The reduced catalyst is highly pyrophoric and must not come in contact with air. After reduction, the hydrogen over the catalyst can be replaced with carbon dioxide and thus lessen the possibility of explosions. A general practice is to suspend the catalyst in oil in which form it is stable.

#### 3.3.2.2. Electrolytic Precipitation

A more recently introduced method of catalyst preparation, which yields a product of very high activity, good

characteristics, and remarkable uniformity, is that of electrolytic precipitation (6, 7). This method involves the corrosion of sheets of metallic nickel in an electrolyte by the passage of a direct current. The nickel is precipitated in the form of nickel hydroxide on kieselguhr suspended in the electrolyte. The superiority of the electrolytic method over other methods of precipitation appears to be due to the fact that by this means the entire mass of catalyst can be precipitated at a constant and controllable pH, whereas in ordinary precipitation by the addition of one solution to another the pH of the precipitant solution continuously varies. Furthermore, the product is usually free of undesirable sulfur compounds.

A sheet of the metallic nickel to be converted to nickel hydroxide is made the anode of the electrolytic cell while another sheet of nickel or other corrosion resistant metal is employed as the cathode. On passing a direct current through the electrolyte (a dilute solution of sodium chloride) the following reactions occur:



In addition to the reactions indicated, a small amount of side reaction occurs: some basic nickel chloride is formed. This tends to increase the pH of the electrolyte as the reaction continues. In the original procedure, as described by Sieck (6), this tendency for the pH to increase was overcome to some extent by employing a



mixture of sodium acetate and ammonium chloride as the electrolyte because of their buffering qualities. Current practice is to introduce an acidic material to control the pH.

The following is one of the proven procedures for preparing electrolytically precipitated nickel catalyst. The nickel sheet to be corroded (anode) is suspended in a vat made of wood or other inert material. Two cathodes (one on each side of the anode) are suspended to within 1 to 4 inches of the anode. The vat is almost filled with a 1% solution of chemically pure sodium chloride, and amount of fine diatomaceous earth equal in weight to the nickel to be corroded is added. The mixture of earth and electrolyte is heated to 50°C; and while it is kept in uniform suspension by mechanical stirring, direct current is passed through the cell at a current density of 44 to 57 amperes per square foot, based on the total anode surface. To produce this current density, about 6 volts is required. The temperature of the electrolyte is maintained at 50°C. The pH is maintained between 9.0 and 9.5 by introducing carbon dioxide at a slow, uniform rate. When the proper amount of nickel has been corroded, electrolysis is discontinued, and the suspended catalyst is separated from the electrolyte by filtration, washed, dried and ground to a fine powder. This unreduced catalyst should contain about 38.5% of nickel. Reduction is accomplished by heating it at 370 to 480°C in a stream of hydrogen for 2 to 4 hours.

### 3.3.2.3 Impregnation (8)

Impregnation is the easiest method of making a catalyst. A carrier, usually porous, is contacted with a solution,

usually aqueous, of one or more suitable metallic compounds. The size and shape of the catalyst particles are that of the carrier. The impregnation technique requires less equipment since the filtering and forming steps are eliminated and washing may not be needed. It is the preferred process in preparing supported noble metal catalysts for which it is usually economically desirable to spread out the metal in as finely divided a form as possible.

There are two methods of contacting. The support is sometimes dipped into an excess quantity of solution, but the composition of a batch of solution will change as additional supports are impregnated. The release of debris into the treating solution can form a mud, which makes it difficult to completely utilize the treating solution. More precise control is achieved by a technique termed by dry impregnation, or impregnation to incipient wetness, which is commonly used industrially. The support is contacted, as by spraying, with a solution of appropriate concentration corresponding in quantity to the total known pore volume of slightly less. This allows accurate control of the amount of the active ingredient that will be incorporated into the catalyst. Good reproducibility from one particle to another may be achieved but the maximum loading obtainable in a single impregnation is limited by the solubility of the reagent. In any event, the resulting catalyst is then usually dried and calcined. In a few cases, in order to obtain more uniform dispersion, the active ingredient may be fixed inside the catalyst by immersing the impregnated catalyst in a reagent to cause precipitation occur.

Oxide supports such as alumina and silica are readily wet by aqueous solutions, as are most activated carbons, which have a

layer of chemisorbed oxygen on them. Capillary forces then ensure that liquid will be sucked up into the entire porous structure. Because of capillary pressure, even pores closed at one end will be nearly filled, and the solution of gas in the liquid assists the process. If the support is not readily wetted, e.g., a carbon that is highly graphitized or without chemisorbed oxygen, an organic solvent may be used or the support may be impregnated under vacuum. These procedures are somewhat more costly to use in the plant than incipient impregnation.

The time required for liquid penetration into a pore may be calculated by equating the capillary force to the viscous drag. For a wetting liquid where the contact angle is zero, the time required for liquid to penetrate a distance  $x$  into a capillary is given by :  $t = 4\eta x^2 / \gamma d$ , where  $\eta$  is the liquid viscosity,  $\gamma$  is the surface tension, and  $d$  is the pore diameter.

### 3.3.3 Leaching Method

Alloys composed of nickel and either aluminum or silicon or both were found by Raney (9) 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 employed. However, for all practical purposes nickel-aluminum alloys containing 42 to 50% of nickel are employed. 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.

Alloys containing 42 to 50% of nickel are prepared by working nickel shot into molten aluminum heated to about 1200°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.

Conversion of the powdered alloy into catalyst is accomplished by digesting it 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 (10) and Bailey (5) are typical for plant-scale hydrogenations, while those described by Adkins and Billica (11) are good for laboratory use.

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 the 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 the 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 at 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

Raney nickel produces hydrogenated oils similar to those made with good wet-reduced or dry-reduced catalysts under comparable conditions of hydrogenation. It is often somewhat deficient in activity as compared with the best reduced catalysts, but it is popular because of the simplicity of the method by which it is activated. It avoids the use of complicated reducing furnaces, etc., and does not even require distilled water in its preparation.

#### 3.4 Catalyst Poisons (4)

A large number of compounds which might be present in the catalyst, hydrogen, or oil employed in a hydrogenation can poison

the reaction, either completely or partially. If the poisoning is partial, the activity of the catalyst is reduced.

Among the strongest poisons for nickel catalysts are the sulfur compounds, hydrogen sulfide, carbon disulfide, and sulfur dioxide, which can occur as impurities in the hydrogen produced by several of the common process. Basic nickel sulfate left in catalyst prepared from nickel sulfate also is a poison. These and certain other sulfur-containing compounds exert their effect by forming nickel sulfide. This not only destroys some of the nickel crystallites but produces a compound which has a low melting point. The effect of sulfur poisoning is irreversible; the catalyst cannot be reactivated.

Bailey (5) has found that when a single catalyst is progressively poisoned by the addition of successive portions of a sulfur-containing compound, the activity of the catalyst after each addition corresponds closely to the residue of active nickel, as calculated from the sulfur added and the sulfur required for complete poisoning. The latter quantity varies, according to the original activity of the catalysts, between 0.5 and 5.0 grams of sulfur per 100 grams of nickel. Sulfur-containing nickel catalysts possess the tendency to produce large amounts of trans-isomers in partially hydrogenated oils. Ordinarily this is an undesirable characteristic, except when margarine oils are produced.

Carbon monoxide, which can be present as an impurity in the hydrogen, is another commonly encountered poison. Its effect, unlike that of sulfur, is reversible. Catalyst poisoned with



carbon monoxide can be reactivated by simply flushing with clean hydrogen the oil-catalyst mixture at the hydrogenation temperature. If the temperature of a hydrogenation is high enough, about 200°c, carbon monoxide poisoning will not occur. On the other hand, if a hydrogenation temperature as low as 100°c is used a concentration of 0.01 % of carbon monoxide in the hydrogen will interfere seriously with the reaction according to Bailey. This situation is explained by the fact that carbon monoxide reacts with nickel to form relatively unstable nickel tetracarbonyl. When this compound is heated in the presence of an inert gas at a lower temperature decomposition to nickel and carbon monoxide results. If the decomposition takes place in oil, the nickel will be catalytically active.

Natural oils contain a number of minor components which act as catalyst poisons. These include phosphatides, oxidized glycerides, proteins and proteinaceous materials, and unidentified gummy materials. Hence natural oils are always refined and bleached before being subjects to hydrogenation. Ordinary refining may not suffice because it tends to leave in the oil traces of alkali soaps which are poisons.

Ueno (12) made an extensive investigation of the hydrogenation of oil with a nickel catalyst and found that in addition to some of the compounds already mentioned the following had a retarding effect : soaps of lithium, magnesium, barium, beryllium, iron, chromium, zinc, cadmium, lead, mercury, bismuth, tin, uranium, and gold. He also found that glycolic and lactic acids, hydroxy-stearic acids, oxalic, succinic, and fumaric acids, and hydroxy acids such as malic, citric and tartaric had a retarding effect. Glycerol,

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gelatin and a number of other compounds were also found to have an inactivating influence. It seems probable, however, that many of these compounds have only a very mild poisoning action.

Among the compounds which had no poisoning effect Ueno found the soaps of calcium, strontium, aluminum, cerium, nickel, manganese, copper, silver, vanadium, thorium, and platinum, as well as nickel acetate, butyrate, stearate, lactate, oxalate, and succinate. Among the nonmettalic compounds having no effect, he included cholesterol, squalene, and glycogen.

### 3.5 Theory of the Hydrogenation of Castor Oil

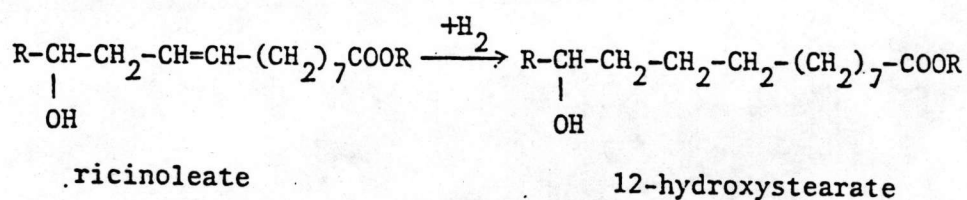
Fully hydrogenated castor oil (castor wax) of high hydroxyl content has a number of desirable properties, viz. high melting point, low solubility in organic solvents, non-toxicity, oxidation stability, high dielectric constant, etc. Castor wax has the above desirable properties only when the ethylenic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

#### 3.5.1 Nature of the Reactions

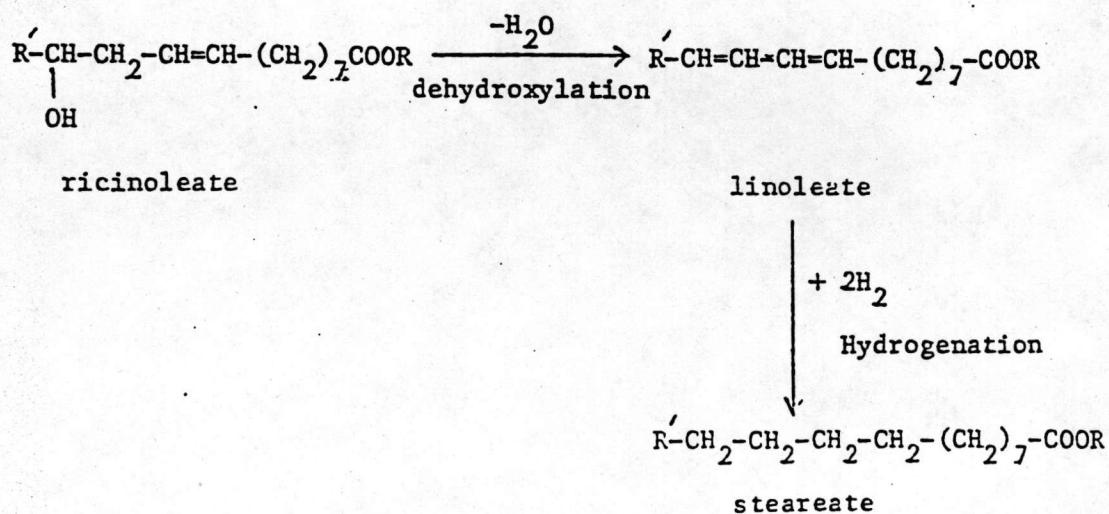
The double bond and the hydroxyl group of ricinoleic acid are the two centers which are affected during hydrogenation. While saturation of the double bonds of the ricinoleic acid chain is undoubtedly the major reaction that occur when castor oil is hydrogenated, it must be pointed out that a number of other reactions can occur even under comparatively mild conditions. These reactions

include conjugated hydrogenation, dehydroxylation, isomerization, hydrolysis, estolide formation, etc.

- Hydrogenation. The hydrogenation of castor oil is the saturation of the double bonds of the ricinoleic acid chain to give glycerides of 12-hydroxystearic acid which can be commercially achieved using of nickel catalyst at about 150°c and 150 psig hydrogen pressure. The hydrogenation reaction occurs according to the following reaction



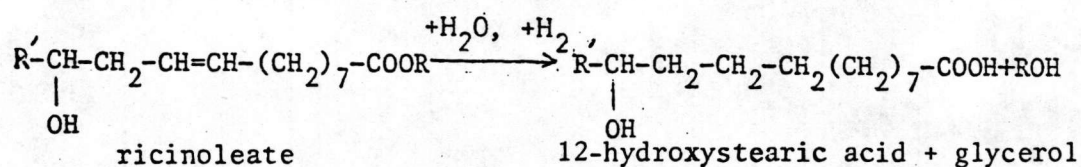
- Dehydroxylation. The dehydroxylation or dehydration of castor oil gives dien products. Castor oil is dehydrated by reacting the hydroxyl group of the ricinoleic acid with an adjacent hydrogen to form water molecule. The products are unsaturated fatty acids with two double bonds of the 9-12 and 9-11 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.



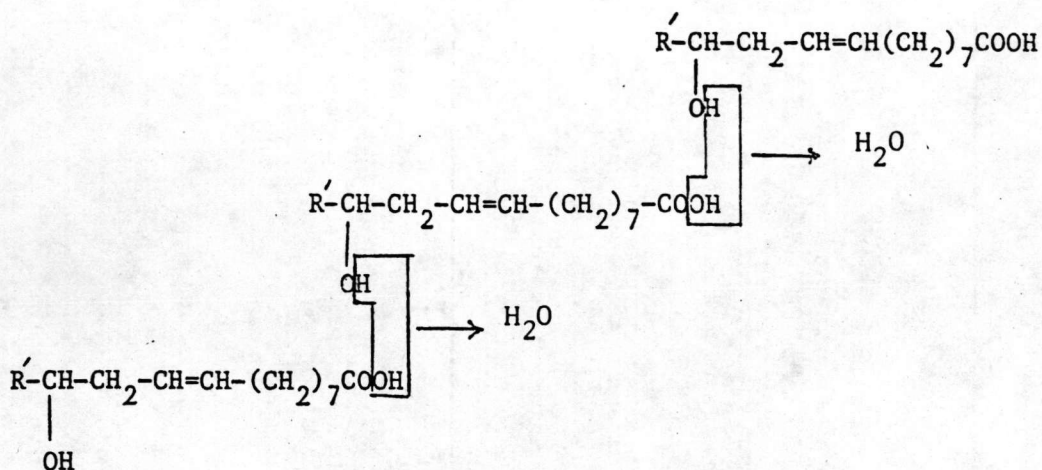


- Isomerization. The isomerization is the formation of isomeric unsaturated fatty acids with properties different from the naturally occurring forms. Such isomers may originate from : (a) the addition of hydrogen at a double bond which is normally not saturated by natural process, (b) the migration double bonds, (c) conversion of natural cis-forms to trans-forms. In the fully hydrogenation of castor oil, the isomerization reaction is negligible.

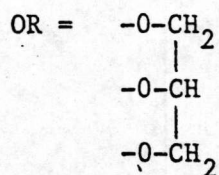
- Hydrolysis. The hydrolysis is caused by splitting of fat molecule to fatty acid and glyceride. The reaction is occurred when there are water and acid catalyst. During hydrogenation, water form the dehydroxylation and acidity of the catalyst cause the hydrolysis. Therefore, increasing the dehydroxylation increases the hydrolysis which is showed by increase in acid value of the hydrogenateed product. The reaction is the following.



- Estolide formation. The estolide formation is caused by condensation of the carboxyl end of one molecule of ricinoleic acid with the hydroxyl group of another. This occurs even at room temperature but can be hastended by heating. The structure of estolide trimer is shown the following.



Note :  $\text{R}' = \text{CH}_3\text{-(CH}_2\text{)}_5$



### 3.5.2 Characteristics of the Hydrogenation Reaction

There are many characteristics of the hydrogenation of castor oil that are the same as other hydrogenation of fatty materials. It is because the reaction is caused by adding 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. Since the three consist, respectively of gas, liquid, and solid, the mechanism by which contact is achieved is somewhat involved. However, many of the characteristics of the hydrogenation reaction are not intelligible without careful consideration of the nature of this mechanism.

### 3.5.2,1 Mechanism of Bringing Reactants Together (3)

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 by the catalyst, which then adsorbs, reacts with, and then desorbs the 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 each an influence on the rate at which hydrogenation proceeds. Furthermore, in special cases any one of the three may become so small in relation to the other two as to control the reaction rate.

Hydrogen pressure and degree of agitation are commonly listed among the factors determining the rate and character of the reaction. There is no evidence, however, that these factors have any effect except to influence the concentration of hydrogen in the liquid phase. The manner in which they exert such influence may be appreciated from a consideration of the mechanic of gaseous diffusion.

The equation defining the rate at which as a gas dissolves in a stirred body of liquid has the form where

$$dp_1/dt = kA(p_g - p_1)$$

$dp_1/dt$  is the rate of solution,  $A$  is the magnitude of the interface between gas and liquid,  $p_1$  is the pressure (corresponding to concentration) of the hydrogen in the liquid phase, and  $k$  is a



constant related to the properties and thickness of the static film of liquid at the interface.

The area of the interface,  $A$ , is a function of the degree to which the oil is agitated (or to which the hydrogen is dispersed during its passage through the oil), and  $p_g$ , the pressure or concentration in the gas phase, is, of course, synonymous with the absolute pressure registered in the system.

In hydrogenation practice the concentration of dissolved hydrogen may vary within wide limits. When an oil has a low iodine number and hence a low concentration of unsaturated fatty acids, or when an oil contains very little catalyst, the concentration of dissolved hydrogen may obviously approach saturation closely if the agitation 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 can doubtless fall very low. Such a condition is particularly likely to occur when a high concentration of catalyst is employed in laboratory hydrogenation. It may be recognized by failure of the reaction to accelerate 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 dissolve in the oil, and hence is independent, within limits of the concentration of either of the other two reactants,

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 the consequent composition of the hydrogenated product. As was implied above, and as will be developed in a later section, there is evidence that agitation, pressure, catalyst concentration, and temperature are interrelated in their influence 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.

#### 3.5.2.2 Operating Variables in the Hydrogenation

While hydrogenation occurs, the plant operator has four variables under his immediate 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 by controlling 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
- (6) Desorption of the saturated bond

The choice of an operating temperature is usually limited to the those between 80 and 200°C. Below this range the nickel catalyst employed possesses in sufficient activity, and above this range there is danger of damaging the oil and also the dehydroxylation 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 is approximately doubled for an increase of 22°. Increasing the temperature at which a hydrogenation is performed increases the dehydroxylation, hydrolysis and also estolide formation.

Agitation during a hydrogenation must accomplish a number of things. It must whip the hydrogen into the reaction mixture so that it can dissolve and, thus, be available. The catalyst must be suspended throughout the oil mixture so that it may come in contact with the hydrogen and with the unsaturated carbon chains. And, also, the agitation must dissipate the heat of the reaction and not allow any over heating or hot spots in the surface of catalyst. Increasing agitation not only decreases external diffusion effect in the interparticle fluid 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<sub>2</sub>O 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 becomes 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 used in the reaction vessel is generally between atmospheric and 200 pounds per square inch gage, within which range 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 to be useful.

### 3.5.2.3 Heat of Reaction

Hydrogenation is an exothermic reaction. Hydrogenation of castor oil yields sufficient heat of reaction to raise the temperature of the oil 1.6-1.7°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).