INTRODUCTION
1.0. **INTRODUCTION**

Hydrogenation is the largest single chemical reaction in the industry that processes oils and fats for edible, e.g., 'Vanaspati', or inedible, e.g. soap, purposes. It consists of addition of hydrogen to the ethylenic linkages or double bonds of the fatty acids in the presence of a suitable metal catalyst.

Hydrogenation is primarily a means of modifying consistency of oils as it converts liquid oils into semi-solid plastic or hard fats which are specially suited for manufacture of margarine and use as shortenings. Besides, it also improves colour and stability of oils and fats, i.e., resistance to deterioration through oxidation or flavour reversion.

The modern hydrogenation process originated from the classical research of Sabatier and Senderens conducted during 1897-1905 to hydrogenate unsaturated organic materials using nickel and other metal catalysts. Wilhelm Normann was perhaps first to obtain a German patent #139457 in 1902 and a British patent #1515 in 1903 for hydrogenation of oils, fats or fatty acids in presence of an appropriate finely divided metal acting as a catalyst. A British firm, Joseph Crossfield and Sons, at Warrington in England built the first hydrogenation plant to Normann's
design in 1906 and employed the process on a limited scale to hydrogenate whale oil to fat useful for soap making and edible purposes. Thereafter, several other designers entered the field and more plants were built within a couple of years in Germany, England, the United States and the Netherlands. The American rights to the Crossfield patents were acquired in 1909 by the Procter and Gamble Company which commercially hydrogenated the cottonseed oil to a plastic edible fat demanded by the American tradition and custom. This shortening, marketed by brand name 'Crisco' was first introduced in 1911 in the American market. Since then several developments have taken place in the theory and practice of hydrogenation of oils and fats which have been summarised elsewhere. Today, a wide variety of hydrogenated oils and fats tailored for specific uses and applications are available on the global shelf.

1.1. Reaction and Process of Hydrogenation

Hydrogenation of oils, as commercially practised in the country and abroad, is a heterogeneous reaction; the unsaturated substrate being in liquid phase, hydrogen in gaseous phase, and metallic catalyst in solid phase.

\[ \text{Unsaturated oil} + \text{Hydrogen} \xrightarrow{\text{Catalyst}} \text{Saturated product} \]

The saturated product is semisolid plastic or hard fat.
The requirement of an appropriate catalyst arises from the fact that direct addition of hydrogen to the double bond of an unsaturated fatty acid involves surmounting a considerable energy barrier. When a chosen catalyst is used, the reactants are chemisorbed on its surface. As a result, the energy barrier becomes much smaller permitting the hydrogenation reaction to proceed at a much faster rate, via surface organo-metallic intermediates. Thus, the heterogeneous hydrogenation reaction involves the following series of steps:

(a) Diffusion of reactants to catalyst surface,
(b) Adsorption,
(c) Surface reaction,
(d) Desorption, and
(e) Diffusion of product(s) from catalyst surface.

The catalyst employed in commercial hydrogenation of oils and fats consists basically of nickel which occurs in nature as a lustrous white ferromagnetic metal having atomic weight of 58.69, atomic number of 28, valence states of 2 and 3, and specific gravity of 8.9. The nickel atoms at the surface of an active nickel catalyst are about 2.5 Å apart. This spacing is close to the spacing of about 2.7 Å units that exists in between carbon atoms of a double bond.

Hydrogenation of monounsaturates, e.g. oleic acid (C\text{18:1} \Delta^9c), proceeds with carbon atoms of its double bond
(9C and 10C) forming absorptive links to the surface of active nickel.

\[
\begin{array}{cccc}
8 & 9 & 10 & 11 \\
H & H & H & H \\
\bullet & \bullet & \bullet & \bullet \\
C & C & C & C \\
H & H & H & H \\
\end{array}
\]

One atom of the hydrogen, previously dissolved in oil and diffused through it to the solid catalytic surface, which is being held absorbed in the vicinity, now links with, say, the 9C atom.

\[
\begin{array}{cccc}
8 & 9 & 10 & 11 \\
H & H & H & H \\
\bullet & \bullet & \bullet & \bullet \\
C & C & C & C \\
H & H & H & H \\
\end{array}
\]

Now one of the following possibilities occurs:

1. The same H atom is lost by 9C before 10C can acquire one H atom, the original 9C-10C cis-double bond reforms and is desorbed, resulting in no change;

2. It is the other hydrogen atom on 9C which is lost before 10C can acquire one H atom, hence a 9C-10C trans-double bond forms and is desorbed resulting in formation of a geometric isomer;
(3) An hydrogen atom is lost from 11C before 10C can acquire one H atom, a 10C-11C cis-double bond forms and is desorbed resulting in formation of a positional isomer; 
(4) The other hydrogen atom is lost from 11C before 10C can acquire one H atom, a 10C-11C trans-double bond forms and is desorbed resulting again in a formation of a positional isomer; or 
(5) The 10C captures an H atom whilst 9C still holds two H atoms; the bond is, therefore, saturated and is desorbed.

If one atom of the hydrogen first links with 10C atom, the possibilities comparable to those indicated above still exist except that this time a 8C-9C cis- or trans-positional isomer is formed.

Hydrogenation of polyunsaturates, e.g. linolic acid \((C_{18}:2 \Delta^{9c,12c})\) and linolenic acid \((C_{18}:3 \Delta^{9c,12c,15c})\), that contain methylene interrupted system of double bonds, proceeds with isomerisation reactions; the polyunsaturates being adsorbed preferentially and more strongly at the catalyst surface than the monounsaturates. The hydrogenation of a methylene interrupted diene on the catalyst surface may involve conjugation before saturation of one of the double bonds as per the following scheme:
(a) Adsorption of one of the double bonds of methylene interrupted diene on catalyst surface

\[ \begin{array}{cccccc}
9 & 10 & 11 & 12 & 13 & 9 \\
H & H & H & H & H & H \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
C & C & C & C & C \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
H & H & H & H & H & H \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\text{Ni- Ni- Ni- Ni- Ni- Ni} & \text{Ni- Ni- Ni- Ni- Ni- Ni} \\
\end{array} \]

(b) Loss of proton from reactive methylene group (11C) and its linking to nickel forming allylic groups

\[ \begin{array}{cccccc}
9 & 10 & 11 & 12 & 13 & 9 \\
H & H & H & H & H & H \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
C & C & C & C & C \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
H & H & H & H & H & H \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\text{Ni- Ni- Ni- Ni- Ni- Ni} & \text{Ni- Ni- Ni- Ni- Ni- Ni} \\
\end{array} \]

(c) Linkage of diene to catalyst surface,

\[ \begin{array}{cccccc}
9 & 10 & 11 & 12 & 13 & 9 \\
H & H & H & H & H \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
C & C & C & C & C \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\text{Ni- Ni- Ni- Ni- Ni- Ni} \\
\end{array} \]
(d) Capture of a proton by terminal \( 9C \) or \( 13C \) atoms.

\[
\begin{array}{cccccccc}
9 & 10 & 11 & 12 & 13 & 9 & 10 & 11 & 12 & 13 \\
H & H & H & H & H & H & H & H & H & H \\
. & . & . & . & . & . & . & . & . & . \\
\text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} & \text{C} \\
. & . & . & . & . & . & . & . & . & . \\
H & H & H & H & H & H & H & H & H & H \\
\text{Ni} - \text{Ni} - \text{Ni} - \text{Ni} - \text{Ni} & \text{Ni} - \text{Ni} - \text{Ni} - \text{Ni} - \text{Ni} \\
\end{array}
\]

(e) Desorption of conjugated system.

\[
\begin{array}{cccccccc}
9 & 10 & 11 & 12 & 13 & 9 & 10 & 11 & 12 & 13 \\
. & \text{CH} : & \text{CH} : & \text{CH} : & \text{CH} : & . & \text{CH} : & \text{CH} : & \text{CH} : & \text{CH} : \\
\text{CH} & \text{CH} & \text{CH} & \text{CH} & \text{CH} & . & \text{CH} & \text{CH} & \text{CH} & \text{CH} \\
\end{array}
\]

The reactive conjugated systems appearing from methylene interrupted diones may have double bonds changed from cis- to trans-configuration. The conjugated fatty acid systems, ready to be hydrogenated, are readSORbed onto the surface of the active nickel catalyst where one of its double bonds is hydrogenated in a manner similar to that of hydrogenation of monoenoic acids. The partial hydrogenation of linoleic acid, thus, results in formation of 9, 10, 11 or 12 cis- or trans- monoenoic; most of the trans-monoenoic contain double bonds at either 10 or 11 positions. These monoenoic are either desorbed from the catalyst surface as such or isomerised and/or hydrogenated at the catalyst surface before being desorbed and diffused into the main body of the oil.
The sequence of reactions in hydrogenation of dienes is summarised in the following model:

\[
\begin{align*}
&\text{(CC)}_{\text{oil}} \quad \text{(C)}_{\text{oil}} \\
&\quad \downarrow \quad \downarrow \\
&\text{(CC)}_{\text{ads}} \quad \text{(C)}_{\text{ads}} \quad \text{(S)}_{\text{ads}} \quad \rightarrow \quad (S)_{\text{oil}} \\
&\quad \downarrow \quad \downarrow \\
&\text{(CT)}_{\text{ads}} \quad \text{(T)}_{\text{ads}} \\
&\quad \downarrow \quad \downarrow \\
&\text{(CT)}_{\text{oil}} \quad \text{(T)}_{\text{oil}}
\end{align*}
\]

where

\[
\begin{align*}
\text{CC} &= \text{cis-cis diene}, \\
\text{CT} &= \text{cis-trans diene}, \\
\text{C} &= \text{cis-monoene}, \\
\text{T} &= \text{trans-monoene}, \quad \text{and} \\
\text{S} &= \text{saturated fatty acid},
\end{align*}
\]

Subscript 'ads' denotes adsorbed species on the surface of the catalyst whereas subscript 'oil' denotes species desorbed from catalyst surface and diffused into main body of the oil.

Hydrogenation of linolenic acid proceeds largely in the aforesaid manners except that the saturation of its central double bond on 12C results in 9, 15 iselinoleate which
is less reactive than normal 9, 12 linoleate. Besides, the migration of double bonds in both directions along the hydrocarbon chain as well as the formation of trans-isomers at each step and also the products of such isomerisation then becoming available for further isomerisation or hydrogenation give rise to complexity of the results and reaction products.

The oils commonly hydrogenated are composed of a mixture of saturated, monoenoic, dienoic and polyenoic fatty acids. Generally, the dienes and polyenes are preferentially adsorbed onto the catalyst surface and hydrogenated until concentration in the oil is considerably reduced; the monoenes are then adsorbed and hydrogenated. Hence, the selectivity of the reaction is important in commercial hydrogenation of fats and oils.

1.2. Selectivity in Hydrogenation Reaction

The term selectivity means a comparison between the rates at which two hydrogenation products are produced when measured over an accepted range of the particular hydrogenation reaction. It clearly implies to comparison of chemical reaction rates or ratios of rate constants; the ratios being independent of the catalyst activity and the overall hydrogenation rate. Although a hydrogenation product is derived by a sequence of reactions, only the net end
result is considered while expressing the selectivity in hydrogenation of fats and oils. Similarly, the positional and geometrical isomers of dienes and monoenes are classed together as the product composite groups.

The terminology commonly used to express selectivities and assigning numerical values to them is as follows:

Selectivity I ($S_I$): This is a comparison of the rate at which oleic acid is produced from more unsaturated fatty acid groups with the rate at which oleic acid is itself hydrogenated further to stearic acid. This term is synonymous to 'linoleic selectivity' and 'selectivity ratio' or $SR$.

Selectivity II ($S_{II}$): This is a comparison of the rate of hydrogenation of linolenic acid to linoleic acid with the rate of hydrogenation of linoleic acid to oleic acid. This term is of value if the oil being hydrogenated contains greater degrees of unsaturation than the two double bonds of linoleate fatty acid group.

Specific Isomerisation ($S_i$): This is the proportion of double bonds isomerised to transform to those saturated with hydrogen. Normally a high $S_i$ is accompanied with a high $S_I$.

Triglyceride Selectivity ($S_T$): This term is an index of random sharing and distribution of the hydrogenation reaction.
over various triglyceride molecules in the bulk oil. When random distribution of hydrogenation occurs, only a little tristearins are formed and a high $S_T$ is indicated. On the contrary, when the random distribution of hydrogenation does not occur, all the stearic groups are confined to tristearin molecules and the $S_T$ sinks to zero. A low $S_T$ is generally accompanied by a low $S_T$.

The selectivity in hydrogenation reaction operates very much according to conditions at the catalyst surface. The dienes and polyenes that are adsorbed on the catalyst surface more firmly have a better chance of obtaining a share of hydrogen adsorbed in the vicinity. Thus, the selectivity is higher when supply of hydrogen is less plentiful. On the other hand, a high concentration of hydrogen creates a mobile situation in which the chances for monoenes and polyenes to hydrogenate are more or less equal. Thus, a rich supply of hydrogen depresses selectivity. Besides, the ease or difficulty of mass transfer within the catalyst pores affects the selectivity; the catalyst with relatively wide pores provides better selectivity than the catalyst with narrow pores. The wide pores of catalyst permit rapid exchange of partially hydrogenated material from pores to the bulk and vice versa, and thereby increase selectivity. On the contrary, the narrow pores allow products of hydrogenation to build up in pores and become saturated, and thereby
decrease selectivity. The catalyst poisons which mainly block the outer catalyst surface and wide pores also reduce selectivity. Besides, the process conditions affect the selectivity in hydrogenation reactions.

1.3. Process Conditions in Hydrogenation Reaction

The four main parameters in hydrogenation of fats and oils are temperature, hydrogen pressure, rate of agitation and catalyst concentration. These parameters exert their influence largely on the concentration of hydrogen at the catalyst surface and thereby affect the rate and selectivity during the course of reaction as indicated in Table 1.1.

1.3.1. Temperature

Hydrogenation is an exothermic reaction; the heat of hydrogenation being 28-29 kcal per double bond which results in an increase in temperature of the oil by 1.6°-1.7°C for each unit decrease in its iodine value. The increase in temperature accelerates the rate of hydrogenation reaction carried out mostly at 100°-240°C in the industry. A high temperature of reaction also increases the formation of trans-unsaturation. The high temperature lowers oil viscosity, increases diffusion and solubility of hydrogen in oil, and increases supply of hydrogen to the catalyst surface. However, a faster rate of hydrogenation reaction partially depletes hydrogen at the catalyst surface which accounts for increase in
isomerisation and selectivity with increases in temperature of the reaction.

1.3.2. Hydrogen Pressure

The industrial hydrogenations of oils are performed under hydrogen pressures of 10-60 psig or 0.7-4.2 Kg/cm². The solubility of hydrogen in oils and its supply to the catalyst surface increases linearly with an increase in hydrogen pressure which increases the rate but decreases the selectivity in the hydrogenation reaction.

1.3.3. Rate of Agitation

The heterogeneous hydrogenation of oils requires agitation to keep the solid catalyst suspended uniformly in the reaction mass, to accomplish distribution of heat or cooling for temperature control, and to facilitate mass transfer of the gas and liquid to and from the solid catalyst surface. The higher rates of agitation help maintaining a high availability of hydrogen at the catalyst surface which increases the rate of hydrogenation reaction but makes it nonselective.

1.3.4. Catalyst Concentration

The catalyst concentrations of 0.02-0.1% (Ni/oil) employed in commercial hydrogenations are largely based on economic considerations. However, as the dose of the catalyst
is increased, the rates of hydrogen uptake and hydrogenation reaction rise due to increased availability of the active surface. This in turn depletes the average hydrogen supply per unit of catalyst surface and thereby increases selectivity in the hydrogenation reaction.

Besides concentration, the nature of catalyst surface is extremely important as it is the catalyst surface that performs the catalytic function in heterogeneous catalysis. The characteristics of nickel catalyst are thus determined by its surface which is submicroscopic in character and has enormous influence on its activity and selectivity.

1.4. Heterogeneous Catalysis and Catalyst Structure

The hydrogenation reaction in heterogeneous catalysis proceeds generally through the formation of unstable intermediate compounds or adsorption complexes in which the catalyst is temporarily combined with one or more of the reactants; the intermediates being invariably decomposed or desorbed to permit the reaction to proceed according to the following scheme:

\[ \text{Catalyst} + \text{reactants} \xrightarrow{\text{adsorption}} \text{catalyst-reactant complex} \xrightarrow{\text{reaction}} \text{catalyst-product complex} \xrightarrow{\text{desorption}} \text{reaction products} + \text{regenerated catalyst} \]
The regenerated catalyst _enters into reaction over and over again_; thus, only a small amount of catalyst is capable of transforming a very large amount of the substrate into the product.

The reaction in hydrogenation of fats and oils is so imperceptibly slow in the absence of a catalyst that the latter is considered an essential element of the reacting system. The catalyst does not initiate but only accelerates the reaction through its influence on the activation energy. A single reaction with a high activation energy is substituted by two successive reactions with relatively low activation energies. It is the lowering of this energy requirement which increases the rate of catalysed reaction in hydrogenation of fats and oils.

The heterogeneous catalysis is a surface phenomenon; its essential requirement being a certain degree and kind of heterogeneity in highly extended surface in an active catalyst. Such a surface is developed by special methods of dry- and wet-reduction of appropriate nickel salts in the catalyst preparation. These reduction procedures create 'active spots' on the catalyst surface. The active spots comprise of metal atoms that possess varying degree of unsaturation. The unsaturation in the metal atoms depends on the extent to which they are elevated above the general
catalyst surface or otherwise relieved of the mutually restraining influence of their neighbouring atoms. The highly unsaturated metal atoms in the active spots at the catalyst surface form adsorptive links with the reactants to catalyse the hydrogenation reaction. Besides, the normal crystal lattice of the metal is slightly expanded at the active spots to fit more exactly the dimensional requirement for two-point adsorption on either side of a double bond.

The active nickel catalyst contains particles or crystallites distributed throughout and/or supported on a porous siliceous material of average particle size of 10 µm. The supported catalysts filter rapidly and also permit repeated filtration on 20-40 subsequent occasions depending upon the type of their use. Besides, the filter aids are employed to facilitate removal of catalyst from the hydrogenated oil. The catalyst becoming inactive or poisoned in repeat uses is discarded as a waste.

1.5. Spent Nickel Catalyst

The 'Vanaspati' and soap industries in India hydrogenate over one million tonnes of oil annually and consume over 1200 tonnes of nickel catalyst containing av 20% metallic nickel. However, there being no reserves of nickel in the country, India imports nickel to meet its requirements.
The valuable constituents of the catalyst rejected from use in the oil hydrogenation industries are metallic nickel and associated fat. The recovery of nickel from the spent catalyst and its reclamation for reuse as a hydrogenation catalyst will not only save the substantial valuable foreign exchange spent every year in importing this metal catalyst but will also alleviate the environmental hazards encountered in disposal of this heavy metal waste. Likewise, the recovery of associated fat from the spent nickel catalyst shall help stretch the supply of oils and fats in the country.

Some of the several scientific studies conducted in the past for recovery of nickel from the spent catalyst considered either recovery of its associated fat by solvent extraction, saponification, or super-critical extraction with carbon dioxide; or removal of the fat by incineration. In these and other studies, the recovery of nickel from the spent catalyst in as such or defatted form was effected by its digestion with organic as well as inorganic acids. The organic acids used were formic acid and acetic acid. The inorganic acids used were hydrochloric acid, nitric acid, sulphuric acid and combinations of the latter with nitric acid or sulfonic acid. However, the techniques are by and large unattractive to the industry for techno-economic reasons. These include:
a) sub-optimal recoveries of nickel with the organic acid,

b) excessive bulk and requirement of longer durations or multiple stages of digestion with dilute solutions of the inorganic acids, and

c) substantial impurities, severe corrosion and handling problems in digestion of the spent catalyst with concentrated solutions of the inorganic acids.

The technical literature on reclamation of recovered nickel from the spent catalyst is scanty though the fresh inorganic and organic nickel salts are normally dry- and wet-reduced, respectively, to prepare active nickel catalysts suitable for oil hydrogenation purposes. Furthermore, the pertinent information on techno-economically feasible process(es) of recovery and reclamation of nickel from the spent catalyst in the country and elsewhere is industrial secret of big business houses. Therefore, this research on reclamation of nickel from spent nickel catalyst by wet-reduction methods was undertaken to generate some relevant and useful information for the benefit of the oil hydrogenation industry.

1.6. **Objectives of Research**

The objectives of the proposed research were:

(1) Quantitative recovery of nickel from spent nickel catalyst under modest conditions.

(2) Reclamation of the recovered nickel by wet-reduction techniques to prepare catalyst of activity comparable to the parent catalyst.
Table 1.1: Influence of process conditions on rate and selectivity in hydrogenation reaction.

<table>
<thead>
<tr>
<th>Increase in Parameter</th>
<th>Surface hydrogen concentration</th>
<th>Reaction rate</th>
<th>Selectivity in reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Hydrogen pressure</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Rate of agitation</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst concentration</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Note: + indicates increase and - indicates decrease.