MATERIALS AND METHODS
3.0. MATERIALS AND METHODS

3.1. Materials

Samples of spent nickel catalyst along with its parent catalyst were obtained from M/s Hindustan Vegetable Oil Corporation, Kanpur.

Acids used for digestion of spent nickel catalyst were hydrochloric acid, LR grade (S.D. Fine Chemicals, Ltd., Boisar, Maharashtra), sulphuric acid, LR grade (Ranbaxy Laboratories Limited, S.A.S. Nagar, Punjab), and nitric acid, LR grade (S.D. Fine Chemicals Limited, Boisar, Maharashtra).

Removal of iron and precipitation of nickel from the acid digests of the spent nickel catalyst were effected using LR grade sodium hydroxide and sodium carbonate, obtained from M/s Ranbaxy Laboratories Limited and M/s S.D. Fine Chemicals Limited, respectively.

Formic acid, oxalic acid, and glacial acetic acid of LR grade (S.D. Fine Chemicals Limited) were used for conversion of recovered nickel into respective salts.

Refined peanut oil (iodine value 101.7 and 99.4) used for wet-reduction of nickel salts and assay of hydrogenation activity of the reclaimed nickel catalysts was obtained from local market; the oil being commercial product of M/s Hindustan Lever Limited, Bombay.
Support materials, viz. aluminium oxide, LR grade (Sarabhai Merk, Baroda), silica-gel without binder, LR grade (BLH India Pvt. Ltd., Bombay), kieselguhr, LR grade (S.D. Fine Chemicals Ltd.), activated carbon and bleaching earth of commercial grade obtained from M/s Hindustan Vegetable Oil Corporation, Kanpur, were used for reclamation of the recovered nickel from the spent catalyst.

Other materials and chemicals used in analytical procedures or experimental work on reclamation of nickel have been specified in respective subsections of the following Section 3.2 of Methods.

3.2. Methods

3.2.1. Proximate Analysis of the Spent Catalyst

Appropriating AOCS procedures\(^5\), the spent nickel catalyst was analysed for its contents of moisture by weight loss from a 5 g sample in its drying in a hot air oven at 101 ± 1°C for 2 h, fat by extracting 5 g sample with petroleum ether (bp 60°C-80°C; S.D. Fine Chemicals Limited) for 3 h in Soxhlet apparatus, ash by incinerating 2 g sample at 600°C ± 15°C for 2 h in a muffle furnace, and acid-insoluble ash by treating the ash in a silica crucible with 5 ml concentrated hydrochloric acid, AR grade (S.D. Fine Chemicals Limited), followed by its water washing on Whatman 42 filter paper and incineration as before.
3.2.2. **Determination of Iron Content**

The iron content of the spent catalyst and its iron-free acid extracts was estimated by thiocyanate method\textsuperscript{51} which is based on oxidation of iron to ferric form and complexing of the ferric iron with thiocyanate ion to produce a red colour in proportion to the amount of iron present (Figure 3.1). The details of this analytical procedure are given below:

**Reagents**

(a) Standard ferric solution: A 0.44 g quantity of Fe(NO\textsubscript{3})\textsubscript{3}.9H\textsubscript{2}O, GR grade (Loba Chemie Indoaustranal Co. Bombay), was dissolved in distilled water and made to 100 ml. This solution was standardised against disodium dihydrogen ethylene-diaminetetraacetate (0.05 M) using Cu-P.A.N. [Copper-1-(2-Pyridylazo)-2-naphthol] as indicator. It was found to contain 0.595 mg Fe\textsuperscript{+++} per ml.

(b) Conc nitric acid, AR grade (S.D. Fine Chemicals Limited).

(c) Ethylene glycol monobutyl ether, AR grade (S.D. Fine Chemicals Limited).

(d) Ammonium thiocyanate, AR grade (S.D. Fine Chemicals Limited): 20\% (w/v) solution in distilled water.

(e) Potassium chlorate, AR grade (Central Drug House Pvt. Limited, New Delhi).
Procedure

Aliquots of standardized ferric nitrate solution in 0.2, 0.4, 0.6, 0.8 and 1.0 ml quantities were taken in 100 ml volumetric flasks. A few drops of conc nitric acid, 2 ml of ethylene glycol monobutyl ether and some distilled water were added to each of these flasks. Thereafter, 5 ml of 20% ammonium thiocyanate solution was added to each flask and its volume was made up to the mark. A blank was prepared using only the reagents and distilled water. The absorbance of the standards was determined against the blank at 472 nm using a Perkin Elmer dual-beam UV-Visible Spectrophotometer (Model No.552; Perkin Elmer Corporation, Norwalk, Conn. 06854, USA).

A 0.5 - 1.0 g sample of the spent catalyst was incinerated at 600° ± 15°C for 2 h. The resultant ash was treated with conc nitric acid (40 ml) and potassium chlorate (1-2 g) on a boiling water bath until it was fully dissolved. After evaporating this solution to dryness, its residue was dissolved in conc hydrochloric acid (10 ml) and again evaporated to dryness. This step was repeated thrice at the end of which the residue was dissolved in conc hydrochloric acid (10 ml), filtered through Whatman 40 filter paper, and made to 500 ml with distilled water washings. A 0.5 ml aliquot of this solution (or iron-free acid extracts of the spent catalyst) was taken in a 100 ml volumetric flask.
to which then a few drops of nitric acid, 2 ml of ethylene glycol monobutyl ether and some distilled water were added. After adding 5 ml of 20% ammonium thiocyanate solution, its volume was made up to the mark. Its absorbance at 472 nm against the reagent blank was taken as before. The iron content of the aliquot analysed was assessed from the standard curve (Figure 3.1).

**Calculation**

The iron content of the spent nickel catalyst was determined using the following relationship:

\[
\text{Iron content (\%)} = \frac{W_1 \times V_1 \times 100}{V_2 \times W_2}
\]

Where
- \( W_1 \) is the iron content of the aliquot analysed,
- \( W_2 \) is the weight of the catalyst sample analysed,
- \( V_1 \) is the total volume of catalyst sample solution prepared, and
- \( V_2 \) is the aliquot of catalyst sample solution analysed.

**3.2.3. Determination of Nickel Content**

The nickel contents of spent-, reclaimed-, and parent- catalysts as well as acid extracts, ferric hydroxide, nickel carbonate and nickel hydroxide were determined by a gravimetric method based on dimethyl glyoxime which
precipitates nickel as nickel glyoxime. The details of this analytical procedure are given below:

**Reagents**

(a) Dimethyl glyoxime: 1.0% solution of dimethyl glyoxime, AR grade (Ranbaxy Laboratories Limited), in distilled ethanol (commercial grade).

(b) Conc nitric acid and hydrochloric acid, AR grades (S.D. Fine Chemicals Limited).

(c) Potassium chlorate, AR grade (Central Drug House Pvt. Limited, New Delhi).

(d) Tartaric acid, AR grade (Sparkle Laboratories Private Limited, Govind Nagar, Kanpur).

(e) Ammonia solution (30%), GR grade (Sarabhai M. Chemicals, Baroda).

**Procedure**

Each of the samples of spent-, parent-, and reclaimed nickel catalysts in 0.5 - 1.0 g quantity was incinerated at 600° ± 15°C for 2 h. The resultant ash was treated with conc nitric acid (40 ml) and potassium chlorate (1-2 g) on a boiling water bath until it was completely dissolved. After evaporating this solution to dryness, its residue was dissolved in conc hydrochloric acid (10 ml) and again evaporated to dryness. This step was repeated thrice at the end of which the residue (or ferric hydroxide, nickel carbonate
and nickel hydroxide in appropriate amounts) was dissolved in conc hydrochloric acid (10 ml), filtered through Whatman 40 filter paper and made to 500 ml with distilled water washings. A 100 ml aliquot of this solution (or the acid extract of the spent catalyst) was boiled with 1-2 g tartaric acid for couple of minutes to tie up its iron and prevent its precipitation with nickel in presence of ammonium hydroxide. After cooling it to room temperature, its nickel was precipitated as nickel glyoxime by mixing with 35 ml of dimethyl glyoxime solution and adding ammonia solution drop wise drop until the mix became slightly alkaline. The scarlet red precipitate of nickel glyoxime was flocculated by heating the mix on a boiling water bath for 2 h. The precipitate was collected on a tared sintered glass crucible (porosity G4) and dried at 120\(^{\circ}\)C for 2 h.

**Calculation**

The content of nickel as metallic nickel in the analysed sample was calculated using the following relationship:

\[
\text{Nickel Content (%)} = \frac{W_1 \times 0.2033 \times V_1 \times 100}{V_2 \times W_2}
\]

Where \(W_1\) is the weight of dried nickel glyoxime precipitate,
\( W_2 \) is the weight of sample analysed, \\
\( V_1 \) is the total volume of sample solution, \\
\( V_2 \) is the aliquot of sample solution analysed.

Note: 0.2033 is conversion factor for nickel glyoxime to metallic nickel.

3.2.4. Recovery of Fat from the Spent Catalyst

The recovery of fat from the spent catalyst was attempted by its extraction with n-hexanes (bp 65\(^\circ\)–70\(^\circ\)C; E.Merck India Limited, Bombay) as well as by saponification with sodium hydroxide followed by acidulation to obtain its fatty acids. In the former approach, the spent catalyst was stirred for 30 min with 4 to 12 folds of n-hexanes (w/v) at \( \sim 50^\circ\)C and filtered. In the latter approach, the spent catalyst was refluxed with 10-18\% (w/w) sodium hydroxide in 6 fold water for 2 h. The soap solution obtained by filtration in hot condition through Whatman 1 filter paper was acidified with sulphuric acid (20\%, w/v); the fatty acid layer at the top was collected, washed and dried.

3.2.5. Determination of Iodine Value

Iodine value of the recovered fat and the mixed-fatty acids from the spent catalyst as well as refined and hydrogenated peanut oils was determined by Wüjs method employing iodine monochloride as reagent and following an AOCS procedure\(^{50}\) (Cd 1-25). The details of this procedure are given below:
Reagents

(a) Glacial acetic acid, AR grade (S.D. Fine Chemicals Limited), free from reducing impurities as assessed by potassium permanganate test (2 ml of acetic acid was diluted with 10 ml distilled water and 2 drops of 0.1 N KMnO₄ solution were added to it. The mix was maintained at 27° ± 2°C for 2 h at the end of which persistence of pink colour was taken to satisfy the test).

(b) Potassium iodide, AR grade (S.D. Fine Chemicals Limited): A 15% (w/v) KI solution was prepared by dissolving 150 g potassium iodide in distilled water and making it to 1 litre. The solution was stored in an amber-coloured glass bottle.

(c) Chlorine gas: Chlorine gas was prepared by allowing HCl (specific gravity 1.19) to drop onto KMnO₄, LR grade (S.D. Fine Chemicals Limited). The gas was dried by passing it through conc sulphuric acid (specific gravity 1.84).

(d) Carbon tetrachloride, AR grade (S.D. Fine Chemicals Limited).

(e) Soluble Starch, AR grade (S.D. Fine Chemicals Limited): 1.0 g starch was made into a homogeneous paste in cold distilled water to which 100 ml of boiling distilled water was added with rapid stirring to
prepare the indicator solution. Freshly prepared solution was used every time.

(f) Potassium dichromate, AR grade (S.D. Fine Chemicals Limited): 4.9035 g of finely ground and dried (110°C for 2 h) K₂Cr₂O₇ was dissolved in distilled water and made to 1 litre at 25°C to prepare 0.1 N solution.

(g) Sodium thiosulphate, AR grade (S.D. Fine Chemicals Limited): 24.8 g Na₂S₂O₃·5H₂O was dissolved in distilled water and made to 1 litre to prepare 0.1 N solution. Its actual strength was determined by titration against standard K₂Cr₂O₇ solution as under:

25 ml of standard dichromate solution (0.1 N) was pipetted into an Erlenmeyer flask. 5 ml HCl and 10 ml KI solution were added to it. The mix was swirled well and allowed to stand for 5 min; thereafter, 100 ml distilled water was added to it. The liberated iodine was titrated against sodium thiosulphate solution using starch solution as indicator. The normality of sodium thiosulphate solution was calculated using \( N_1V_1 = N_2V_2 \) relationship.

(h) Iodine, AR grade (Sarabhai M. Chemicals Limited, Baroda).

(i) Wijs solution (Approximately 0.2 N): 13 g iodine was dissolved by gentle heating in 1 litre glacial
acetic acid. The strength of iodine in the solution was determined by titration with standard sodium thiosulphate solution. A 50 ml aliquot of this solution was kept aside in a cool place for later use. In the remaining solution, dry chlorine gas was passed until the characteristic colour change occurred and the halogen content nearly doubled as ascertained again by titration. If the halogen content was more than double, it was reduced by adding requisite quantity of iodine-acetic acid solution as a slight excess of iodine could be tolerated but not the excess of chlorine.

The iodine content of Wijs solution was determined by taking 5 ml solution into a 500 ml Erlenmeyer flask containing 150 ml water saturated with chlorine and some glass beads, boiling it briskly for 10 min, cooling, and adding 30 ml of 2% $\text{H}_2\text{SO}_4$ and 15 ml of 15% potassium iodide solution, mixing it well and titrating the liberated iodine with standard sodium thiosulphate using starch solution as an indicator.

The total halogen content of the Wijs solution was determined by taking 5 ml solution into a 500 ml Erlenmeyer flask containing freshly boiled and cooled 150 ml distilled water, adding 15 ml of 15% potassium iodide solution and
titrating the liberated iodine with standard sodium thiosulphate solution using starch solution as an indicator.

The titer for total halogen content (B) should be 1.95 to 2.0 times the titer for the iodine content (A) of the Wijs solution. If \( B > 2A \), the iodine-acetic acid solution previously set aside is added in requisite quantity. If \( B < 1.95A \), more chlorine gas is passed into the Wijs solution.

Procedure

Melted, clear and dry oil, fat, or mixed-fatty acids sample was taken in 0.25 to 0.5 g quantities that varied in accordance with expected iodine value as per the following schedule:

<table>
<thead>
<tr>
<th>Iodine value</th>
<th>Sample weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 ± 10</td>
<td>0.4231 - 0.5288 g</td>
</tr>
<tr>
<td>80 ± 10</td>
<td>0.3173 - 0.3966 g</td>
</tr>
<tr>
<td>100 ± 10</td>
<td>0.2538 - 0.3173 g</td>
</tr>
</tbody>
</table>

The sample was dissolved in 20 ml carbon-tetrachloride in an iodine value flask especially designed for the purpose. After adding 25 ml Wijs solution to it and swirling well, the reaction mix was stored in a dark place for 30 min at 25° ± 5°C. Thereafter, 20 ml of potassium iodide solution and 100 ml of distilled water were added to the flask and
the liberated iodine was titrated against standard sodium thiosulphate solution using starch solution as an indicator. A blank determination on reagents was accordingly made without using the sample.

**Calculation**

\[
\text{Iodine value} = \frac{(B - S) \times N \times 12.69}{\text{Weight of sample}}
\]

Where
- \(B\) is the titer of blank,
- \(S\) is the titer of sample,
- \(N\) is the normality of sodium thiosulphate solution.

3.2.6. *Determination of Refractive Index*

The refractive index of melted samples of the recovered fat and mixed-fatty acids was determined by Abbé refractometer and corrected to \(\eta_D\) values for 40\(^\circ\)C using an AOCS procedure\(^{50}\) (Cc 7-25). The details of the procedure are given below:

**Materials**

(a) Toluene and cotton for cleaning the prism.
(b) Clearly filtered and dried sample of fat or mixed-fatty acids (melting point \(\leq 40\(^\circ\)C).
Procedure

The prism was cleaned and dried. The temperature of the refractometer was adjusted to 40°± 0.1°C by circulating water from a precisely thermostatically-controlled water bath with the help of a motor driven pump. The instrument was standardised as per the instructions of the manufacturer. Several drops of the liquid sample were placed on the lower prism. The prisms were closed and tightened firmly with the screw head. After allowing to stand for 1-2 min for sample to attain the temperature of the instrument, the instrument and the light were adjusted to obtain a most distinct reading possible. The refractive index was then determined by taking two or more readings on the sample and calculating their average.

Whenever required, temperature correction was made using the following equation:

\[ R = R' + K(T' - T) \]

Where
- \( R \) is the reading reduced to the temperature \( T \),
- \( R' \) is the reading at \( T' \),
- \( T \) is the standard temperature (°C)
- \( T' \) is the temperature (°C) at which the reading \( R' \) is made,
- \( K = 0.000365 \) for fats and \( 0.000385 \) for oils.
3.2.7. Determination of Acid Value

The acid value of the recovered fat and mixed-fatty acids was assessed using AOCS procedure\textsuperscript{50} (Ca 5a-40) in which 5-10 g sample of fat or 0.5 - 1.0 g sample of mixed-fatty acids was taken in 50 ml neutralized ethanol (95%), the mixture was brought to boiling and titrated with 0.1 N KOH using phenolphthalein as an indicator.

\[ \text{Acid Value} = \frac{56.1 \times N \times V}{W} \]

Where \( N \) is the normality of KOH solution,
\( V \) is the volume of alkali consumed (ml), and
\( W \) is the weight of sample (g).

3.2.8. Determination of Specific Gravity

The specific gravity of the recovered fat and mixed-fatty acids was determined against water at 25°C using a specific gravity bottle of 25 ml capacity and following an AOCS procedure\textsuperscript{50} (Cc 10b - 25).

3.2.9. Determination of Slip Point

The slip points of the recovered fat and mixed-fatty acids as well as the experimental hydrogenated peanut oils were assessed by open-tube capillary-slip method\textsuperscript{53} (IS : 548 Part I - 1964). The details of the method are given below:
Apparatus

(a) Melting point tubes - thin walled, uniformly bored capillary glass tubes open at both ends and with dimensions of 50-60 mm length, 0.8-1.1 mm ID and 1.2-1.5 mm OD.

(b) Thermometer - 0°-100°C range and calibrated to 0.5° subdivisions.

(c) Thiele melting point tube.

(d) Spirit lamp.

Procedure

The recovered fat or mixed-fatty acid, or the experimental hydrogenated peanut oil sample under test was melted completely. It was then filtered to remove any impurities including last traces of moisture. A clear capillary tube was inserted into the molten sample to force it a column of the material of ~10 mm length. The sample in the capillary tube was chilled in a refrigerator at 4°-8°C for 1 h and thereafter attached to a thermometer with a rubber band in such a manner that the lower end of the tube was even with the bottom of the bulb of the thermometer. This thermometer with the sample was suspended in the centre of a thiele tube containing chilled water at ~8°C; the lower end of the sample column was kept 30 mm below the surface of water. The side tube of the thiele apparatus was heated gently to raise the temperature of its
water at a rate of ~0.5°C/min. The temperature at which the sample column commenced to rise in the capillary tube was recorded as slip point of the sample under test.

3.2.10. Extraction of Nickel from the Spent Catalyst by Acid Digestion

The spent catalyst in 25 g quantities taken in a three-necked flask; fitted with a stirrer rotating at 100-150 rpm, a condenser, and a thermometer pocket; was digested with 1-3 N HCl, HNO₃, H₂SO₄ and mixtures thereof (3:1, 1:1, and 1:3, v/v) in 1-3 stages for durations ranging from 1-3 h at 100°C ± 1°C using various proportions of the spent catalyst to acid ranging from 1:3 to 1:8 (w/v). The acid digest was filtered hot (at ~50°C) under reduced pressure and the residue on Whatman 1 filter paper was washed with 20 ml aliquots of hot water (~50°C) twice admixing the washings with the filtrate (acid extract).

3.2.11. Removal of Iron from the Acid Extracts

The acid extracts obtained using HCl, H₂SO₄ and mixtures thereof were treated in 25 ml aliquots with 2 ml sodium hypochloride, LR grade (Burgoyne Burbidges and Company, Bombay-13), and boiled for 2 min to convert their content of iron from ferrous to ferric form. The acid extracts obtained using HNO₃, HNO₃ + HCl and HNO₃ + H₂SO₄ contained iron in ferric form and did not require this treatment.
In order to ensure maximum removal of iron from the acid extract as ferric hydroxide without appreciable loss of nickel, optimisation experiments were carried out in which the acid extracts in 25 ml aliquots were adjusted to pH 4.50, 4.75, 5.00, 5.25, 5.50, 5.75, 6.00, 6.25, 6.50, 6.75 and 7.00 with 10% (w/v) sodium hydroxide solution using a Systronics digital pH meter (Type 335, Sr.No. 895, Systronics Instruments Company Limited, Ahmedabad). The dispersions were then heated to boiling for ~5 min to precipitate their iron as ferric hydroxide. Following filtration through Whatman 1 filter paper under reduced pressure, the precipitates were analysed for their content of nickel and the filtrates were analysed for their content of iron by the aforesaid gravimetric and colorimetric thiocyanate methods, respectively (refer sections 3.2.2 and 3.2.3). The results of these experiments revealed that the pH of 6.0 was optimum for removal of iron from the acid extracts. Therefore, the bulk of each of the experimental acid extract of the spent nickel catalyst was adjusted to pH 6.0 with 10% (w/v) sodium hydroxide to precipitate out most of its iron without appreciable loss of nickel in the ferric hydroxide precipitate; the precipitated iron was removed by filtration through Whatman 1 filter papers.
3.2.12. Precipitation of Nickel from the Iron-freed Acid Extracts

The iron-freed acid extracts of the spent catalyst were adjusted to pH 8.5 ± 0.5 with either 50% (w/v) NaOH or anhydrous sodium carbonate and heated to ~70°C. The resultant precipitates of nickel hydroxide and nickel carbonate were washed twice with distilled water at room temperature and recovered by filtration using Whatman I filter paper under reduced pressure.

The recovery of nickel from the spent nickel catalyst in the aforesaid manner was assessed from the weights of the recovered precipitates of nickel hydroxide and nickel carbonate and their nickel content determined by the aforesaid gravimetric method (refer section 3.2.3).

3.2.13. Conversion of Recovered Nickel to Salts

Nickel Hydroxide to Nickel Formate

Assuming quantitative recoveries of nickel, the nickel hydroxide precipitate in as such form was converted into the nickel formate by refluxing for 30 min with stoichiometric amounts of formic acid (10%, w/v) which actually amounted to about 5% excess addition on the basis of actual recovery of nickel from the spent catalyst. Alternately, the nickel hydroxide precipitate dried at 105° ± 1°C for 2 h was converted into nickel formate by refluxing its 25 g
quantities with formic acid (10%, w/v) in 10% or 20% excess to stoichiometric amounts for 30 min in a three-necked flask assembly fitted with a stirrer. The reaction mix which was a clear solution without any sediment was evaporated to dryness on a boiling water bath to crystallise nickel formate as \((\text{HCOO})_2\text{Ni}.2\text{H}_2\text{O}\).

**Nickel Carbonate to Nickel Formate**

The nickel carbonate dried at 105\(^\circ\)C for 2 h was converted into nickel formate by refluxing 25 g quantities with formic acid (10%, w/v) in 10% excess to stoichiometric amounts for 30 min. The reaction mix which was partly in solution and partly in insoluble form was fractionated; the soluble and insoluble fractions were dried separately on a boiling water bath and in an oven, respectively.

**Nickel Carbonate to Nickel Oxalate**

The dried nickel carbonate was converted into nickel oxalate by refluxing 25 g sample with oxalic acid (10%, w/v) in 10% excess to stoichiometric amounts for 30 min. The reaction mix containing bluish green crystals of nickel oxalate was filtered through Whatman 1 filter paper. The precipitate of nickel oxalate was washed with distilled water and dried in an oven at 105\(^\circ\)C for 2 h.
**Nickel Carbonate to Nickel Acetate**

The dried nickel carbonate was converted into nickel acetate by refluxing 25 g sample with acetic acid (10%, v/v), in 10% excess to stoichiometric amounts for 30 min. The reaction mix which was a clear solution without any sediment was evaporated to dryness on a boiling water bath to crystallise nickel acetate as \((\text{C}_2\text{H}_3\text{O}_2)_2\text{Ni}.4\text{H}_2\text{O}\).


**Nickel Formate**

Appropriating method of Vogel\(^5\) the experimental nickel formate solution (2.5 g/l), in 25 ml aliquots, was treated with excess of saturated solution of sodium carbonate and heated to \(\sim 60^\circ\text{C}\). The liberated formate was titrated against 0.1 N \(\text{KMnO}_4\) until the liquid became distinct pink in colour. After acidifying it strongly with dilute sulphuric acid, 25 ml of 0.1 N sodium oxalate was added to it. The reaction mix was then warmed to completely dissolve the precipitate of nickel carbonate. The resultant solution was again titrated, while warm, with 0.1 N \(\text{KMnO}_4\) solution. A blank determination was also carried out simultaneously. The purity of the prepared salt was assessed by determining its nickel formate, \((\text{HCOO})_2\text{Ni}.2\text{H}_2\text{O}\), content as follows:

\[
\text{Nickel formate } (\lambda) = \frac{(S - B)}{W} \times N \times 4.617
\]
Where $S$ is the volume of KMnO$_4$ solution consumed for sample,

$B$ is the volume of KMnO$_4$ solution used in blank determination,

$N$ is the normality of KMnO$_4$ solution, and

$W$ is the weight of the sample in aliquot analysed.

**Nickel Oxalate**

Appropriating method of Vogel$^{54}$, the experimental nickel oxalate solution (prepared by dissolving 2 g nickel oxalate in distilled water containing 50 ml concentrated H$_2$SO$_4$ and making its volume to 1 litre), in 25 ml aliquots, was titrated against standard KMnO$_4$ solution at ~60°C until a faint pink colour appeared and persisted for 30 sec.

The purity of the prepared salt was assessed by determining the nickel oxalate, $(C_2O_4)_2Ni.2H_2O$, content as follows:

\[
\text{Nickel Oxalate} = \frac{V}{W} \times N \times 9.137
\]

Where $V$ is the volume of KMnO$_4$ solution used in titration,

$W$ is the weight of the sample in aliquot analysed, and

$N$ is the normality of KMnO$_4$ solution.

**Nickel Acetate**

Appropriating method of Scott$^{55}$, 2.3 g of experimental nickel acetate was taken in a Kjeldhal flask connected to a condenser and a receiving flask containing 50 ml
of 0.5 N NaOH. 20 ml of concentrated phosphoric acid, AR grade (S.D. Fine Chemicals, Limited), and 150 ml of distilled water were added to the Kjeldhal flask and its contents were heated gently to distill off the liberated acetic acid. More distilled water was added to the flask and ~ 800 ml of the condensate was collected in the receiving flask. The contents of the receiving flask were refluxed for 10 min for removing off its dissolved carbon dioxide content, if any. After cooling, 25 ml of 0.5 N acetic acid was added to the flask and its excess acetic acid was titrated against 0.5 N NaOH using phenolphthalein as an indicator. The purity of the prepared salt was assessed by determining its nickel acetate, \((\text{C}_2\text{H}_3\text{O}_2)_2\text{Ni}.4\text{H}_2\text{O}\), content as follows:

\[
\text{Nickel acetate} = \frac{V}{W} \times N \times 12.44
\]

Where \(V\) is the volume of standard alkali used for neutralisation of liberated acetic acid from the sample,

\(W\) is the weight of sample analysed, and

\(N\) is the normality of NaOH solution.

3.2.15. Wet-reduction of Nickel Salts

Experimental dispersions of the recovered nickel formate, nickel acetate, and nickel oxalate were prepared without any support material in commercial sample of refined
peanut (groundnut) oil (50:50, w/w). The reduction of these dispersions in 100 g quantities was attempted while stirring at 125 ± 25 rpm in a 500 ml capacity three-necked flask assembly at temperatures ranging from 230°C to up to 290°C for periods of up to 1.5 h under a stream of hydrogen bubbling through the reaction mass at 50 ml/min. While the dispersions of nickel formate reduced easily as was evident from blackening of the reaction mass, difficulties were encountered with dispersions of nickel acetate and nickel oxalate as the former produced a lumpy mass at 250°C which is its reported temperature of reduction while the latter could not be reduced appreciably in 1.5 h even at 290°C as was evident from light chocolatey colour of the reaction mix which did not flake on pouring over a chilled glass surface. Consequently, experimental work with nickel acetate and nickel oxalate was abandoned while that with nickel formate was continued.

3.2.16. Wet-reduction of Nickel Formate for Kinetic Studies

Experimental dispersions of the recovered nickel formate in refined peanut oil (50:50, w/w) were reduced under a stream of hydrogen in the glass assembly at 230°C–270°C for 0.25–1.50 h. After cooling to 150°C in atmosphere of hydrogen, the catalyst was flaked by pouring on a chilled glass surface.
Approaching AOCS procedure (Ca 17-76), the nickel formate reduced to active catalyst was assessed for its hydrogenation activity by determining the drop in iodine value of refined peanut oil hydrogenated for 15 min in a Parr pressure reactor (Model 4522 M, capacity 2000 ml, Parr Instruments Company, Moline, IL 61265, USA). The hydrogenation vessel/bomb of this reactor weighing 14.5 Kg was made up of 316 stainless steel and had a working capacity of 1.5 litres. The maximum rating of the bomb was 1900 psi (134 Kg/cm²) at 350°C. Its internal diameter was 4'" (10.16 cm) and depth was 10.5'" (26.67 cm). The vessel was provided with a stirrer to maintain an uniform suspension of catalyst and distribution of hydrogen in the oil throughout the course of the hydrogenation reaction. The stirrer, with a drive shaft diameter of 3/16'" (0.48 cm), was provided with two impellers (with six blades on each of the impeller) and was driven by a 1/15 HP motor. The vessel was also provided with an exterior heater consisting of 1500 Watt sheathed calrod element built in rugged stainless steel and aluminium housing. It was also provided with an automatic temperature controller that operated in conjunction with a thermocouple and was installed in a thermowell attached to the bomb head. Spiral and serpentine cooling coils were also built in the bomb for cooling of reaction mass by circulation of water, if required. The vessel was equipped with
a pressure gauge capable of reading up to 2000 psi (141 Kg/cm²) with a least count of 20 psi (1.4 Kg/cm²).

The reactor vessel was charged with refined peanut oil (1 Kg) and nickel catalyst (0.05% as metallic nickel by weight of oil). It was then evacuated to ~15 mm pressure with the help of a mechanical vacuum pump. The reaction mix was agitated at 425 rpm and its temperature was raised to 175°C. The hydrogen gas, standard grade (Indian Oxygen Limited, Kanpur), was then introduced at 20 psig (1.4 Kg/cm²) and hydrogenation was carried out at 175°C for 0.25 h. The hydrogenated oil samples obtained at the termination of the experiment were analysed after filtration for iodine value (refer section 3.2.5).

Since it was not possible to directly determine the actual extents of reduction of nickel formate to catalytically active metallic nickel at various temperatures as a function of time, an indirect method was appropriated for the purpose. In this method the reduction of nickel formate to active catalyst was taken as completed at 270°C in 1 h; its basis being the maximum drop in iodine value of the oil observed on its hydrogenation with this catalyst under the aforesaid test conditions. Using this as a standard, the extents on reduction of nickel formate to active catalyst in other experimental samples were assessed as a
function of time at 230° - 270°C from the relative drops in iodine value of the oil effected in its hydrogenation with each one of the respective catalytic preparations. This in turn provided residual proportion and quantum of nickel formate in experimental dispersions reduced at 230° - 260°C for 0.25-1.5 h and at 270°C for 0.25-0.75 h for kinetic studies of its wet-reduction to active catalyst.

The logarithms of the ratios $A_0/A$ (where $A_0$ is initial quantum of nickel formate taken for wet-reduction and $A$ is its residual quantum after time, 't') were plotted as a function of time (t) for reduction temperatures of 230°, 240°, 250°, 260°, and 270°C which indicated the wet-reduction of nickel formate to be a first order reaction and provided the reaction rate constants. The reaction velocities were plotted as a function of temperature in accordance with the Arrhenius equation ($K = Ae^{-E/RT}$ where $K$ is the rate constant of the reaction, $E$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature; the logarithmic form of this equation is: $\log_{10}K = \log_{10}A + \frac{E}{2.303R \cdot 1/T}$) to obtain activation energy for wet-reduction of nickel formate under the experimental conditions.
3.2.17. **Wet-reduction of Nickel Formate to Catalytically Active Nickel for Hydrogenation of Oil**

Experimental dispersions of the recovered nickel formate in commercial sample of refined peanut oil were prepared in a pestle and mortar without any support material (50:50, w/w) and with support materials, viz. aluminium oxide, silica-gel, kieselguhr, activated carbon, or bleaching earth, in nickel formate : oil : support ratio of 50 : 45 : 5 (w/w), respectively. These dispersions were reduced under a stream of hydrogen bubbling through the reaction mass at the rate of 50 ml/min at 250°C for 2 h while stirring in a glass assembly. After cooling to 150°C in atmosphere of hydrogen, the catalyst was flaked by pouring on a chilled glass surface. The reclaimed nickel catalyst was assessed for its hydrogenation activity (refer section 3.2.16) by determining the iodine value (refer section 3.2.5) and slip point^53 (refer section 3.2.9) of the refined peanut oil hydrogenated for 1.5 h in the Parr pressure reactor using 0.05% catalyst concentration (as metallic nickel by weight of oil) at 175°C under 20 psig (1.4 Kg/cm²) hydrogen pressure and agitation at 425 rpm.

The hydrogenation activity of experimental samples of the reclaimed catalyst was also assessed in the aforesaid manner after its storage for six months in sealed polyethylene bags under ambient conditions. The storage
studies revealed that the catalyst supported on kieselguhr was the most stable, and therefore, subsequent studies were carried out only on the kieselguhr-supported catalyst.

The temperature for the reduction of nickel formate to active nickel catalyst was optimised by dispersing the recovered nickel formate in refined peanut oil on kieselguhr support (50:45:5, w/w) and reducing it in a stream of hydrogen for 2 h at 230°-270°C under agitation. The optimum temperature of reduction was found to be 260°C.

The proportion of kieselguhr for the reclamation of nickel was optimised by reducing dispersions of the recovered nickel formate in refined peanut oil on this support (50:49:1 to 50:40:10, w/w) at 260°C for 2 h. The hydrogenation activity of the catalyst preparations was assessed by the procedure described above. The studies revealed that the dispersion in the proportion of 50:43:7 (w/w) of nickel formate : Oil : kieselguhr provided catalyst of maximum activity.

The optimum time for the reclamation of nickel in refined peanut oil on kieselguhr support was assessed by reducing the recovered nickel formate at 260°C for 0.25 to 2.75 h and assessing the hydrogenation activity of the catalyst. The hydrogenation activity of the parent nickel catalyst was also assessed in a manner identical to that
used for that of the reclaimed catalyst.

3.2.18. **Determination of Fatty Acid Composition**

The control and the hydrogenated peanut oil samples were analysed for their fatty acid composition by gas-liquid chromatography of their fatty acid methyl esters as follows:

**Gas-liquid Chromatograph**

The gas-liquid chromatograph (Model No. 741-S; Chromatograph and Instruments Company Limited, Baroda) provided with a flame ionization detector (FID) was used for the determination of fatty acid composition of refined peanut oil and its hydrogenated samples. A stainless steel column of 3 mm ID x 2 m length packed with 20% DEGS (diethylene glycol succinate) on Chromosorb W (80-100 mesh) was used for separation of methyl esters of fatty acids while maintaining the injection port at 220°C and oven at 190°C. The flow rates for the carrier nitrogen gas (IOLR-2; Indian Oxygen Limited, Kanpur) as well as the hydrogen gas (Standard: Indian Oxygen Limited, Kanpur) for the flame ionization detector were adjusted at 30 ml/min.

**Reagents**

(a) 0.2 N sodium methoxide solution in methanol: A 4.6 g quantity of metallic sodium, AR grade (Allied Chemicals
Limited, Kanpur), was treated with 1 litre methanol, AR grade (S.D. Fine Chemicals Limited), under ambient conditions.

(b) 2 N sulphuric acid solution: 52.2 ml of conc sulphuric acid, AR grade (Ranbaxy Laboratories Limited), were diluted in distilled water and made to 1 litre.

(c) Methyl orange indicator: 1% solution of methyl orange (S.D. Fine Chemicals Limited), in distilled water.

(d) Saturated solution of sodium chloride: Sodium chloride, LR grade (S.D. Fine Chemicals Limited), was dissolved in distilled water to maximum possible extent at room temperature.

(e) Petroleum ether (bp 40°-60°C), LR grade (S.D. Fine Chemicals Limited).

(f) Sodium sulphate (Anhydrous), AR grade (S.D. Fine Chemicals Limited).

(g) Diethyl ether, AR grade (S.D. Fine Chemicals Limited).

Procedure

A 5.0 g sample of oil with 16 ml solution of 0.2 N sodium methoxide (in methanol) was refluxed for 40 min in a 250 ml round-bottom flask on a boiling water bath. The reaction mix was cooled and acidified with 2 N sulphuric acid using methyl orange as an indicator. The contents of the flask were poured into an equal volume of saturated
sodium chloride solution in a separatory funnel and the methyl esters were extracted with 3 x 10 ml portions of petroleum ether. The combined extracts were washed with 10 ml portions of ice-cooled distilled water until the washings were neutral. The acid-free extract containing methyl esters was dried for 30 min over anhydrous sodium sulphate and filtered. The bulk of the petroleum ether of the extract was removed by evaporation on a boiling water bath and its last traces were removed under vacuum.

A 10% solution of methyl esters was prepared in diethyl ether and analysed by injecting its 0.4 µl aliquots with the help of a high pressure hypodermic syringe into the gas chromatograph operating under stabilised isothermal conditions. Gas chromatograms of the authentic samples of fatty acid methyl esters were also obtained for reference purposes. The fatty acids in chromatograms of the experimental samples were identified by their retention time in comparison to that of the reference fatty acids in their standard chromatogram.

Calculation

The fatty acid composition of the experimental oil samples was calculated by triangulation method in which the area of each peak corresponding to a fatty acid was calculated by multiplying its height with width at half height,
adding the area of all peaks (total area), and expressing the area of a particular peak as a percent of the total area.

3.2.19. Determination of Trans-isomers

The control and the hydrogenated peanut oil samples were also analysed for their content of trans-isomers by infra-red spectroscopy\(^5\) (AOCS : Cd 14-61) as follows:

**Equipment**

The infra-red spectrophotometer (Perkin Elmeyer 599B; Perkin Elmeyer Corporation, Norwalk, Conn. 06854, U.S.A) covering 9-11 µ spectral region with wave length scale readable to 0.01 µ and equipped with cell compartment for holding 0.5 mm cells was used for determination of isolated trans-isomer content of refined peanut oil and its hydrogenated samples.

**Reagents**

(a) Carbon disulphide, AR grade (J.T. Bakers Company, Phillipsburg, NJ 08865).

(b) Primary standard methyl elaidate : Prepared by esterification of elaidic acid (Approx. 99%; mp 44°-45°C; Sigma Chemical Company, Saint Louis, MO 63178, USA) with methanol in presence of sulphuric acid as catalyst.
Procedure

The methyl esters of experimental oil samples were prepared by trans-esterification method (refer section 3.2.18). The standard solutions of the methyl esters of fatty acids of experimental samples as well as the primary standard were prepared by dissolving an accurately weighed sample (~0.2 g) in carbon disulphide and making its volume to 10 ml mark in a volumetric flask. Keeping the matching absorption cells in an upright position, one was filled with carbon disulphide (blank) and the other with a prepared standard solution with the help of a hypodermic syringe. The cells were placed in the reference and sample beam sample holders of the spectrophotometer. The wavelength transmittance curves for the experimental samples as well as for the primary standard were obtained.

From the wavelength transmittance curves, the percent transmittance of a sample at 10.36 µ was calculated by drawing a base line from 10.02 µ to 10.59 µ and measuring the distance from zero line of the recorder chart to the absorption peak ('ab') and distance from zero line of the recorder chart to the base line ('ac').

Calculation

The percent trans-isomer contents of the samples were calculated using the following relationship:
Trans as methyl elaidate (\( \chi \)) = \( \frac{a_{\text{sample}}}{a_{\text{methyl elaidate}}} \times 100 \)

Where \( a \) is the absorptivity, \( \chi/\beta c \),

\( A \) is the absorbance, \( \log_{10} 100/T \),

\( b \) is the internal cell length in cm,

\( c \) is the concentration of the solution of sample or standard in carbon disulphide in g/l,

\( T \) is the percent transmission, \( \frac{ab}{ac} \times 100 \)

Where \( 'ab' \) is distance from zero line of the recorder chart to the absorption peak, and

\( 'ac' \) is distance from zero line of the recorder chart to the base line.

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Figure 3.1 Standard curve for iron (Fe^{+++}) by thiocyanate method.

\[ Y = 0.0064 + 1.3487x \]

\( r = 0.9997 \)