Hydrogenation of Triglycerides (Oils)
Introduction

Oils and fats are essential nutrients in both human and animal diets. The fats are nothing but oil molecules with higher melting point; therefore, they are solid at ambient conditions. The principle source of oils and fats are meats, poultry, fish, dairy products, fruits and nuts. Major components of oils and fats are triglycerides i.e. esters of glycerine and fatty acids (Fig 1). The properties of different triglycerides (oils and fats) are dictated by the chain length of the fatty acid (mostly C4 - C24) and as well as the presence of number of double bonds per molecule.

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H \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \quad 11 \quad 12 \quad 13 \quad 14 \quad 15 \quad 16 \quad 17 \quad 18 \\
\text{H-C-O-OC-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \\
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\text{H}
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Fig. 1 : Structure of triglyceride (oil) molecule - an ester of glycerine and 3 fatty acids (C18)

Hydrolysis of triglyceride results in breakage of its molecule into glycerine and free fatty acid. Fatty acids, thus obtained are used as raw material to manufacture large number of oleo chemicals.

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\text{H} \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \quad 11 \quad 12 \quad 13 \quad 14 \quad 15 \quad 16 \quad 17 \quad 18 \\
\text{H-C-OH} \quad \text{HO-OC-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH} = \text{CH}\text{-CH}_2\text{-CH}_2\text{-CH} = \text{CH}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \text{ Stearic} \\
\text{H-C-OH} \quad \text{HO-OC-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH} = \text{CH}\text{-CH}_2\text{-CH} = \text{CH}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \text{ Oleic} \\
\text{H-C-OH} \quad \text{HO-OC-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH} = \text{CH}\text{-CH}_2\text{-CH} = \text{CH}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3 \text{ Linoleic} \\
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Glycerine 3 Fatty Acid Molecules of C18 Chain

Fig. 2 : Glycerine and fatty acids obtained after hydrolysis of triglyceride (oil) molecule
Fatty acid chains in triglycerides having double bonds are susceptible to attack by atmospheric oxygen, resulting in rancid odour, which is not acceptable to consumers. Oils and fats molecules having multiple (2 to 4) double bonds are more prone to rancidity as compared with those having single or nil double bond. Hence, to restrict deterioration of oil, it is necessary to minimize number of double bonds; this can be achieved by hydrogenating multiple double bonds to give single bond.

Conversion of 2 – 4 double bonds per fatty acid molecule to 1 double bond per molecule by hydrogenation process not only enhances stability of oils and fats but also offers improved taste due to softness of hydrogenated solid product. Edible products such as margarines, low fat spreads, cake shortenings and confectionery fats are made with oils containing certain concentration of solid fat content (SFC) that could give good mouth feel during consumption. Depending on the end use, SFC in the fat product could be modified during the hydrogenation of oil by selecting suitable catalyst as well as specific hydrogenation conditions.

In today’s world, oils and fatty acids hydrogenation is carried out using supported nickel as most appropriate catalyst to decrease the unsaturation. Though supported noble metal catalyst could be used for similar applications, nickel catalyst offers comparatively higher performance / price ratio.

Industrially, hydrogenation is used in large number of applications:

- Hydrogenation of palm oil using nickel catalyst changes the melting point of the triglycerides to the desired level in food applications (chocolates, pastry, ice-cream, puffs, vanaspati).

- Partial or brush hydrogenation of soybean oil using specially designed nickel catalyst gives product suitable to use as salad oil.

- Complete hydrogenation of castor oil is carried out at relatively lower temperature using highly active nickel catalyst to obtain a product that is suitable in manufacture of premium grade lubricants and greases.

Monarch Catalyst Pvt. Ltd. has developed indigenous technology for the production of dry reduced nickel catalyst for hydrogenation of edible oils and fatty acids. Now, it is a market leader in manufacture of different grades of such specialty nickel catalysts in India.
Hydrogenation of various feed stocks

Soybean Oil

Soybean oil is obtained from bean plant “Glycine max” and used for edible purpose. Unlike most common edible oils, it has higher concentration (7-8%) of linolenic acid (3 double bonds in a C18 fatty acid chain). Refined soybean oil contains low levels of catalyst poisons (phosphatides) and it requires lower dosage of nickel catalyst for hydrogenation as compared to other oils such as mustard and rice bran oil.

During hydrogenation, it was found that the initial rate of reaction is completely controlled by the rate of transport of hydrogen molecules from the bulk oil to the external surface of the catalyst. While in the final stage of the reaction to achieve very low iodine value, chemical kinetics plays an important role.

Hydrogenated soybean oil is used in manufacture of margarines or shortenings and also as cocoa butter substitute. Brush hydrogenation of soybean oil gives a product which is used as salad oil. Performance of different grades of catalysts and product quality obtained was measured in the lab using soybean oil under varying hydrogenation conditions.

MONCAT®3921 is selective for the hydrogenation of soybean oil to manufacture vanaspati and MONCAT®1061 is selective for making low-trans salad oil.

Fig. 3: Soya seeds

Fig. 4: Hydrogenation of Soybean Oil ($P = 1.0 – 1.5$ bar, $T = 180 – 190^\circ C$)
Palm Oil (refined CPO)

Palm tree (*Elaeis guineensis* Jacq.) is originated from West Africa and now it is cultivated in south-east Asia and South America on a large scale. Around 1848 the palm tree came to South-East Asia from West Africa for ornamental purpose and now it has become main crop of the country.

Palm tree produces large number of palm fruits in the form of a bunch. These fruits are made up of a hard kernel (seed – a white portion in the middle of the fruit) inside a shell (endocarp) that is surrounded by a yellow fleshy mesocarp. The palm oil is extracted from the fleshy mesocarp which contains about 56% of oil. The palm oil comprise 49% saturated fatty acids (i.e. ester of palmitic acid + stearic acid = 46.5% and ester of Myristic+lauric acid = 2.5%) and 51% of unsaturated triglyceride (ester of oleic + linoleic acid = 51%). The palm oil with initial iodine value of about 55 needs negligible level of hydrogenation to give a vanaspati grade fat.

![Bunch of palm fruits](image1)

![Cut palm fruit showing kernel in the middle](image2)

Also, palm oil is known to contain significant amount of the symmetrical Stearic+Oleic+Stearic - type triglyceride, but with a higher amount of oleic acid. This enables palm oil to undergo partial hydrogenation of oleic to stearic acid for the production of cocoa butter equivalent fats with the desired M.P. and hardness.

The palm oil with initial iodine value of about 55 needs negligible level of hydrogenation to give a vanaspati grade fat. Small quantities of MONCAT®3921 and MONCAT®2021 catalysts along with large quantities of spent catalyst are used in industry for manufacture of vanaspati from palm oil. However, most of the vegetable oils (including palm oil) are hydrogenated using relatively higher dosage of MONCAT®1051 for manufacture of hard vanaspati without increasing the melting point of the fat.
Fig. 7: Hydrogenation of Palm Oil (P = 1.0 – 1.5 bar, T = 180 – 190°C)

The palm kernel i.e. white portion in the middle of the fruit is obtained after the removal of flesh from the palm fruit and it is known to contain 46-48% oil. The palm kernel oil composition is rich in saturated fatty acids viz., Lauric and Myristic acid (I.V. = 18) similar to that of coconut oil (I.V. = 11), therefore, is a cost effective substitute for crude coconut oil in the production of premium grade soap). As this oil is rich in lauric acid, it is used in the synthesis of lauryl alcohol. Nickel catalyst is used to hydrogenate PKO to obtain a fat which is used in the manufacture chocolates.
Palm Stearine (PS)

Palm oil contains almost equal concentration of palm stearine and palm olein. Palm stearine is a triglyceride of saturates (stearic and palmitic acid) and it is white soft semi-solid in appearance. During fractionation of crude palm oil by cooling and settling process, the crude palm stearine (CPS) settles at the bottom as a soft solid layer. The top layer found to contain mainly palm olein which is a triglyceride of unsaturates (oleic and linoleic acid) and appears as clear wine red liquid.

Refined palm olein (after removing FFA and other impurities) is used directly for edible purpose and it could also be used for manufacture of vanaspati by catalytic hydrogenation.

Complete hydrogenation of palm stearine (triglyceride) gives a product with very low I.V. and with lower concentration of nickel soap in the product. Splitting of such low I.V. product gives palm stearine fatty acid and glycerine. Hydrogenation of refined palm stearine and blending with other oils is practiced in manufacture of margarine, shortening, soap, oleo chemicals and specialty fats (for coating in confectionery industries). The impurities present in palm stearine are removed during refining, bleaching and deodorizing stages. Therefore, refined, bleached and deodorized palm stearine (RBDPS) is comparatively easier to hydrogenate completely (IV < 0.6) using nickel catalyst.

**MONCAT® 2021** is a selective catalyst, best suited to hydrogenate RBDPS to achieve complete hydrogenation to achieve I.V. < 0.6).

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**Fig. 8:** Hydrogenation of Palm Stearin – CPS (P = 18 – 19 bar, T = 180 – 190°C, 60 min)
Castor Oil

Castor plant (Ricinus communis) is native to the Ethiopian region of tropical East-Africa, it has become gradually naturalized in tropical and warm temperate regions throughout the world. Weather in India and Brazil is suitable for castor cultivation. Also, south-western United States and China are known for production of castor oil.

The spiny seed pod or capsule is composed of three sections or carpels which split apart at maturity. Each section (carpel) contains a single seed, and as the carpel dries and splits open, the seed is often ejected with considerable force.

Although the seeds or beans are extremely poisonous, they are the source of numerous economically important products and are one of earliest commercial products. Castor beans have been found in ancient Egyptian tombs dating back to 4000 BC, and the oil was used thousands of years ago in wick lamps for lighting.

Castor oil is extracted from castor beans by either pressing or solvent extraction and it is used in making soap, inks, and plastics; for preserving leather; as an illuminant; in Turkey red oil for dyeing and finishing textiles; and in brake fluids and certain insecticidal oils. Castor wax, a hard wax produced by the hydrogenation of pure castor oil (using nickel catalyst), is used in polishes, electrical condensers, carbon paper, and as a solid lubricant.

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**Fig. 10:** Fatty acid chain in castor oil molecule showing CHOH group

Presence of hydroxyl group at C-12 position in castor oil provides opportunity for large number of applications after low temperature (125 – 145°C) hydrogenation. Higher temperature (> 145°C) could result in hydrogen starvation condition in the reactor (autoclave) and loss of hydroxyl value in the product which has less commercial value. **MONCAT®2021** is suitable to hydrogenate castor oil (to a final iodine value of 2 – 3) at low temperature (125 – 145 °C) and to retain hydroxyl value (around 159) in the product.
Fig. 9: A bunch of castor fruits

Fig. 10: Dried castor fruit and seed within

Fig. 11: Hydrogenation of Castor Oil ($P = 10 – 12$ bar, $T = 125 – 135^\circ C$),
$Time = 6 - 8$ hours

Higher pressures ($10 – 12$ bar) and lower temperatures ($125 – 145^\circ C$) are beneficial to retain high OH value and good colour in the product. Though the temperature at the end of reaction (final IV < 10) could be relaxed to $145 – 155^\circ C$, it is crucial to maintain < $145^\circ C$ during the IV drop from 88 to 10.
General Applications

MONCAT®2021 and MONCAT®3921 are used to hydrogenate cotton seed, sunflower, rapeseed, rice bran and mustard oils. Depending upon the product end use and hydrogenation facilities available in the plant one can select the particular grade of catalyst and dosage pattern. Our technical team is available to provide appropriate suggestions for application of different grades of catalysts for various oils and fatty acids.

Fig. 12: Cotton flower

Fig. 13: Cotton seeds with and without lintel

Fig. 14: Sun flower

Fig. 15: Sunflower seeds
Catalyst Grades

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Application</th>
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<tbody>
<tr>
<td>MONCAT®3921</td>
<td>Catalyst for Vanaspati / Edible fat (partial hydrogenation)</td>
</tr>
<tr>
<td>MONCAT®1061</td>
<td>Catalyst for Low trans fat / Salad oil (brush hydrogenation)</td>
</tr>
<tr>
<td>MONCAT®1051</td>
<td>Catalyst for trans selective speciality fat (partial hydrogenation)</td>
</tr>
<tr>
<td>MONCAT®2021</td>
<td>High active catalyst for hydrogenation of mustard, palm stearine and other triglycerides (oils). Also, Catalyst suitable for Low temperature hydrogenation of Castor oil</td>
</tr>
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Post Hydrogenation Filterability

When compared with competitor’s catalysts for filterability after hydrogenation, MONCAT® catalysts give quite comparable results when tested under identical conditions (i.e. using same filtration equipment & other parameters).
MONCAT® catalysts handling Information

Physical form:

MONCAT® catalysts are manufactured in pastil form. The pastils are nothing but small droplets made up of dispersion of active metal species in hydrogenated vegetable oil (solid at room temperature). Catalyst pastils are not only easy to handle but also give no dusting while transferring or charging the catalyst. Also, coating of metal with vegetable fat renders active nickel metal less prone to exposure to air and thereby minimizes loss in activity during storage.

Packaging:

Catalyst pastils are packed in standard metal or HDPE drums. Also, they are packed in customer specific packaging materials (Small bags, Jumbo bags & Paper bags) to match the handling facility / practices at the customer’s end.

Shelf Life:

➢ Catalyst stored in closed container retains performance for minimum one year.

➢ Store catalyst in cool and dry place.

➢ Refer our MSDS for safety instructions.

➢ Catalyst is Kosher Certified ★
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