

Technological Approaches to Minimize *Trans* Fatty Acids in Foods

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Trans fatty acids can be produced by isomerization of *cis* unsaturated fatty acids (UFAs) from a natural source that is enzymatic hydrogenation or biohydrogenation) and or industrial source for example, mainly partial catalytic hydrogenation (PCH). The overconsumption of trans fatty acids except some conjugated linoleic acid could predispose the consumer to a higher risk of cardiovascular diseases as well as to other non communicative pathologies (that is cancer, and type 2 diabetes).

Occurrence of *trans* fatty acids

With rare exceptions, almost all edible fats and oils of plant origin contain unsaturated fatty acids in the *cis* conformation. TFA are found naturally, in low levels, in meat and dairy products as the result of microbial hydrogenation of *cis*-unsaturated fatty acids in the stomach of ruminant animals. However, the major source of TFA is products containing industrially produced partially hydrogenated vegetable oils. In addition, small amounts of TFA isomers are found in refined edible oils due to the high temperatures used during the deodorization procedure. *Trans* fatty acids content in different food products is as follow:

Natural sources (Meat and dairy products)	
Product	g/100g
Beef	1
Beef tallow	5-6
Butter	2-7
Whole Milk	0.07-0.1
Partially hydrogenated oil based products (10 to 60%)	
Shortenings	10-33
Margarine/Spread	3-26
Bread/Cake product	0.1-10
Cookies and creakers	1-8
Salty snacks	0-4
Cake frostings and sweets	0.1-7

As the trans fatty acids possess cardiovascular diseases, so there is a need to minimize these trans fatty acids in food products. The following technologies can be used to modify trans fatty acids in foods:-

1. Modification of hydrogenation process
2. Fat interesterification
3. Genetic modification
4. Fractionation

Fat hydrogenation

Vegetable oils have a high content of polyunsaturated fatty acids (eg, linoleic and linolenic acids) and are prone to oxidation. Industrial hydrogenation is performed to increase the stability, resistance to oxidation, and shelf life of the oil. In addition, hydrogenation raises the melting point of unsaturated vegetable oils, which are liquid at room temperature, converting them into solid/semisolid fats suitable for products such as shortenings and margarines for which a solid fat structure is essential.

The edible oil industry has relied heavily on nickel (Ni) catalysts to manufacture partially hydrogenated vegetable oils. These catalysts offer several advantages, including high activity, tailored linoleic and linolenic selectivities, low cost, and ease of separation from the processed oil. Unfortunately, these catalysts also isomerize the naturally occurring *cis* double bonds of unsaturated fatty acids to the *trans* configuration. A simplified description of the hydrogenation process sheds light on the formation of *trans* isomers, and provides a logical starting point for exploring techniques to reduce *trans* isomers in a partially hydrogenated oil product.

The hydrogenation process consists of a series of reaction steps. When the fat molecule is adsorbed to the surface of the Ni catalyst, the double bond (the point where the molecule is unsaturated) bonds with the active site on the catalyst. The activated fat molecule can then react with a hydrogen molecule adsorbed on the catalyst surface, eliminating the unsaturation. If no hydrogen is available, the double bond can reform and leave the catalyst surface. The double bonds of a fat molecule have an almost equal chance of reforming either in the *cis* or the *trans* form. Thus half or more of the molecules that contact the catalyst where hydrogen is not available will form *trans* fats.

This leads to three strategies for reducing *trans* formation during hydrogenation to produce a partially hydrogenated oil with increased saturation:

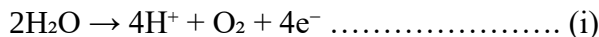
1. Increasing the hydrogen pressure so as to increase the amount of hydrogen on the catalyst surface.
2. Using a less active catalyst with fewer active sites, so as to ensure that the catalyst surface always has enough absorbed hydrogen near the active sites. This can be achieved by producing catalysts with smaller surface area and less activation, or by pre-poisoning the catalyst and by blocking most of the active sites with a catalyst poison such as sulphur.
3. Slowing the reaction down so as to allow more hydrogen movement to the catalyst surface before the fat molecule is released by the catalyst. This is most simply done by decreasing the temperature of the reaction.

ii) Electrochemical hydrogenation

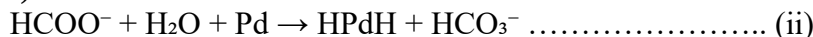
Use of electrochemical hydrogenation instead of gas hydrogenation has been developed. Many studies have demonstrated that electrochemical hydrogenation offers an advantage of producing final product with *trans* isomer fatty acids at lower levels than gas hydrogenation and subsequently much less thermal degradation, which could significantly reduce the consumer's concerns. In the process of electrochemical hydrogenation, the charge carried by the electron is involved in the reactions of various hydrogen donors and solvents, and the hydrogen concentration on the catalyst surface can be partially controlled by the applied current. Since hydrogen is generated in situ directly over the catalytic surface, there is no need for enhancement of hydrogen transfer rate, thereby eliminating the requirements to operate at high temperature (up to 150–225°C) and high pressure (10–60 psig) that are required by the traditional gas hydrogenation. Most importantly, the expected targets of reducing TFAs while increasing the selectivity of unsaturated fatty acid can be achieved.

Principle

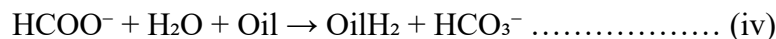
Inside the electrochemical reactor where reduction and oxidation reactions occur at the cathode and anode, respectively, the electrons move from the anode to the cathode via the circuit and the protons migrate through the Nafion 117 cation membrane to the cathode under the applied current. In the present study, H₂O is electrochemically oxidized to electrons and protons at the anode area as shown in reaction



Meanwhile, in the cathode chamber, the sequential chemical reactions between the formate ions and unsaturated fatty acids of oil in the presence of Pd as a hydrogenation catalyst occur (as shown in reaction ii, iii) and the overall oil hydrogenation reaction could be summarized (reaction iv & v)



Overall reaction:



The product bicarbonate ions of reaction (can then be reduced electrochemically to formate ions at low pH on the surface of cathode, which regenerates the formate ions (v)

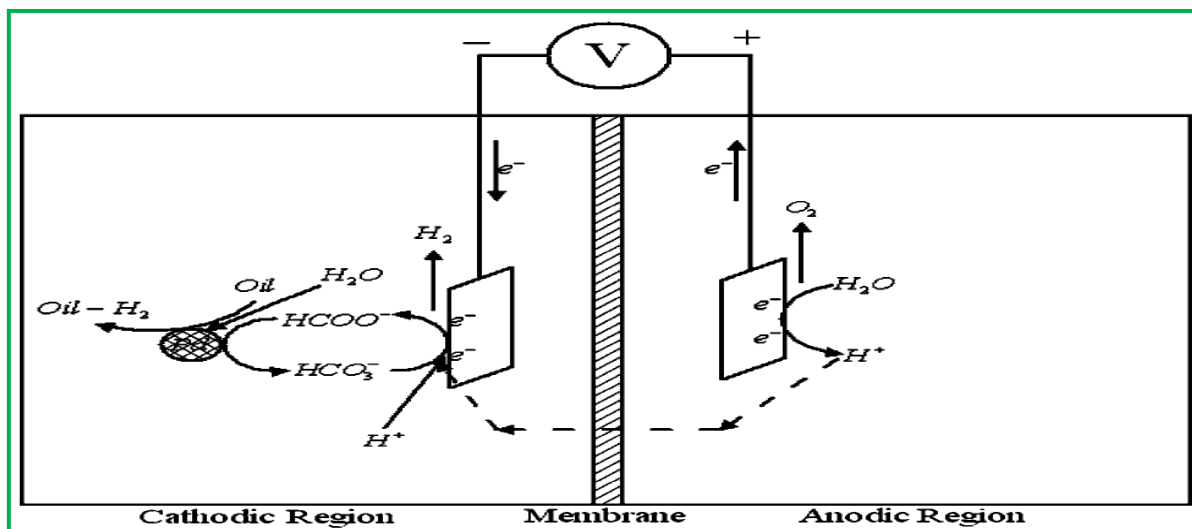


Fig : Principle of the diaphragm hydrogenation with formate

iii) Hydrogenation using supercritical carbon dioxide

Hydrogenation using supercritical CO_2 provides an alternative to partial catalytic hydrogenation. Supercritical carbon dioxide is used as a reaction medium for hydrogenation reaction in batch/continuous mode and heterogenous/homogenous phase. Improved reaction rate, higher catalyst efficiency, improved process safety, tunable reaction selectivity are some of the advantages experienced on carrying out the reaction in supercritical carbon dioxide. Supercritical hydrogenation provides the more stereospecific *cis* configuration comparative to *trans*.

Fat Interesterification

The technique involves exchanging fatty acids between the TAGs in a mixture. It is a catalytic reaction, involving the hydrolytic release of some fatty acids, and their random reattachment to the glyceride. The reaction is catalyzed chemically or by enzymes. Chemical interesterification (CIE) lacks specificity and several TAG products which may not be desired are produced in the blend. Interesterification reaction somewhat, by removing desired, high melting point fractions as the reaction proceeds. Chemical interesterification is relatively inexpensive and is in industrial practice, particularly in Europe, to produce plastic saturated fats with zero or low trans fat levels.

Enzymatic interesterification (EIE) offers more control over the reaction products that form. Enzymes are highly specific, and may be selected to cleave specific ester bonds in terms of their position on the molecule. EIE can be carried out at lower temperatures than CIE, so less thermal degradation occurs. Unlike chemically interesterified oils, enzymatically interesterified oils do not require washing and bleaching. Low or zero trans plastic or solid interesterified fats produced by either chemical or enzyme interesterification will contain the saturated fats of the original feed stocks.

Genetic modification

Modern mutation and transgenic technologies have opened the possibility for plant breeders to incorporate a range of fatty acid oil profiles and other traits of economic importance into oilseed crops. New fatty acid profiles that are fundamentally different to the composition of the normal (original) oil have been identified in many oilseed species. Genetic molecular biology tools offer a more direct way to modify fatty acid profile by altering the enzymatic pathway involved in the polyunsaturated fatty acids biosynthesis in the plants. Thereby, the expression of *FAD₂* genes, which encode delta 12 (Δ-6) fatty acid desaturase involved in oleic acid (18:1) biosynthesis can be inhibited in order to significantly increase oleic acid concentration in seed oil.

Fractionation

Fractionation is widely used to improve the functionality of fats and results in products with differing melting points, solid fat contents, and hardness. Plastic fats with zero trans fatty acids but having high levels of saturates can be prepared by fractionating palm, mango kernel and mahua fats and recombining the fractions in different proportions. The fractionating of high stearic canola and soybean oils to recover saturated fat fractions with useful properties for manufacturing margarine and shortening has been demonstrated. Fractionation involves selectively crystallizing TAG species with higher saturates and separating them from the liquid oil. This technique is used during the “winterization” of oils to remove high melting TAGs which would otherwise crystallize during storage. Fractionation of palm oil results in the unsaturated palm olein and saturated solid fractions having desirable melting properties for use in confectionary applications. Palm olein has high oxidative stabilities suitable for frying. The higher melting fractions are used as cocoa butter substitutes or basestocks in margarines and shortenings.

Conclusion

The high temperature in the partial hydrogenation process leads to production of trans fatty acids. The various technological interventions like modified hydrogenation, interesterification, genetic manipulation and fractionation can be used for reducing trans fatty acid content in fat. Enzymatic interesterification appears to be the most versatile and least cost process available to oil refiners to reduce or eliminate trans fats from the food supply