Crucial ingredient in h

Catalysts are an essential part of the hydrogenation process of vegetable oils as, without them, the necessary reactions would not be possible. Dr Paul Hudson of Johnson Matthey explores the basics of catalysts, including what catalysts are, why they are needed, how they work and what are the properties of the best catalysts for different applications

Successful catalytic hydrogenation of edible oils began with the work of Wilhelm Norman in 1902. Catalytic hydrogenation was important in giving a new route to manufacture solid fats required for margarine production which, until Norman's invention, were at risk of being in short supply. The invention meant a wider choice of raw materials was available to make margarine at the right consistency than just the animal fat that had been mostly used until that point.

Though the invention of techniques for converting liquid oils into solids fats was significant, the ability to scale up hydrogenated fat production took time to catch up. Norman helped Joseph Crosfields develop a full-scale plant for the production of hydrogenated fats in Warrington, England, in 1907.

In 1911, Norman was instrumental in the commissioning of the Oelwerke Germania fat hardening plant at Emmerich, Germany, where nickel hydrogenation catalysts continue to be manufactured to this day.

Early catalysts were variable, having poor activity/selectivity, and – in combination with low-quality hydrogen – poorly pre-refined oils and the use of relatively simple plant equipment meant the process was far from optimised, with reactions taking a long time and leading to variable products.

Nickel was used as the catalyst of choice even from the early days of oil hydrogenation. It remains the metal of choice for most edible oil hydrogenation reactions due to it being cost-effective and versatile, working across a wide range of feeds.

The what and why of catalysts

A catalyst is a substance that accelerates a chemical reaction but is not consumed in the reaction and does not affect its equilibrium. A catalyst effectively reduces the energy barrier to a reaction, which allows the reaction to take place. Without a catalyst,

the reaction may be very slow or not possible at all (*see Figure 1, page 20*).

Catalysts used for edible oil hydrogenation are processing aids and not food ingredients, which means they are used in the processing of foodstuffs but are entirely removed from the products in post-processing. In the case of edible oil hydrogenation, it may appear that the catalyst is consumed during the reaction as reuse of the catalyst is only possible to a limited extent.

Although hydrogenation catalysts require regular replacement, they are not technically consumed. Rather, they are deactivated and hence need replacing.

Hydrogenation of fatty acids in triglyceride feeds can be performed for edible oil applications where hydrogenated fats are required or for technical applications where hydrogenated fatty acids are the product. Hydrogenation of edible oils is done to improve the oxidative and flavour stability or melting behaviour of oils.

High levels of unsaturation in oils lead to a large number of double bonds in the triglycerides, which decreases the oxidative and flavour stability for the oil. The amount of unsaturation is characterised by the iodine value (IV) of the oil, with higher IV indicating more unsaturation, or more double bonds present.

By hydrogenating the oils to reduce the number of double bonds (increase saturation/decrease IV), the shelf life and flavour stability of the oil can be greatly increased, which improves both the sustainability of edible oils, by reducing waste, and the profitability for oil producers and vendors.

The amount of or type of unsaturation present in oils also influences the melting behaviour of the oil. Increased unsaturation means a lower melting point, so when an oil is hydrogenated – which decreases the amount of unsaturation – the melting point of the oil increases.

Through catalyst selection and process

hydrogenation process

optimisation, it is possible to produce oils and fats with increased melting points or potentially more demanding melting profiles.

Hydrogenation of oils generates fats used in a wider variety of products than would be possible with an unmodified oil feedstock, such as high melting point frying/bakery fats and steep melting curve confectionery fats through to salad oils that do not have solids present at room temperature but do have improved oxidative stability.

What makes a good catalyst?

A catalyst is formulated to optimise effectiveness in particular applications. A nickel hydrogenation catalyst for triglycerides/fatty acids is essentially made up of three parts: active nickel, support and the encapsulating fat.

It is the nickel surface area that is responsible for the activity of the catalyst and catalyses the reaction between hydrogen and the double bond in fatty acids.

The support is present to allow a high dispersion of the nickel so that more activity can be obtained using effectively lower levels of nickel.

Modern hydrogenation catalysts are usually supplied pre-reduced and encapsulated in a hardened fat. The pre-reduction of the catalysts means an easy start-up of the hydrogenation process, which increases efficiency and reduces cost for the user by eliminating a lengthy reduction step. The encapsulating fat protects the reduced nickel metal from air, which makes the handling of the catalysts safe and easy.

Hydrogenation of oils is a three-phase reaction, where hydrogen gas is mixed into the liquid oil with the solid catalyst also dispersed through the mix. The hydrogenation reaction takes place when the hydrogen and a triglyceride adsorb onto the nickel located on the catalyst surface.

Without the presence of the catalyst, no reaction would take place. Various parameters govern the effectiveness of the hydrogenation reaction, including the oil feedstock, the catalyst and process parameters. Many properties can be used to describe a catalyst:

Activity

The primary function of the catalyst is to allow the reaction between hydrogen and the double bonds in the oil to take place. The activity of a catalyst describes how effectively a catalyst will drive a reaction, all else being equal.

A more active catalyst will mean faster reactions, whereby the IV drop is more rapid. However, the maximum activity of a catalyst might only be realised if the reaction feedstock is sufficiently 'clean' and the process used is sufficiently optimised.

Nickel loading and surface area

The nickel content of a catalyst is easily quantifiable and tells the user what proportion of a catalyst is nickel metal. In the past, higher nickel content may have meant a higher performance hydrogenation catalyst.

However, with improved formulations and better manufacturing of catalysts, it is not just the amount of nickel in a catalyst but how the nickel is present in a catalyst that determines how active the catalyst will be.

For the same amount of nickel in a catalyst, a higher dispersion of the nickel leads to smaller nickel crystallites on the catalyst surface and a higher overall 'nickel surface area' for the same amount of metal (*see Figure 2, page 20*).

Increased nickel surface area means it is possible to squeeze extra performance per mass of nickel. This is to be balanced with the ability of a catalyst to resist deactivation.

More highly dispersed nickel may be more highly active to begin with, but may be more sensitive to deactivation, for example by water.

Polyene selectivity

Catalysts are described by selectivity of two types. The first is polyene selectivity which is the ability of a catalyst to effectively hydrogenate fatty acids sequentially so that the hydrogenated product has a more desirable fatty acid profile (*see Figure 3, page 22*).

A highly polyene selective catalyst will preferentially hydrogenate the most unsaturated fatty acids first, such as linolenic acid (C18:3), which increases the proportion of linoleic acid.

Afterwards, the linoleic acids (C18:2) will preferentially be hydrogenated to oleic acid (C18:1).

Finally the oleic acid is hydrogenated to saturated stearic acid (C18:0).

A polyene selective catalyst is useful for increasing oxidative stability of an oil by removing the linolenic acid while producing minimal saturated fat, for example.

Trans selectivity

Trans selectivity describes how effectively hydrogenation of oils takes place without producing the *trans* configuration of double bonds in the product.
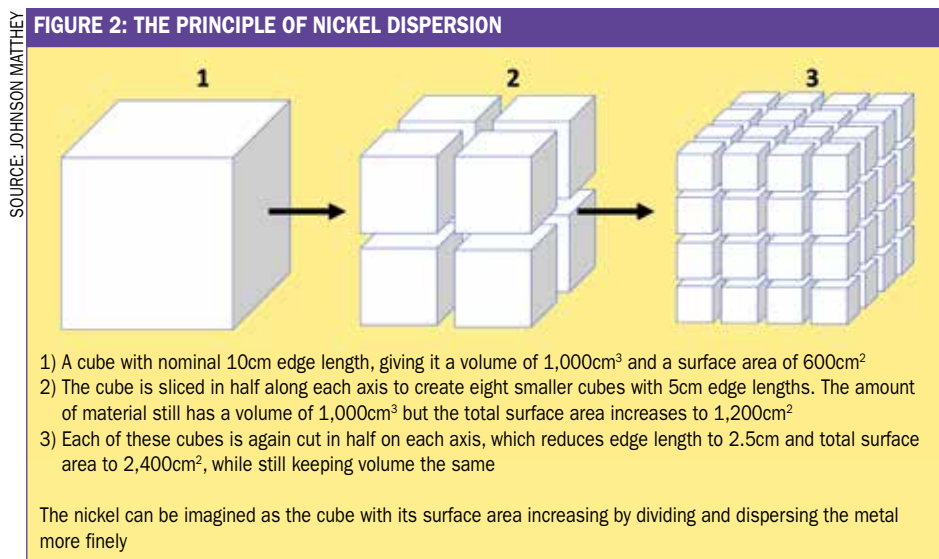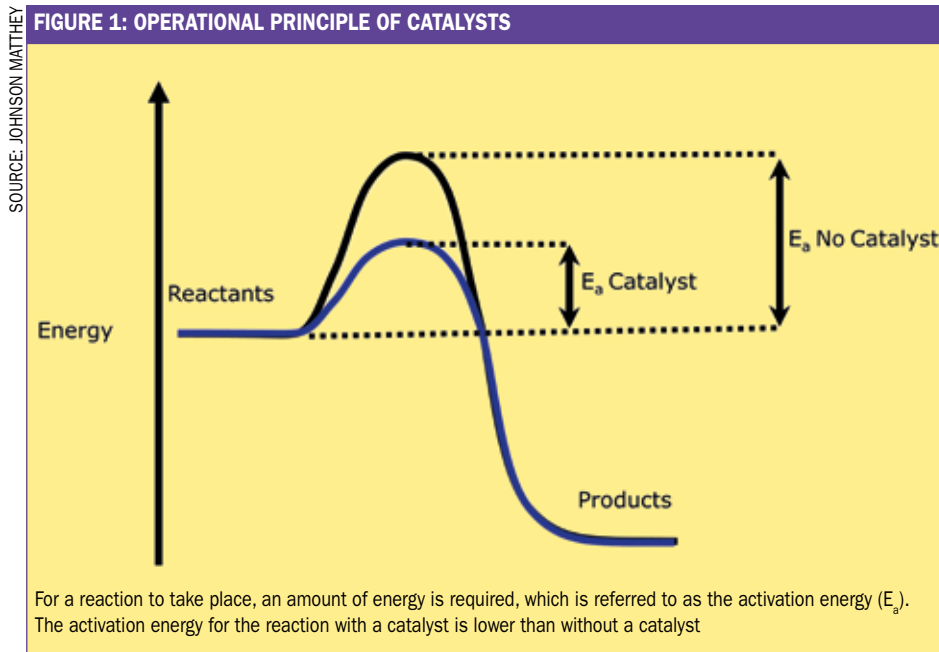
Minimising *trans* formation during hydrogenation is largely a question of process optimisation. *Trans* fats form when the catalyst surface enters a state of being hydrogen-starved.

When insufficient hydrogen is available at the surface of a catalyst, double bonds that adsorb onto the catalyst surface may not be hydrogenated.

In this case, the molecule may desorb and diffuse back into the bulk oil unchanged.

Otherwise, the double bond in the molecule may isomerise to a *trans* configuration before desorption. This is how *trans* fats are formed.

To reduce the proportion of *trans* fats that are produced, it is important to maintain saturation of the catalyst surface with hydrogen.

FIGURE 1: OPERATIONAL PRINCIPLE OF CATALYSTS

SOURCE: JOHNSON MATTHEY

For a reaction to take place, an amount of energy is required, which is referred to as the activation energy (E_a). The activation energy for the reaction with a catalyst is lower than without a catalyst

FIGURE 2: THE PRINCIPLE OF NICKEL DISPERSION

SOURCE: JOHNSON MATTHEY

1) A cube with nominal 10cm edge length, giving it a volume of 1,000cm³ and a surface area of 600cm²
2) The cube is sliced in half along each axis to create eight smaller cubes with 5cm edge lengths. The amount of material still has a volume of 1,000cm³ but the total surface area increases to 1,200cm²
3) Each of these cubes is again cut in half on each axis, which reduces edge length to 2.5cm and total surface area to 2,400cm², while still keeping volume the same

The nickel can be imagined as the cube with its surface area increasing by dividing and dispersing the metal more finely

Resistance to deactivation

Some substances act to reduce catalytic activity. Examples in edible oils are sulphur- or phosphorous-containing materials.

A high level of such materials in a hydrogenation feed (due to lower quality/'dirty' feed being used) will increase the time required for the hydrogenation to take place – if it is possible to attain target specifications at all – or the amount of catalyst required for the hydrogenation reaction.

Increased catalyst loading is required due to the catalyst effectively cleaning the oil by absorbing the substance which acts to deactivate it. Excess catalyst over and above that required to clean the oil retains catalytic activity and performs the hydrogenation reaction.

Differentiation of catalysts

Nickel hydrogenation catalysts are not all alike. Extensive R&D efforts mean catalysts are researched and formulated for specific applications and to make specific products from particular feedstocks. For example, catalysts for hydrogenating triglyceride feeds will not be suitable for hydrogenating fatty acid feeds.

Highly technical modern catalysts are formulated to have higher activity per amount of metal, although higher metal loading does not guarantee a better catalyst.

Differentiation between catalysts for the same application comes from the effectiveness of the catalysts in consistently achieving the desired product in the desired time in a cost-effective manner overall. The catalyst is likely the most expensive material in the production of hydrogenated fats and, with modern manufacturing practices, a high quality catalyst should behave as expected time and time again.

Hydrogenation is possible with a wide range of feeds – from highly unsaturated soyabean through to more highly saturated oils such as palm oil. The same catalysts may be used across the range of feeds but the feedstock itself can introduce variability in terms of the outcome of the reactions.

Oil feeds from different plants have varying fatty acid profiles, levels of free fatty acids and levels of deactivating substances in their makeup. These can even vary for oil from the same plant depending on how the plant was grown and the level of refining of the oil.

Palm oil is an example of an oil with a greater proportion of saturated fat than other plant-based oils. This is compared to soyabean oil, which can have relatively high levels of linolenic fatty acid.

Soyabean oil is usually considered an example of a 'clean' oil, usually having relatively low levels of substances that inhibit catalyst activity, such as sulphur and phosphorous, whereas canola oil is relatively 'dirty', having higher levels of deactivating materials. Effective refining of oil prior to hydrogenation not only means a higher quality final product but also protection for the hydrogenation catalyst from deactivation during the process.

Variability in the composition and level of contaminants in an oil mean hydrogenation of oils can, at times, give surprising changeability in the apparent effectiveness of a catalyst even when using high quality catalysts and in a well-controlled process.

Hydrogenation process parameters

Hydrogen has low solubility in feed oils, so working with high hydrogen pressure in a reactor increases the amount of hydrogen available to react with the oil at the catalyst surface. If the amount of hydrogen is low, the reaction rate will be low and increased *trans* fat will be formed, which may be undesirable.

Conversely, if high hydrogen pressure is used, the reaction will be shorter/faster and less *trans* fat will be formed. The tradeoff is that polyene selectivity of the reaction is reduced under higher pressure, meaning more saturated fat will likely be produced, which again may be undesirable.

A high temperature reaction will increase the hydrogenation reaction rate, leading to shorter reaction times to hit the target IV.

However, increased temperature will also decrease hydrogen solubility in the oil, meaning less will be available for reaction at the catalyst surface, which in turn means the proportion of *trans* fat produced during the reaction will likely increase.

Mixing is an occasionally overlooked aspect of the hydrogenation reaction but it is critical in ensuring that the mixing of the solid/liquid/gas is effective enough to maximise the efficiency of the hydrogenation reaction.

Good mixing means hydrogen is optimally available at the catalyst surface and the reaction can proceed with maximum efficiency. If mixing is poor, the catalyst surface can become hydrogen-starved, which will reduce the reaction rate and lead to increased *trans* fat formation.
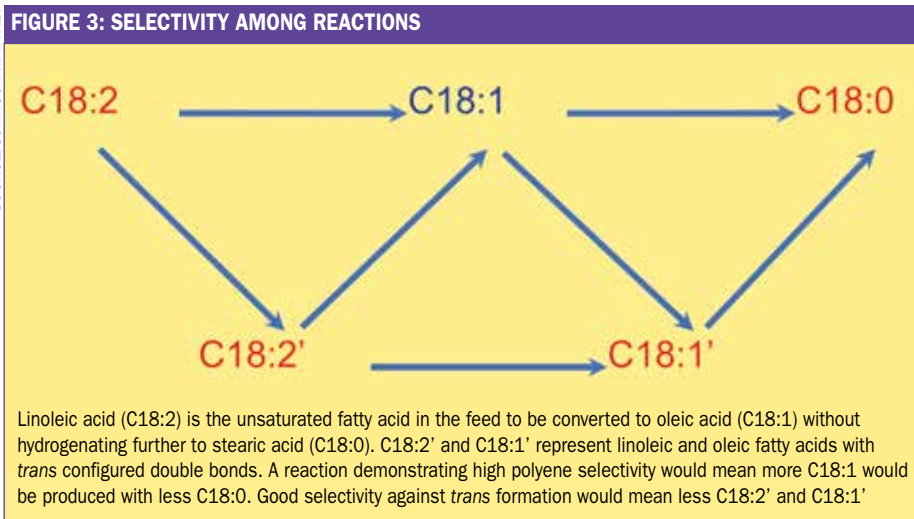
Limitations and expectations

Modern plant equipment allows detailed monitoring, control and accurate metering of raw materials, which means product IV is straightforwardly targeted for a hydrogenation reaction.

The volume of hydrogen consumed in a reaction can be monitored and the volume of hydrogen required to achieve a specified IV is easily calculated prior to reaction. Therefore, when that known volume of hydrogen is consumed, the reaction is stopped knowing the IV target has been achieved.

The IV of the product is closely related to the melting point of the fat, which, in turn, can be better characterised by a solid fat content (SFC)

SOURCE: JOHNSON MATTHEY

FIGURE 3: SELECTIVITY AMONG REACTIONS

Linoleic acid (C18:2) is the unsaturated fatty acid in the feed to be converted to oleic acid (C18:1) without hydrogenating further to stearic acid (C18:0). C18:2' and C18:1' represent linoleic and oleic fatty acids with *trans* configured double bonds. A reaction demonstrating high polyene selectivity would mean more C18:1 would be produced with less C18:0. Good selectivity against *trans* formation would mean less C18:2' and C18:1'

measurement. Targeting a low IV for complete hydrogenation is straightforward and the reaction simply continues until the IV is achieved according to the hydrogen consumption.

Targeting an intermediate IV is likely to be required for improving oxidative stability or specific melting behaviour.

Using slip melting point as a target is again straightforward, as the hydrogenation can be adjusted through iterative testing to achieve the required melting point.

Achieving more complex product properties, like solid fat content at varying temperatures, is a highly demanding application that may be difficult or impossible to achieve with hydrogenation alone. Some amount of product formulation or compromise on product properties may be required, as well as the hydrogenation of the feed.

Types of hydrogenation catalysts

There are multiple ways hydrogenation catalysts can be employed depending on the application of the hydrogenated fat. Full or dead-end hydrogenation involves the removal of effectively all double bonds from an oil feedstock by a highly active catalyst.

Full hydrogenation is used where maximum oxidative stability or fully hardened fats with high melting points are required, such as for use as frying fats, for further formulation into products such as margarine, or in non-food applications such as naturally-derived candles. In modern times, fully hydrogenated fats are also used as interesterification feedstock.

Partial hydrogenation refers to hydrogenation where the target is removal of *some* of the double bonds in the feed oil. An example of partial hydrogenation would be preferential conversion of linolenic fatty acid groups in a feed to linoleic/oleic fatty acids whilst producing as little stearic (fully saturated) fatty acid as possible. Partial hydrogenation improves the properties of oils but has the downside that it produces *trans* fats.

In some applications, such as cocoa butter substitutes/replacements (CBS/CBR), the steep melting profile of *trans* fat is the only way to achieve desired product properties.

CBR/CBS require steep melting curve fats to ensure the fats in confectionery goods remain solid at room temperature for transport and storage, but melt completely when being consumed as they would otherwise diminish the pleasant mouthfeel and sensory experience consumers enjoy. Hydrogenation of oil using sulphided nickel catalysts allows fats to be produced with preferential *trans* fat production, which can then be further formulated into products.

Fatty acid hydrogenation can be performed before or after splitting the triglyceride into fatty acids and glycerol. Fatty acids are also hydrogenated to increase oxidative stability and alter melting behaviour, but the catalysts used are different to those used for triglyceride feeds.

Hydrogenation of fatty acid feeds and feeds high in free fatty acids (FFAs) can lead to nickel soap formation during the reaction. Soap formation not only reduces catalyst activity, but the hydrogenated products may also require more post-reaction clean up to remove nickel soaps formed by the FFAs.

Vacuum distillation or neutralisation of oils prior to hydrogenation will help reduce FFAs and protect the catalysts and product from the problems of nickel soap formation.

Use of specialist catalysts resistant to soap formation will give superior results versus more conventional nickel catalysts and will lead to more effective hydrogenation of the feed.

Hydrogenation of triglycerides and fatty acids is a complex reaction, but it is better understood now more than ever. Advanced catalyst formulations and process design/control mean reactions can be optimised to high efficiency, giving predictable results and consistent products in a cost-effective manner.

With an increasing world population and a drive for sustainable use of resources, hydrogenation of oils and fatty acids will continue to be required to support the global need for oils and fats in foodstuffs as well as naturally derived ingredients for consumer products like detergents and cosmetics. ●

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PHOTO: JOHNSON MATTHEY

JOHNSON MATTHEY'S CATALYST MANUFACTURING FACILITY IN EMMERICH, GERMANY