

SCI LECTURE PAPERS SERIES HYDROGENATION – USE IN FRYING OILS

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The process for the liquid-phase hydrogenation of fatty oils was patented in 1903 by W. Normann, with hydrogenation being first carried out on a limited scale in the UK around 1906 for the modification of Whale Oil. It was not until 1909, when Procter and Gamble acquired the American rights to the Normann patent, which by this time had been passed to Joseph Crosfield and Sons, that hydrogenation on an industrial scale first began to take off.

In 1911, P+G launched Crisco, a hydrogenated Cottonseed shortening. The launch was met by a storm of controversy eventually leading to the American courts invalidating the P+G patent claim. This in turn cleared the way for the manufacture of hydrogenated products by other companies. Since this time hydrogenation has become, and still remains, the most popular method for modifying oils.

Over the past 85 years the actual process of hydrogenation has changed very little, the main advances have been in the area of catalysts, allowing for increasingly sophisticated products to be made.

The main objectives of hydrogenation can be summarised as follows:

- improve stability
- change melting characteristics/behaviour
- improve colour

For the purpose of this paper we will be concentrating on the first of these points, improving stability, and relating it to oils and fats used in frying.

For light duty frying (home or occasional restaurant) where the oil is used once and then discarded, a standard well refined vegetable oil will suffice. For heavy duty, multiple use applications such as deep frying a higher degree of stability is required and typically these products will be hydrogenated.

There are many types of solid, liquid and semi-liquid frying shortenings available on the market today, all however are manufactured to very much the same criteria.

Key requirements of a Frying Oil:

- oxidative stability
- flavour stability
- acceptable shelf life
- good fry life
- nutritionally acceptable
- low in saturates
- low in *trans*
- acceptable eating quality

Oxidative stability

The rate of oxidation can be linked directly to type and extent of unsaturation.

Oxidation rate linked to unsaturation

C18:0	=	1
C18:1	=	10
C18:2	=	100
C18:3	=	200
C18:3 (c,t,t)	=	800

C18:3 linolenic acid with its two reactive methylene groups (at C11 and C14) is 200 times more prone to oxidation and the development of off flavours than C18:0 stearic, hence the need for hydrogenation to produce the more stable linoleic or oleic acid. In industrial frying oils, the level of polyunsaturates must be low, and in particular the level of C18:3 should be less than 1% and ideally absent, if performance and shelf life requirements are to be met.

Traditionally, most hydrogenated vegetable frying oils used in the UK are based on either Soyabean or Rapeseed, very occasionally Sunflower. In their natural state all of these are 'liquid oils', containing high levels of polyunsaturated fatty acids.

Reducing the levels of polyunsaturation to ensure acceptable results in multi-use frying can be achieved with relative ease using standard hydrogenation conditions and catalysts. The result is typically a solid frying shortening (melting point 35–45°C).

The general public are becoming increasingly aware, and concerned, not only about the amount of fat in their diet but also the type of fat which they eat. Solid frying shortenings containing typically high levels of saturates and/or *trans* fatty acids are now seen as undesirable and as such are becoming less popular. This, linked with the demand for an ever more convenient to use products has prompted the development of a range of frying oils which have become known as "longlife" oils.

Fatty acid profile – liquid oils

	C16:0	C18:0	C18:1	C18:2	C18:3
Rapeseed	6.0	1.5	58.0	21.0	11.0
Soyabean	11.0	4.0	22.0	54.0	8.0
Sunflower	7.0	4.0	22.0	66.0	<0.3
Palm Olein	40.0	4.5	40.0	11.0	<0.3

Tending to be either liquid or semi liquid oils at room temperature, ‘Longlife oils’ offer the fry-life benefits of a solid shortening but with improved nutritional characteristics. Most longlife oils like their solid counterparts are based mainly on Soya or Rapeseed and, as such, still need to be hardened to reduce the level of polyunsaturates. Now, however, there is the added complication that the end product must have a liquid/pourable nature. To achieve this, the formation of saturates and *trans* during hydrogenation must be kept to a minimum and the process more tightly controlled

Melting point of fatty acids

	°C
C16:0	65.0
C18:0	73.0
C18:1 <i>cis</i>	5.5
C18:1 <i>trans</i>	42.0
C18:2 <i>cis</i>	-13.0
C18:3 <i>cis</i>	-24.0

Partial hydrogenation (sometimes referred to as touch or brush hardening) is usually carried out in conjunction with a selective catalyst.

The catalysts used in most commercial hydrogenation in the UK are Nickel based, although catalysts based on other metals such as copper, palladium, zirconium are also being used.

Selectivity basically means that the reaction is guided toward a particular unsaturated bond in preference to another unlike a non-selective catalyst where the reaction is more random. Manufacture of the ‘Longlife’ type products is based on the use of a selective catalyst which has the ability to reduce C18:3 to C18:2 or C18:1 with the minimum formation of C18:0. In this way the oxidative/flavour stability is greatly improved whilst the liquid nature of oil is retained.

By comparing the rate of hydrogenation of C18:3 to C18:2 with the rate of hydrogenation of C18:2 to C18:1, we obtain what is classed as SII or linolenate selectivity. The S1 or linoleic selectivity being the ratio of C18:2 to C18:1 conversion versus the rate at which C18:1 oleic is hardened further to the C18:0 stearic acid.

Nutritional

A largely unavoidable consequence of hydrogenation is the formation of *trans* geometric isomers.

Trans isomers are undesirable in frying oils both from the nutritional standpoint and also because of their high melting points.

The extent to which *trans* isomers are formed depends on many factors including, hydrogen pressure, reaction temperature, catalyst type, even reactor design. The effect of these factors on *trans* formation can be summarised as follows:

Effect of variables on *trans*-isomer formation

- Increasing Temperature increases *trans*-isomer formation
 - Increasing Pressure decreases *trans*-isomer formation
 - Increasing Agitation decreases *trans*-isomer formation
 - Increasing catalyst concentration decreases *trans*-isomer formation
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So, to minimise the level of *trans* isomer formation, hydrogenation should be carried out at low temperature (110–140°C), high hydrogen pressure (4–5 bar) in conjunction with a fresh, highly SII selective catalyst with good poison resistance.

In this chart we can see the effect of temperature and catalyst selectivity on the solid fat content at 10°C. As we have previously mentioned, it is important for the oxidative stability of the oil to reduce the C18:3 content to below 1%, however, equally important for convenience and ease of pouring the solid fat content should be kept to a minimum.

Eating quality

Whilst it is the stability of the frying oil which is important to the operation of the fryer, it is the properties of the fat itself which will influence the consumer appeal of the finished product.

The amount of solid fat can greatly influence both the visual appeal and eating quality of the food. Crisp manufacturers for instance believe that it is important to have a dry surface appearance whilst manufacturers of some breaded or battered foods would argue that a shiny appearance is more desirable.

The degree of hardness of the fat can also influence the mouthfeel and overall enjoyment of the fried food. If the level of solid fat is too high in the region 35–40°C, then the food can leave a rather undesirable fatty cling in the pallet. Although, this may not seem to be so important for products such as chips which are consumed hot it is worth bearing in mind that the meal is often served with a cold drink!

In other applications, such as donut manufacture, the solid fat content can be critical to the manufacturing process. If the fat is too hard at the temperature at which sugar is applied, the sugar will not adhere, too soft the oil will penetrate the sugar layers giving a poor appearance.

Another factor that should be taken into account is the flavour imparted to the food by the frying oil. Although most refined oils are referred to as being bland, certain oils can give characteristic flavour notes. For example, liquid Rapeseed Oil is often described as giving a ‘grassy’ note whilst Soyabean oil is said to be ‘beany’. Hydrogenated oils, on the other hand, tend to have less of a characteristic taste.

For the user, convenience, i.e. ease of use pouring, storing and fry-life are very important. To the consumer however, food quality, taste, and nutritional characteristics are key. The use of hydrogenation is key in meeting both requirements.