Review

A New Generation of Frying Oils

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Abstract

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Traditional edible oils have high polyenoic acid contents, mainly linoleic acid, sometimes with a smaller amount of linolenic acid. Consequently, they are unstable against oxidation, especially under deep frying conditions. Novel high-oleic vegetable oils have been developed which contain low amounts of polyenoic fatty acids. Their relative resistance against oxidation is lower at deep frying temperatures in comparison with storage conditions, however, high-oleic oils were found advantageous for deep frying. High-oleic oils are more stable than low-linolenic oils. High-oleic sunflower, safflower or peanut oils have the best prospects for large-scale applications. The stability can be improved by the addition of antioxidants such as tocopherols.

Keywords: deep fat frying; frying oils; high-oleic oils; oxidation

Deep frying in oil has become one of the most favoured procedures for the culinary preparation as the process is easy, rapid, relatively energy saving, and the resulting meal has an agreeable and intensive flavour. The main disadvantage of deep frying is the rapid degradation of frying oil at high temperatures. As the oxidation products are objectionable from both sensory and food safety aspects, the oil used has to be replaced by fresh oil from time to time which is rather expensive. The use of antioxidants or special frying equipment is only a partial solution. Therefore, the use of more stable frying oils would be desirable.

Traditional frying oils

Traditional frying medium in Central Europe was pork lard, but it is rather expensive and rich in saturated fatty acids and cholesterol. High price is objectionable in the case of olive oil. Refined edible oils prepared from oilseeds are the main edible oils now such as soybean, rapeseed, sunflower, or peanut oils (Erickson 1996) which have high contents of polyenoic fatty acids, mainly linoleic and sometimes also linolenic acids. They may be used for pan frying in which frying oil is used only once and is immediately consumed. However, they are not suitable for deep fat frying where frying oil is used many times, as they are easily oxidised at high frying temperatures. Palm kernel or coconut oils are more stable but their saturated fatty acid content is very high.

Hydrogenated vegetable oils were used almost exclusively until recently for deep fat frying (Erickson 1996). Hydrogenation substantially reduces the polyenoic acid content, and the stability against oxidation under frying conditions is thus improved. Their stearic acid content is moderately increased by hydrogenation but stearic acid appears to be neutral or to have only a little effect on the LDL-cholesterol rising potential of blood plasma as compared to fats containing palmitic, myristic, and lauric acids (HAUMANN 1998a). Hydrogenated vegetable oils contain also trans unsaturated fatty acids which are formed as by-products during hydrogenation. As they are now considered as a health risk, there is a tendency to replace them by mixtures of edible oils with palm oil or interesterified oil fractions.

Search for new frying oils

Traditional low-linoleic high-oleic vegetable oils could be used for deep frying, e.g. olive oil, hazelnut, avocado, or almond oils, as they are very stable in storage and even at high frying temperatures. Their disadvantage is their high price. Fortunately, sources of several traditional polyenoic acid oils such as sunflower seed, peanut, soybean, and rapeseed have been recently bred to obtain high-oleic oils with only a low linoleic acid content (WILSON *et al.* 1989), and these have become available now on the market (POKORNÝ & SAKURAI 2000). Nutritional advantages were recognied of oils rich in oleic and other monounsaturated fatty acids with a reduced linoleic acid content and low contents of saturated acids (NESTEL *et al.* 1994). Diets with high contents of oleic acid are connected with low levels of low-density lipoprotein (LDL) cholesterol in blood plasma. Their consumption may thus reduce the risk of coronary heart diseases (GRUNDY 1986; NOAKES *et al.* 1996).

The deep fried flavour is due to the degradation products of linoleic acid (POKORNÝ 1989), so its intensity can be lower if the food is fried in oil with a very low linoleic acid content. Some fried flavour compounds are, however, produced even from oxidised oleic acid esters (WARNER *et al.* 2001).

These modified oils have fatty acid compositions similar to that of olive oil. They are moderately more expensive than the traditional oils but still cheaper than olive oil or other traditional high-oleic oils. The content of triacylgycerols containing bound polyenoic fatty acids is only low while triacylglycerols containing solely oleic and saturated fatty acids are the major fractions. These triacylglycerols free of polyenoic fatty acids are much more resistant against oxidation than triacylglycerols containing bound linoleic or linolenic acids (PÁNEK *et al.* 2000).

High-oleic sunflower and safflower oils

High-oleic sunflower oil was developed about twenty years ago and its nutritional and chemical characteristics were defined (PURDY 1986; YODICE 1990). The safety of using high-oleic sunflower oil as a good alternative to palm oil and partially hydrogenated vegetable oils in the industrial frying of potato chips and French fries was confirmed by a European Union AAIR project (SÉBÉDIO *et al.* 1996). High-oleic sunflower oil containing 80–82% oleic acid and 9–11% linoleic acid is very satisfactory as a medium for deep frying. High-oleic sunflower oil used for frying potato crisps had nearly the same stability against degradation as palm olein during subsequent storage of the fried product (LAHTINEN *et al.* 1996). Potato crisps and French fries could be stored at room temperature for at least six months, contrary to the product fried in conventional sunflower oil (MARTIN-POLVILLO *et al.* 1996). High-oleic sunflower oil was used for frying different food products without replenishment or with frequent replenishment with fresh oil (CUESTA *et al.* 2001). The oleic acid content was found suitable as a marker of changes in frying oil extracted from the fried product.

Extremely high-oleic oil (about 91% oleic acid and only 3% linoleic acid) is also produced but it is expensive and not easily available, therefore it has only a limited application for frying. Medium-oleic sunflower oil is still more advantageous than high-oleic oil in the view of price, and still satisfactory for frying (FRANKEL 1998). SCHWARZ *et al.* (1996) compared 12 frying oils and observed a negative correlation between the degree of unsaturation and the relative deep frying stability.

Mixtures of virgin olive oil and high-oleic sunflower oil are preferred in the Mediterranean countries because of the flavour. These mixtures were found excellent with regard to thermoxidation under frying conditions (ROMERO *et al.* 1998a, 1999; DOBARGANES *et al.* 1993). The use of traditional olive oil in the Mediterranean countries has recently sharply declined in favour of other edible oils for frying purposes and snack food preparation (ROMERO *et al.* 1998b, 1999). Although more stable than the conventional sunflower oil, high-oleic sunflower oil has still the disadvantage of being moderately more expensive and less stable than other high-oleic edible oils developed for alimentary uses such as high-oleic safflower oil (FULLER *et al.* 1971; PURDY 1985), available for more than two decades. Other high-oleic oils will be discussed later.

The oxidation products of polyunsaturated oils form dark compounds by interaction with amino acids and proteins (Pokorný & Sakurai 2002). The use of high-oleic peanut oil caused less browning on oxidation than traditional peanut oil (Uematsu *et al.* 2002). With regard to the light colour of the fried material (Baixauli *et al.* 2002), high-oleic low-linoleic sunflower oil was thus more suitable for frying meat, especially fish containing such polyunsaturated lipids as battered squid rings.

High-oleic corn oil

For continuous high-temperature applications, such as deep fat frying, corn oil (extracted from corn germs) is usualy stabilised by hydrogenation. As an alternative to hydrogenation, new cultivars of corn with elevated levels of oleic acid and reduced levels of linoleic acid were developed (WO 1995). High-oleic corn oil was shown to have significantly better flavour as a salad oil and a good oxidative stability in both storage test at 60°C and frying test at 180°C than conventional or hydrogenated corn oil (Warner *et al.* 1997). High-oleic corn oil was found much more stable in French-frying than both conventional corn oil and hydrogenated corn oil, and even high-oleic sunflower oil (Warner & Knowlton 1997), probably also because of the high tocopherol content. High-oleic corn oil also demonstrated good fried-food flavour intensity compared to some other high-oleic oils.

High-oleic peanut oil

Conventional peanut oil is also unstable in storage as it contains about 30% linoleic acid. Genetically modified peanut cultivars rich in oleic acid were developed with the use of modern breeding methods. The modified peanut oil contains 80% oleic acid or even more (Haumann 1998b). The novel oils have shown the shelf life at least four times longer under storage conditions. Their stability under frying conditions is naturally not so good but still substantially better than that of the conventional oil (Sakurai *et al.* 1999; Parkányiová *et al.* 2000). High-oleic peanut oil shows a preventive effect against hyperlipidemia and chemically induced lung tumorigenesis in mice (Sakurai *et al.* 2000; Yamaki *et al.* 2002, 2003).

High-oleic linolenic acid-containing oils

Novel oils developed from traditional soybean or rapeseed have either a lower linolenic acid content, or a lower linoleic content, or both. Edible oils containing linolenic acid are still less suitable for frying than oils in which linoleic acid is the most unsaturated fatty acid. Soybean, rapeseed, and linseed oils belong to this group of oils. Novel oils were developed in which not only linoleic acid content but also that of linolenic acid were reduced. The reduction of linolenic acid levels through genetic modification was shown to extend the shelf life of foods fried in modified soybean oil (O'Keefe *et al.* 1993; Miller & White 1988; Liu & White 1992). The flavour of potatoes fried in low-linolenic soybean oil was better than that of potatoes fried in traditional or hydrogenated soybean oil (Mounts *et al.* 1994).

Good experience was obtained with novel low-linolenic canola (low-erucic rapeseed) oil (Hawrysh *et al.* 1995; Warner *et al.* 1994). Potato chips fried in high-oleic, hydrogenated, and low-linolenic canola oils had a better flavour quality after storage as compared to those fried in conventional canola oils (Warner *et al.* 1994; Petukhov *et al.* 1999; Xin *et al.* 1999). With regard to significant performance advantages and nutritional value, high-oleic canola oil (called Monola) whith a low linolenic acid content (only 2.5%) was found to be very well suitable for deep frying (Xu *et al.* 1999, 2000). From the standpoint of stability of fried potato chips in storage, high-oleic or hydrogenated canola oil were more suitable than conventional or low-linolenic canola oils (Petukhov *et al.* 1999). On the contrary, no substantial diference was observed between frying of shoestring potatoes or fish nuggets in traditional and low-linolenic soybean oils (Tompkins & Perkins 2000). Even novel linseed oil was reported as suitable for deep frying purposes.

Further stabilisation of novel frying oils with antioxidants

As already mentioned, the performance of high-oleic frying oils is significantly better than that of traditional oils but, some further improvement on their resistance against degradation would be still desired. The oil degradation during frying was retarded by decreasing the oxygen content in the atmosphere to 2% (Fujisaki *et al.* 2001b). Water spraying increased the rate of frying oil degradation (Fujisaki *et al.* 2001a).

The stability of frying oils depends not only on the unsaturation degree of fatty acids present but also on the level of antioxidants, especially of natural tocopherols. Changes during frying depended on the tocopherol content more significantly than on that of linoleic acid (Barrera-Arellano *et al.* 2002). The fatty acid composition data give thus only indicative information about the oxidative stability of the respective frying oils. Potatoes fried in conventional sunflower oil containing 100 mg/kg tocopherol at the end of frying were oxidised less rapidly during storage at 60°C than potatoes fried in high-oleic sunflower oil containing only 10 mg/kg tocopherols at the start of storage (Márquez-Ruiz *et al.* 1999). The stabilisation of high-oleic oils by the addition of antioxidants was studied (Calvo *et al.* 1996); the stabilised oils are both economically and nutritionally more desirable than saturated oils. High-oleic peanut oil was efficiently stabilised by the addition of α- and γ-tocopherols which were gradually destroyed during the heating by oxidation (Pokorný *et al.* 2002, 2003). The natural way of improving the oxidative and flavour stability of frying oils and fats is the addition of natural antioxidative components and precursors present in the plant kingdom such as virgin olive oil, sesame seed oil, or rice bran oil. A variety of natural antioxidative components present in these oils include tocopherols and tocotrienols, special sterol esters, and sterols such as 5-avenasterol, squalene, sesamolin sesamol, sesaminol and related compounds, phenolic acids and various polyphenols, etc.

Tocopherols are the most important natural antioxidants for vegetable oils. Both α- and γ-tocopherols were found to increase the oxidative stability of high-oleic sunflower oil containing 70% and 20% linoleic acid (Carrick & Yodige 1993). At high temperatures, γ-tocopherol was much more efficient as an inhibitor of polymerisation than α-tocopherol (Lampi & Kamal-Eldin 1998). It means that high-oleic/high-γ-tocopherol oils, such as high-oleic canola oil, may be better frying oils than high-oleic/high-α-tocopherol oils, such as high-oleic sunflower oil. High-oleic soybean varieties may be particularly interesting since they contain considerable amounts not only of γ-tocopherol but also of δ-tocopherol which is still more efficient than γ-tocopherol (Kamal-Eldin & Appelqvist 1996). The presence of tocopherols and their interactions with other frying oil stabilisers including trace metal chelators (e.g. phospholipids, citric acid and some phenolic compounds), tocopherol regenerating agents (e.g. ascorbyl palmitate), or oxidation inhibitors (e.g. silicone oils) as well as processing effects (processing temperature) and the frying practices used (replenishing of the used oil), all play an important role in affecting the stability of frying oil. The addition of natural antioxidant components and their synergistic action in frying oil, their stability during frying exert a strong effect on its oxidative frying stability (Gertz *et al.* 2000; Kochhar 2000; Normand *et al.* 2001). The use of antioxidants to stabilize high-oleic oils is a way of making them economically more interesting for frying purposes.

Conclusions

The use of high-oleic frying oils reduces the oxidation rate and the need for their replacement with fresh oil, even though the relative resistance against oxidation is not as high as under the storage conditions.

The degradation of high-oleic frying oils depends on the contents of tocopherols and other natural antioxidants and is improved by the addition of more antioxidants.

The fried flavour originates from the volatile oxidation products of linoleic acid; thus, the intensity of fried flavour may be lower if products are fried in high-oleic oil with a very low linoleic acid content.

The widespread use of high-oleic oils for deep frying is still partially prevented by their higher price. Another difficulty is poor experience of technologists as welll as the not secured availability on the market. Nevertheless, it may be assumed that, in the long run, they will become substantially more important.

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Tradiční jedlé oleje mají vysoký obsah polyenových mastných kyselin (většinou obsahují kyselinu linolovou, někdy též linolenovou). Jsou proto málo stálé proti oxidaci, zvláště za podmínek smažení v tuku. V poslední době byly vyšlechtěny nové odrůdy s nízkým obsahem polyenových mastných kyselin a s vysokým obsahem kyseliny olejové. Cílem bylo zvýšit jejich stabilitu proti oxidaci. Za podmínek smažení jsou sice relativně méně stálé než za podmínek skladování, ale přece znamenají podstatné zlepšení. Oleje s vysokým obsahem kyseliny olejové jsou vhodnější než oleje s nízkým obsahem kyseliny linolenové, ale s normálním obsahem kyseliny linolové, zvláště modifikovaný sójový a řepkový olej. Nejlepší perspektivy pro využití ve větším měřítku mají slunečnicové oleje se středním nebo vysokým obsahem kyseliny olejové, světlicový a podzemnicový olej s vysokým obsahem kyseliny olejové. Jejich stabilitu je možné dále zvýšit přídavkem vhodných antioxidantů, zvláště tokoferolů.

Klíčová slova: oleje; kyselina olejová; oxidace; smažení v tuku; smažicí oleje

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