# Current advances in sunflower oil applications

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## ABSTRACT

The fatty acid and triglyceride molecular species of a given oil determine its physical, chemical, and nutritional properties. Thus, applications for a specific oil depend mainly on its fatty acid composition and the way in which the fatty acids are arranged in the glycerol backbone. Minor components, such as tocopherols, could also modify oil properties, such as thermo-oxidative resistance. Sunflower seed commodity oils predominantly contain linoleic and oleic fatty acids, with lower contents of palmitic and stearic acids. High-oleic sunflower oil, which could actually be considered as a commodity oil, contains oleic acid of up to around 90%. New sunflower varieties with different fatty acids and tocopherols compositions have been selected. Due to these modifications, they possess new properties and are much better adapted for direct home consumption, food industry and other applications such as biolubricants and biodiesel production.

**Key words**: biodiesel – fatty acids – oil quality – oxidative stability – tocopherols – triglycerides.

## INTRODUCTION

Oils are mainly constituted by triglycerides, but also contain small quantities of diglycerides, polar lipids, tocopherols, free fatty acids, etc. Triglycerides, which account for more than 95% of total oil, consist of a glycerol molecule with three fatty acids esterified in the hydroxyl residues, one in the central position of the glycerol molecule and the other two at the terminal positions. The most common fatty acids forming these triglycerides in sunflower are: saturated palmitic and stearic acids, monounsaturated oleic acid and polyunsaturated linoleic acid. The final use of each type of oil is defined by both its physical and chemical characteristics, which depend on its fatty acids and triglyceride composition. For instance, the difference between oils and fats is due to the amount of their saturated fatty acids. Their thermo-oxidative stability depends mainly on the amount of polyunsaturated fatty acids they contain (oils with a high content of these unsaturated fatty acids are more unstable), and their content and type of tocopherols. Therefore, the performance of an oil for a specific use will depend on these characteristics. Considerable research efforts are being put into the following aspects. On the one hand, more stable sunflower oils are being obtained by increasing their content in monounsaturated fatty acids (oleic acid) and decreasing their content in polyunsaturated fatty acids (linoleic acid). These oils are also suitable for biolubricants. Their stability could also be increased by modifying their tocopherol content. On the other hand, healthy substitutes for animal, tropical or hydrogenated fats required by the food industry are being obtained by increasing their content in saturated fatty acids, mostly stearic, which does not modify the plasma cholesterol content.

## DISCUSSION

*Sunflower oils*

Depending on their particular use, oils or fats must have a specific composition to fulfill the requirements of each application. Deep-frying, and other industrial processes for food preparation, require fats and oils with a high thermo-oxidative stability. In these applications, due to easy storage and pouring, oils are better than fats. For margarine, spreads, confectionery, and related products, fats with a certain degree of plasticity are required. For biolubricant production, oil liquid at temperatures below 0ºC with a good thermo-oxidative stability is required. Biodiesel production only requires a minimal stability and standard sunflower oils are equally as good as canola or other vegetable oils, but, probably for this application, palm oil is even better.

By lowering the content of unsaturated fatty acids or modifying minor components, such as tocopherols, the stability of oils could be enhanced, making them suitable for deep frying and biolubricant uses. Increasing the saturated fatty acids content will increase the proportion of solid fat and, therefore, its melting temperature. With the exception of animal fats, palm oil fractions and lauric oils, natural fats hardly fulfill the requirements of most industrial processes. Nevertheless, the above mentioned fats are considered unhealthy by many authors and by the World Health Organization (WHO, 2003) because of their high content in palmitic, myristic and lauric fatty acids, so they have been substituted by hydrogenated vegetable oils. However, the hydrogenation process generates *trans* isomers of unsaturated fatty acids, which are also considered to be nutritionally undesirable. In general, dietary recommendations encourage the intake of unsaturated fatty acids, such as oleic and linoleic, and stearic as a saturated fatty acid (Kelly et al., 2001; Mensink, 2005; WHO, 2003).

Different sunflower lines with modifications in the fatty acid composition of their oils have been obtained (Table 1). Since the selection of the high-oleic mutant by Soldatov (1976), several new fatty acid mutants have been obtained by ionization, radiation or chemical mutagenesis, among them three independent high-palmitic lines, with around 30% of palmitic acid in their oils, two in standard high-linoleic background and another in high-oleic background (Ivanov et al., 1988; Osorio et al., 1995; Fernández-Martínez et al., 1997), and some high-stearic acid in high-linoleic background (Osorio et al., 1995; Fernández-Moya et al., 2005) have been obtained. Lines with high-stearic in high-oleic background were obtained later by recombination (Fernández-Moya et al., 2005). In spite of their higher saturated acid content, these sunflower oils have a low content of saturated fatty acid in the middle position of the triglyceride (Alvarez-Ortega et al., 1997), differentiating them completely from animal, palm and hydrogenated fats.

**Table 1.** Fatty acid composition of several sunflower oil mutant lines with modifications in their oils, compared to the standard sunflower oil.

| Sunflower line | Oil phenotype | Fatty acid composition (%) | | | | |
|---|---|---|---|---|---|---|
| | | 16:0 | 16:1 | 18:0 | 18:1 | 18:2 |
| Standard | Normal | 7 | | 6 | 29 | 58 |
| HA-OL9[a] | High oleic | 5 | | 3 | **90** | 2 |
| CAS-4[b] | Medium stearic | 6 | | **12** | 28 | 53 |
| CAS-3[b] | High stearic | 5 | | **26** | 15 | 53 |
| CAS-30[c] | High stearic | 6 | | **30** | 10 | 50 |
| CAS-15[c] | High stearic-oleic | 6 | | **24** | **62** | 5 |
| CAS-5[b, d] | High palmitic | **31** | 5 | 3 | 12 | 48 |
| CAS-12[e] | High palmitic-oleic | **32** | 6 | 4 | **54** | 3 |

[a]Soldatov, 1976; Fernández-Martinez et al. 1993.
[b]Osorio et al. 1997.
[c]Fernández-Moya et al. 2005.
[d]Ivanov et al. 1988.
[e]Fernández-Martínez et al. 1997.

New research has been carried out to obtain fractions with improved properties from these oils. Thus, high stearic and oleic sunflower oils have been cold-fractionated to obtain stearin and olein fractions (Table 2). In this case, because of the unimpaired distribution of triglycerides species between the fractions, fatty acid composition analysis is not a satisfactory method to characterize them, and, instead, the triglyceride composition has to be determined. Table 2 shows the triglyceride subclasses of these fractions; the liquid olein fraction has mostly triunsaturated triglycerides, mainly OOO, (see Table 2 for abbreviations) and OOL, and monosaturated triglycerides, mainly EOO, and in a lesser amount POO and EOL, whereas the stearin has a higher content of disaturated triglycerides than the olein fraction, EOE and POE being the principal triglycerides. The melting properties of the stearin, measured as the solid content at different temperatures by differential scanning calorimetry are similar to cocoa butter.

**Table 2.** Triglyceride subclasses composition of the liquid fraction (olein) and solid fraction (stearin) obtained from high stearic and oleic sunflower oil[1].

| Sunflower | Oil Fraction | TAG Types (%) | | |
|---|---|---|---|---|
| | | SUS | SUU | UUU |
| HEHO | Olein | 3.1 | 56.7 | 40.2 |
| HEHO | Stearin | 73.3 | 17.9 | 8.8 |

[1]SUS, disaturated triglycerides; SUU, monosaturated triglycerides; and UUU, triunsaturated triglycerides. S, saturated; U, unsaturated; HE, high stearic acid; HO, high oleic acid.

Tocopherols, good antioxidant molecules, are one of the minor components of sunflower oil, with α-tocopherol, or vitamin E being the standard in commodity sunflower oil, new lines with modified profiles of tocopherols have been obtained (Table 3). These new lines have been obtained from germplasm of wild and cultivated sunflower (Demurin, 1993; Velasco et al., 2004). The tocopherols accumulated in these lines mainly depend on modifications on the genes which control the biosynthetic pathway. The oils containing γ-tocopherol and δ-tocopherol have the advantage of a higher oxidative stability, but a reduced vitamin E content.

**Table 3.** Tocopherol composition of oils extracted from modified sunflower lines.

| Oil Type | Tocopherol composition (%) | | | |
|---|---|---|---|---|
| | α-T | β-T | γ-T | δ-T |
| Standard α-T | 95 | 4 | 1 | 0 |
| Medium β-T[a] | 50 | 50 | 0 | 0 |
| High β-T[b] | 75 | 25 | 0 | 0 |
| High γ-T[a] | 5 | 0 | 95 | 0 |
| High δ-T[b] | 5 | 0 | 30 | 65 |

[a]Demurin, 1993
[b]Velasco et al., 2004

*Sunflower oil applications*

Standard sunflower oil possesses good properties for low temperature and general food applications (salad dressings, emulsions, etc), but for high temperature applications and deep frying, oils with a lower content of polyunsaturated fatty acids are required, and these are the high-oleic oils. The oil properties at a high temperature also depend on the tocopherols, oils with a higher content of γ and δ-tocopherols being more stable than oils with α and β-tocopherols. Margarine and plastic fat production demands oils with high contents of saturated fatty acids such as palmitic or stearic acids, preferably stearic because of the unhealthy effect of palmitic acid, as stated in Kelly et al. (2001): “The food industry might wish to consider the enrichment of foods with stearic acid in place of palmitic acid and trans fatty acids”.

Thermo-oxidative treatments to test oil stability are usually carried out at 180 °C for 10 h monitorizing the formation of polar and polymer compounds. TAG polymerization in the different oils increased with time (Fig. 1). In this regard, oils could be classified into three groups; standard oils, with a high content of polymerised TAGs, up to around 17% after 10 h treatment; high-oleic sunflower and palm olein oils with around 10% of polymerised TAGs after the same treatment; and the high-palmitic and high-oleic sunflower oil with only 6% of polymerised TAGs at the same time. This indicates that oils with the higher content of oleic and palmitic acids are the best for high temperature applications. Rejection levels of 12% of polymers have been recommended in current regulations for discarding used frying fats for human consumption (GFSR, 2000). As a result, commodity oils, soybean, canola and standard sunflower oils must be rejected after 8 h at 180ºC, while high-oleic sunflower could still be used after 10 h and the high-palmitic and high-oleic oil would be even further from rejection.

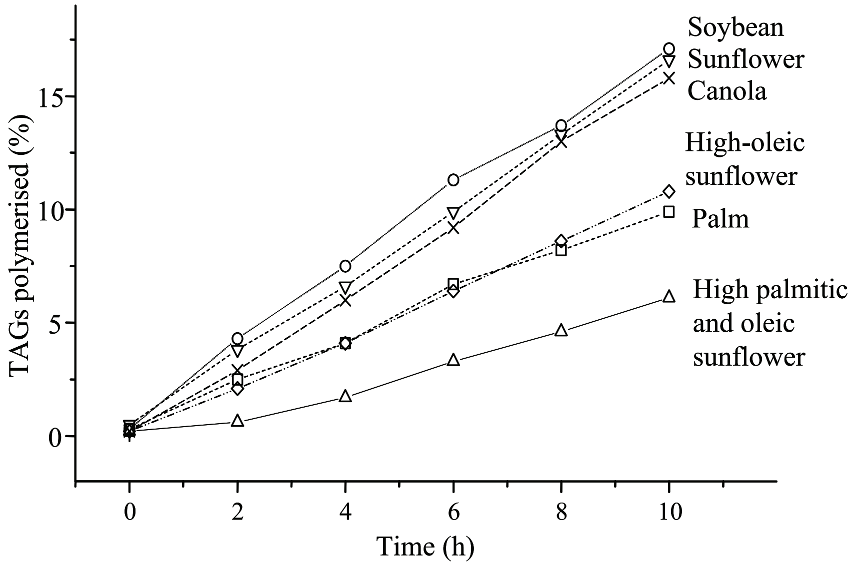


**Fig. 1.** TAG polymerization at 180ºC of oils of vegetal origin. Soybean, canola and sunflower are the standard commodity oils, palm is a commercial palm olein, and high-oleic and high-palmitic high-oleic sunflower oils are genetically modified sunflower oils (Marquez et al., 1999).

As stated above, tocopherols could also modify the thermo-oxidative stability of the oils. Fig. 2 shows the polymerised TAGs at 180ºC of genetically modify sunflower oils. Oils tested in this experiment were standard, high-oleic containing α-tocopherol, high-oleic and high-palmitic containing α-tocopherol and high-oleic and high-palmitic containing γ-tocopherol.

After 10 h at 180ºC, standard and high-oleic sunflower oils have 17.4% and 8.2% of polymerised TAGs, while the high-palmitic and oleic oils have only 2.3% and 1.4%. Furthermore, after 25 h of experiment, the polymerised TAGs were only 8.7 and 4% of polymerized TAGs and had less than 12% of polymers and were therefore still suitable for human consumption (Marmesat et al., 2008). These two high-palmitic oils have a very high oxidative stability and the oil with γ-tocopherol is the best as it always has less than half of the polymerised TAGs than the same oil with α-tocopherol and, even more, after 25 h it was less polymerised than the standard sunflower after 2 h, making this oil extremely stable.

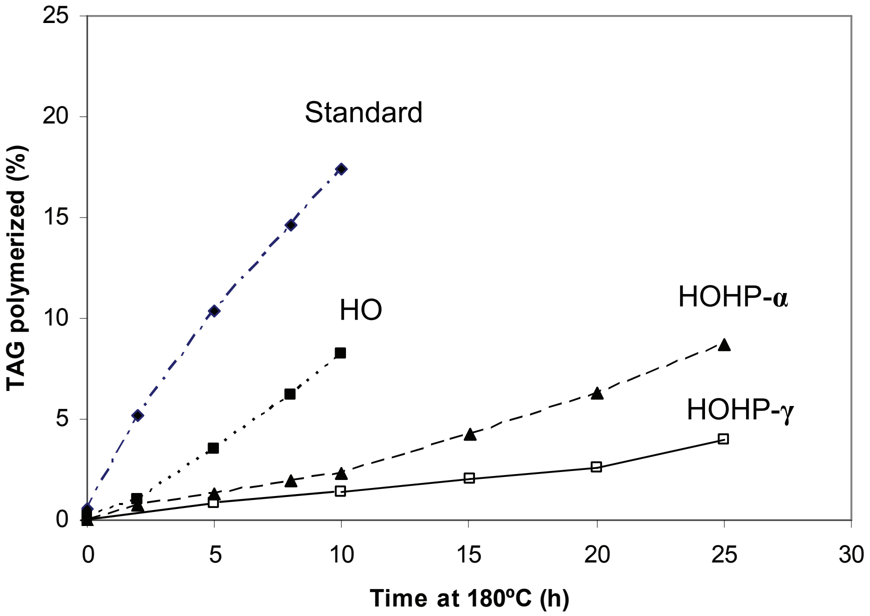


**Fig. 2.** TAG polymerization at 180ºC of standard sunflower oils compared with high-oleic oil (HO), high-oleic and high-palmitic oil containing α-tocopherol (HOHP-α), and high-oleic and high-palmitic oil containing γ-tocopherol (HOHP-γ).

High-stearic high-oleic sunflower oils, and also the liquid fraction obtained from them by cold fractionation, have good thermo-oxidative stabilities. These oils have a reduced content of polyunsaturated fatty acids, high content of oleic and some stearic acid. Experiments made to determine their oxidative stability have shown the total modified TAGs after 10 h at 180ºC of these oils in comparison with high-oleic and high-oleic and palmitic with different tocopherol contents (Table 4). Due probably to the different origin of oils and authors, differences were found in the data for standardising the results. The data presented here were corrected according to the results obtained with respect to the high-oleic oil present in all experiments, 1 being the value assigned to the high-oleic oil.

For oils with a high saturated content, which could be solid at relatively high temperatures, a new parameter must be defined, i.e. the cloud point which is the temperature at which the liquid became turbid. Oils with a cloud point of above 0ºC are difficult to transport and need special factory requirements. In winter during transport storage oil could become solid, and so good deep frying oils must have a good oxidative stability and be liquid, at least up to 0ºC. The high-stearic and high-oleic oils are very stable, but they are solid at room temperature, and the high-palmitic oils are also quite solid at temperatures of between 0 and 10ºC. High-oleic sunflower oil and olein fractions from HSHO sunflower are probably the best oils for deep frying, mainly if they contain γ-tocopherol instead of α-tocopherol.

**Table 4.** Total modified TAGs and cloud point of sunflower oils with different fatty acid and tocopherol compositions.

| Fatty acids<br>Phenotype | Total modified TAG<br>High oleic = 1 | Cloud point (ºC) |
|---|---|---|
| Standard | 1.29 | -8 |
| High oleic | 1.00 | -8 |
| High oleic and palmitic α tocopherol | 0.61 | 6 |
| High oleic and palmitic γ tocopherol | 0.48 | |
| High oleic and stearic | 0.59 | 24 |
| Oleine from HSHO[1] | 0.76 | -4 |

[1]High saturated, high oleic acid

For the elaboration of some food products the industry needs solid or semisolid fats, whose traditional sources have been animal and some tropical fats, such as palm and lauric oils (palm kernel and coconut). Studies in human health have demonstrated that these fats are unhealthy due to their elevated contents of medium and long chain saturated fatty acids (mainly myristic and palmitic acids). Their intake increases the plasma levels of LDL-cholesterol (bad cholesterol), which generates an increment in the risk of suffering cardiovascular diseases. The effect of fats on cholesterol levels depends on their fatty acid composition (Mensink et al., 2003). The relationship between plasma cholesterol levels and cardiovascular diseases is well-known. The ingested fatty acids modulate the lipoprotein levels (and therefore the type of cholesterol). In general, unsaturated fatty acids (oleic, linoleic, and linolenic acids) increase the HDL and diminish the LDL, and for that reason they are considered as being healthy. On the other hand, saturated fatty acids (lauric, myristic and palmitic) increase both the LDL and the HDL and therefore the ratio LDL/HDL. But stearic acid, in spite of being saturated, does not have any effect on the cholesterol content (Kelly et al., 2001; WHO, 2003; Mensink, 2005). In conclusion, the ingestion of stearic, oleic or linoleic acid does not modify the profile of lipoproteins (Thijssen and Mensink, 2005). The main reason for this is that stearic acid is transformed very quickly into oleic acid in the liver (Pearson, 1994).

To solve the problem regarding the use of hydrogenated vegetable fat, animal fat or tropical fats, a research project has been carried out with the aim of obtaining natural sunflower oils that could be used directly in the food industry for the production of margarine and similar products without the need of any chemical manipulation. New lines have been selected by classic methods, without the application of genetic engineering techniques, just the same as the high-oleic sunflower mutant. Sunflower lines with a high-stearic acid content together with oleic or linoleic acids are a healthy alternative to these unhealthy fats. In Table 4, the clouding point of some sunflower oils is shown. Among these, setting a good example, the high-stearic and oleic fat from sunflower has a clouding point of 24ºC, making it suitable for the manufacture of margarine, spreads, bakery and other products where a plastic fat is needed.

The triglyceride composition of these new oils is different to those of the standard sunflower oil, making them appropriate for industry demands (Table 5; Fig. 3). High-stearic lines contain a considerable percentage of triglycerides with two saturated fatty acid molecules, EOE and POE being the most abundant species in high-stearic high-oleic oils, and ELE and PLE those in the lines with a high-linoleic background. These triglycerides have linoleic or oleic acids in the central position of the triglyceride, which makes them appropriate for the production of margarines. With fats constituted by these types of triglycerides and keeping in mind the effect on the levels of cholesterol of these fatty acids, besides the fact that they do not contain saturated acids in the central position of the triglyceride, we can guarantee that a fully vegetable and healthy margarine can be manufactured for the first time with the healthy stearic acid (WHO, 2003) and no saturated fatty acids in the middle position of triglycerides (Renaud et al., 1995).

**Table 5.** Triglyceride subclasses composition of standard sunflower (RHA-274), high-oleic (CAS-9), high-stearic and high-linoleic (CAS-30) and high-stearic and high-oleic (CAS-15) oils. SUS, disaturated triglycerides; SUU, monosaturated triglycerides; and UUU, triunsaturated triglycerides. S, saturated; U, unsaturated fatty acids.

| TAG type | RHA-274 | CAS-30 | CAS-9 | CAS-15 |
|---|---|---|---|---|
| SUS | 1.8 | 29.0 | 0.9 | 18.4 |
| SUU | 30.7 | 57.0 | 21.5 | 61.9 |
| UUU | 67.5 | 13.8 | 77.5 | 19.1 |

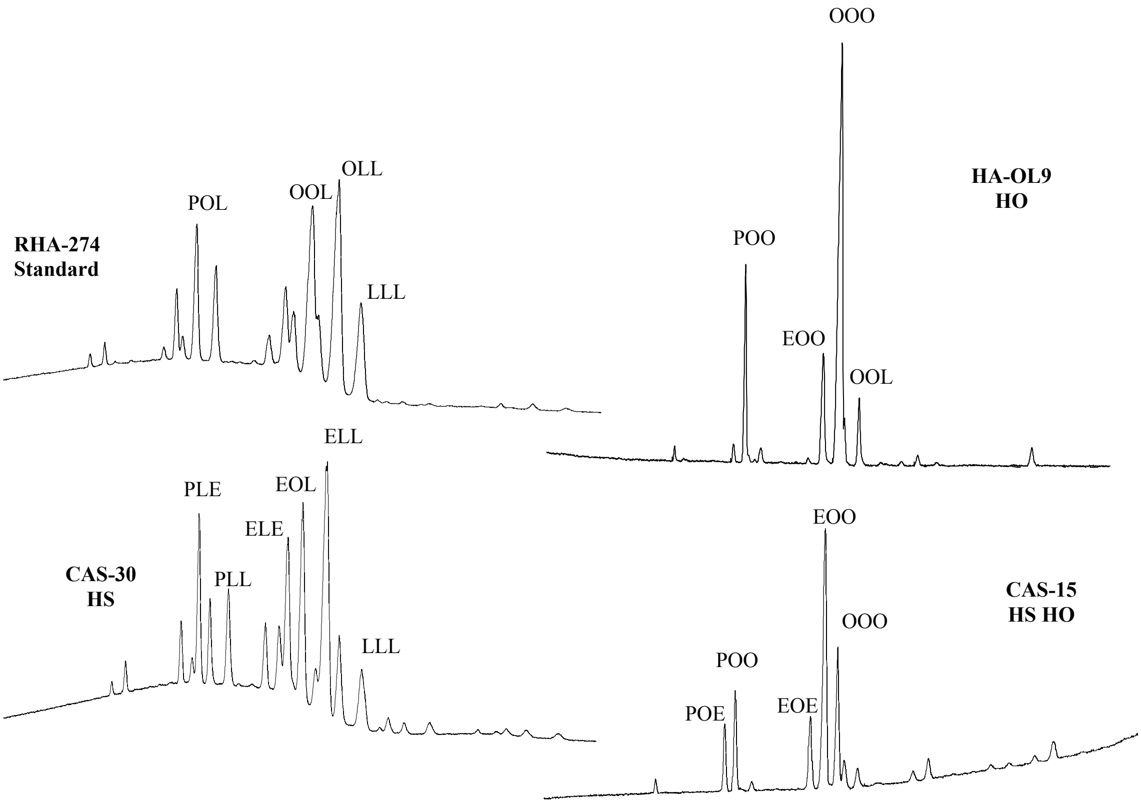


**Fig. 3.** Triglyceride chromatographs of standard RHA-274, high-oleic HA-OL9, high-stearic CAS-3 and high-stearic and oleic CAS-15 sunflower oils, showing the main triglycerides molecular species of each oil. P, palmitic; E, stearic;, O, oleic; and L, linoleic fatty acids.

To sum up, these new sunflower oils, with modified tocopherols and fatty acid composition, which were developed as a feedback for the food industry requirements to offer healthier products, together with the two others available nowadays (normal and high-oleic) could cover the requirements of the food industry without any chemical manipulation, with the aim of increasing the consumers' quality of life.

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