

# Healthy oils: a process to obtain diglyceride-rich edible vegetable oils

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Among edible vegetable oils, the most healthful choices are those containing monounsaturated and polyunsaturated fatty acids with 1, 2, and 3 unsaturations in the molecule, such as oleic, linoleic, and linolenic. However, it is well known that vegetable oils found in nature are mostly triglycerides, or triacylglycerols (TAG), and that a long-term diet rich in lipids containing TAG may result in body fat accumulation and obesity.

- Healthful synthetic edible oils are obtained catalytically by upgrading vegetable oils in a four-phase reactor, without the use of solvents.
- Oil glycerolysis promoted by an inexpensive and fully recoverable solid base (magnesium oxide) increases the total diglyceride content up to 54 wt.%, with 67% of this fraction being the 1,3-diglyceride isomer.
- The distinct metabolic pathway of 1,3-diglyceride is believed to prevent body fat accumulation.

Recently, several studies showed that the regular intake of oil diglycerides, or diacylglycerols (DAG), as substitutes for TAG helps prevent obesity and related conditions such as diabetes, hypertension, stroke, and cardiovascular problems, among others. Although DAG are present as minor components in various edible oils, vegetable oils are not a significant source of DAG. Thus, for a diet rich in DAG, the DAG must be consumed from other sources. DAG have been traditionally used as food emulsifiers, which take advantage of the amphiphilic properties derived from the unique combination of hydrophilic and hydrophobic functions in the molecule. Other food uses of DAG are in cocoa butter substitutes, in bakery and confectionery industries, and in milk fat analogues.

Nevertheless, consumption of unspecific DAG does not guarantee prevention of obesity, since only one of the two possible DAG isomers—1,2-DAG and 1,3-DAG—are considered to be a healthful option. Taking into account that the energy contents of TAG and DAG are similar (~9 kcal/g) and that there is no difference in their absorption rates in the human body, the effect of 1,3-DAG intake on the reduction of weight gain is ascribed to its distinct metabolic pathway in the small intestine as compared to TAG or 1,2-DAG. During digestion, TAG and 1,2-DAG are hydrolyzed to 2-mono-glycerides, or 2-monoacylglycerols (2-MAG), and free fatty acids (FFA), from which TAG are immediately re-synthesized and released to the lymphatic system. In contrast, during 1,3-DAG metabolism, 1-MAG and FFA are formed, thereby avoiding the 2-MAG pathway that leads to re-synthesis of TAG and the consequent deposition of fat in body tissues.

## REACTING TAG WITH GLYCEROL

Synthetic edible oils enriched with 1,3-DAG can be obtained by different routes. Recently, we showed that glycerolysis of vegetable oils promoted by solid catalysts is a suitable and practical process for this purpose. In our process, the TAG of the oil are reacted with glycerol, without the use of solvents, to give DAG. The catalyst, magnesium oxide, can be

recovered and recycled. Therefore, the total number of oil purification steps is significantly reduced compared with the enzymatic route.

Countries that produce vegetable oils and biodiesel have the potential to develop this technology as well as an incentive to produce innovative value-added foods that would improve the economics of existing oil or biodiesel production.

Products derived from leguminous plant farming, in particular the TAG of the oil, are a profitable and abundant biore-source for many countries. For instance, South America is one of the largest producers of soybean oil, with Argentina and Brazil contributing 30% of world production and 62% of total exports in 2017. However, South American consumers prefer other oils, such as sunflower, olive, or corn. In this sense, the situation of Argentina is noteworthy since in spite of having one of the world's largest and most efficient developments combining soybean farming and milling facilities in a concentrated area, the country's oil production is mainly industrialized as margarine, exported (\$850/ton) or used for biodiesel production in nearby integrated plants.

On the other hand, biodiesel production by oil or fat transesterification totals about 26 million tons per year. Among edible oils, major biodiesel feedstocks around the world are rapeseed, corn, palm, and soybean oils. The latter is the main biodiesel feedstock in the Americas, involved in about 80% of the biodiesel produced worldwide. During biodiesel synthesis by transesterification, glycerol, or glycerine (Gly) is obtained as the main co-product, representing ~10% of the biodiesel production. Thus, more than 2 million tons per year of bio-glycerol are made available by this technology alone. Consequently, there is a considerable Gly surplus, and since the market for industrializing Gly is limited, this product is mostly sold and exported as crude (\$100–\$400/ton) or refined (\$900/ton) glycerine.

Thus, new applications intended to convert bio-glycerol and oil into novel value-added products are welcome. In this context, glycerolysis of oils is an attractive option to transform these abundant biomass-derived resources into functionalized foods.



### THE REACTION IN DETAIL

The four-phase reactor used in the glycerolysis reaction is sketched in Figure 1. At the beginning of the reaction, the bottom liquid layer is pure Gly, whereas the layer on top of it is the "oily phase." The reaction occurs in the latter, since Gly is slightly soluble in TAG but TAG are not soluble in Gly. The solid catalyst is distributed in both layers, and a continuous flow of  $N_2$  is supplied during reaction. The complex reaction system entails concerns related to thermodynamic limitations, presence of competitive reactions, DAG isomer interconversion, product degradation, and catalyst deactivation.

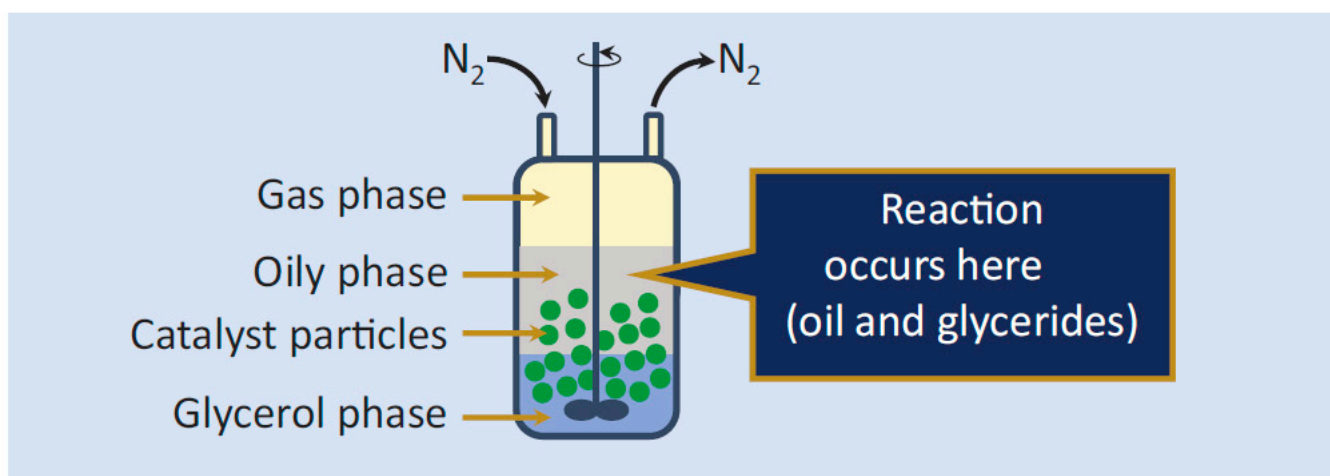


FIG. 1. Scheme of the four-phase glycerolysis reactor

TABLE 1. Composition of fresh edible vegetable oils and of oils after glycerolysis

Entry	Oil	Composition (wt.%)									
		Fatty acid distribution				Glyceride content					FFA
		16:0 <sup>b</sup>	18:1 <sup>c</sup> ( $\omega$ -9)	18:2 <sup>d</sup> ( $\omega$ -6)	18:3 <sup>e</sup> ( $\omega$ -3)	MAG	DAG	TAG	1,2-DAG	1,3-DAG	
1	Sunflower	7.1	29.9	63.0	-	1.1	1.6	97.3	0.4	1.2	0.04
2	Soybean	11.1	25.2	54.8	8.9	0.6	3.4	96.0	1.0	2.4	0.02
3	Sunflower <sup>a</sup>	7.7	36.6	55.7	-	15.3	49.3	35.4	16.0	33.4	2.6
4	Soybean <sup>a</sup>	16.6	19.3	59.2	4.9	18.4	46.6	35.0	15.0	31.6	3.2

<sup>a</sup> after the 8h-reaction at 220°C and Gly/TAG=0.6, without any further purification treatment; <sup>b</sup> palmitic; <sup>c</sup> oleic; <sup>d</sup> linoleic; <sup>e</sup> linolenic

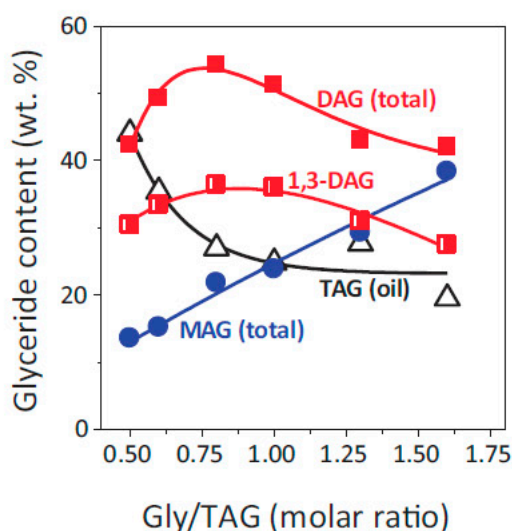


FIG. 2. Effect of the Gly/TAG ratio on the glycerolysis reaction [sunflower oil, magnesium oxide, T= 220°C, 8 h, 9 g catalyst/mol oil, 70 mL N<sub>2</sub>/min]

Table 1 presents an analysis of the fatty acid distribution in soybean and sunflower oils after the glycerolysis reaction at 220°C, showing no significant changes compared with the fresh oils. Furthermore, the TAG content decreases to 35% after reaction with a concomitant increase of the total DAG content to almost 50%, 68% of which are the dietary 1,3-DAG isomer.

The reacted oils also contain MAG, mainly as 1-MAG. This is explained by the fact that glycerolysis is a stepwise process, starting from the initial formation of equimolar amounts of MAG and DAG, Eq. (1), followed by different possible reaction steps that might take place depending on the Gly availability in the reaction zone. The preferred consecutive pathway is the reaction between TAG and MAG toward DAG, Eq. (2). Thus, care has to be taken to select the most satisfactory experimental conditions, mainly with respect to reaction temperature and Gly/TAG ratio in the reactor feed, since both parameters define the concentration of available Gly.

The reaction steps and the overall reaction, Eq. (3), can be written as:



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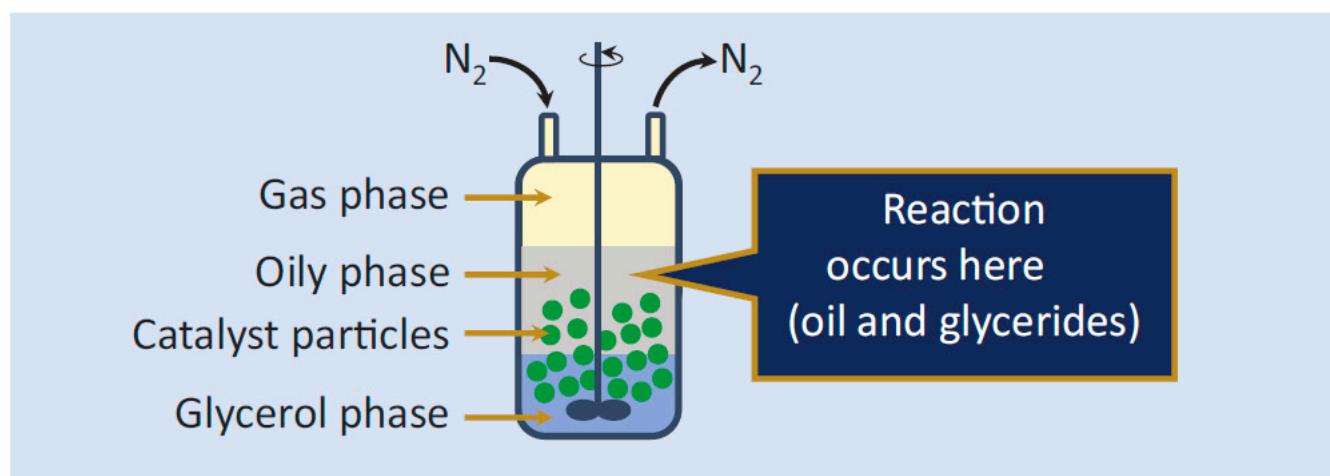


FIG. 1. Scheme of the four-phase glycerolysis reactor



FIG. 4. Commercial sunflower oil before and after glycerolysis and bleaching

commercial vegetable oils. Figure 4 compares a commercial sunflower oil before and after glycerolysis followed by treatment with bleaching earths.

Potential food applications of these healthy oils are in oil-in-water type emulsions, such as mayonnaise and salad dressings, and in water-in-oil type emulsions represented by margarine, spreads, and buttercream fillings.

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### Further reading

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