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MODERN APPROACHES TO VEGETABLE OIL FRACTIONATION

BY

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Abstract. This study analyses the fractionation of vegetable oils using the methods known up to this point and examines the use of these fractions in various industries. Emphasis was placed on sunflower oil due to its high-oleic acid content, which has health benefits. As a novel fractionation method, the work primarily focuses on molecular distillation, a method that leads to high purities, advantageous for heat-sensitive or easily degradable substances and has been studied up to pilot scale until now. Three sunflower oil samples were subjected to experimental and empirical analysis. The results were compared with available literature data and process simulators outputs.

Keywords: vegetable oils, oil fractionation, sunflower oil, molecular distillation, methanol transesterified oil fractionation.

1. Introduction

Vegetable oils mainly consist of complex lipids, mainly triacylglycerols, whose composition determines their physicochemical properties (Gunstone, 2011). Sunflower oil is primarily composed of triacylglycerols (98–99%), with a

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small amount of phospholipids and non-saponifiable matter (tocopherols, sterols, and waxes, etc.). Regular sunflower oil has a high content of linoleic acid in the form of trilinolein (36.3%) and oleo-dilinolein (29.1%) of the total triacylglycerol content (Grompone, 2011; Yayla, 2025). High-oleic sunflower oil is valuable both nutritionally and technologically. The Food and Agricultural Organization (FAO) recommends its consumption due to its stability and health benefits, including cholesterol reduction and protection against arteriosclerosis (Salas *et al.*, 2015).

This study presents the results obtained from the characterization of three sunflower oil samples through both experimental and empirical analysis. This stage is essential for determining the composition of the oil that will subsequently undergo fractionation.

2. Oil fractionation

Fractionation represents a fundamental technological process within the vegetable oil industry, enabling the separation of oils into targeted fractions for specialized applications. These fractions are extensively utilized in the food, cosmetic, pharmaceutical, and industrial sectors, contributing to enhanced product quality and functionality (Yayla, 2025; Kellens *et al.*, 2007).

There are three main fractionation methods: dry, solvent, and detergent-assisted. Dry fractionation is the most widely used due to its eco-friendliness and cost-effectiveness (Timms, 2005). Solvent fractionation provides a more precise separation but raises environmental concerns. Detergent fractionation yields high-purity fractions but involves complex waste management (Yayla, 2025).

Fractionation of methanol-transesterified oil is a process used to separate the components formed during transesterification, mainly to obtain biodiesel and glycerol (Mumtaz *et al.*, 2017). The biodiesel fraction can be obtained by decanting the glycerol or by simple washing with acids and the use of absorbents (Atadashi *et al.*, 2011).

Another method of fractionating vegetable oil is molecular distillation, a method that was developed for the removal of free fatty acids from vegetable oils but can also be used for the recovery of other volatile compounds such as squalene or tocopherols. The process is based on molecular distillation, where volatile compounds evaporate upon contact with the evaporation surface and subsequently migrate to a cold surface to obtain a distillate product. This method minimizes oil losses, can be applied to oils with varying acidities and compositions, and reduces the need for wastewater treatment (Ștefan *et al.*, 2021; Changwatchai *et al.*, 2022).

Molecular distillation does not lead to the formation of difficult-to-manage waste and does not require complicated steps or a certain viscosity of the medium to achieve separation, such as in detergent fractionation and dry fractionation methods. Solvent fractionation requires very high investment and operating costs, being applied only to high-value oils. Molecular distillation is a solvent-free technique applicable to a wide range of oils, with its effectiveness depending primarily on the oil's composition. In contrast, the other methods have been tested only on specific types of oils. For example, dry distillation has been used to separate the olein and stearin fractions from palm oil, and recently, it has been applied to other vegetable oils, such as coconut oil. This method is limited by the viscosity of the oil.

Furthermore, it should be considered that the method is intended for future industrial-scale application and all the disadvantages mentioned above prevent it from being realized with an advantageous profit.

3. Experimental

For oil characterization by experimental analysis, the acidity index, saponification index, iodine index and density of two cold-pressed sunflower oil samples and one refined commercial oil sample were determined. For Sample 1, the oil was extracted from sunflower seeds after four months of storage and was characterized six months after extraction. In the case of Sample 2, the oil was extracted after eight months of seed storage and characterized two months later.

The methods used for characterization were those available in the Department of Bioresources and Polymer Science at the National University of Science and Technology Politehnica Bucharest (Călinescu *et al.*, 1999).

From the chromatographic analysis of the oil samples, the percentage composition of the oil sample with an acidity of 4.89% was considered, consistent with the results obtained in the experimental analysis: acidity, molar mass and type of oil - with a high content of oleic acid, according to data from the literature.

Oil characterization by empirical analysis: Choosing molecular distillation as the fractionation method, the aim is to remove components such as free fatty acids and tocopherols from the oil sample. These components have high boiling points at atmospheric pressure.

To prevent oil degradation, it is necessary to reduce the pressure until the boiling temperatures of the target compounds are sufficiently lowered. Since experimental data at low pressures are not available in existing databases, certain properties are estimated using the group contribution method. Boiling temperatures at a pressure of 1 atm were estimated by the Ceriani method (Ceriani *et al.*, 2004). Boiling temperatures were also estimated by the group contribution method implemented in the Aspen Plus software. The estimated temperatures were compared with literature data. Aspen Plus software is a process simulation tool used for monitoring, analysis, optimization, and conceptual design of industrial processes, particularly in the chemical industry.

4. Results and discussion

The results of the characterization of the three oil samples by experimental analysis (acidity index, saponification index, iodine index, density) are presented in Table 1. Each property will indicate an important aspect about the analysed oil.

It can be observed that the density of the three samples is similar and comparable to the data in the literature. The values obtained for the iodine index correspond to the oil with a high oleic acid content (Tiefenbacher, 2017; Gunstone, 2011). The saponification index can be used to calculate the molar mass of the oil. It can be observed that oil Sample 2 exceeds the maximum allowable acid value for cold-pressed oil and therefore requires refining.

By comparing the 3 types of oils, major differences in color and clarity can be observed between the first two samples and the last one. Visual differences were observed in the viscosity of the samples, with the last sample being less viscous compared to the others. Another noteworthy observation was the strong sunflower seed odor in the golden-colored oils, suggesting the presence of carotenoid compounds and trace amounts of chlorophyll (Grompone, 2011).

Sample 2 exhibited the highest acidity, suggesting a significant presence of free fatty acids, with a harmful effect on human health due to the presence of trans double bonds, requiring refining of the oil. Consequently, the oil requires refining before it can be marketed. It is important to note that both the duration of seed storage and the oil's storage period after extraction contributed to the increase in free fatty acid content.

Table 1

Properties of sunflower oil samples

Oil sample	Sample 1	Sample 2	Refined commercial oil	Data from the scientific literature	Literature reference
Acidity index, mg KOH/g sample	3.05	4.89	0.30	max 0.6 for refined oils; max 4.0 for cold pressed oil	CODEX STAN 210-1999 (2025)
Saponification index, mg KOH/ g sample	184.28	183.46	180.91	182-194	CODEX STAN 210-1999 (2025)
Iodine index, g iodine/g sample	77.58	77.76	79.78	81-91; 78-90	Tiefenbacher, 2017; CODEX STAN 210-1999 (2025)
Density, g/mL	0.913	0.921	0.912	0.918	Sagiroglu *et al.*, 2011

Some of the results of the calculation of the boiling points of the components of sunflower oil Sample 2 are given in
Table 2. The estimates obtained using the Ceriani method exhibit good agreement. For fatty acids, the values reported in the literature are comparable to those predicted by group contribution methods, with errors tend to increase as the complexity of the acylglycerol structure grows. The results generated and those provided by Aspen Plus software show only minor discrepancies.

Table 2
Boiling temperatures of sunflower oil components at 1 atm and 0.1 Pa pressure

Oil component	Tf, °C at 1 atm pressure			Literature reference	Tf, °C at 0.1 Pa pressure	
	Estimated by group contributions (Ceriani method)	Aspen Plus	Literature		Estimated by group contributions (Ceriani method)	Aspen Plus
palmitic acid (16:0)	349.5	350	351.5	PubChem, 2024a; Fisher Scientific, 2024b; Oreopoulou *et al*., 2015	79.59	78
oleic acid (18:1)	361.8	359.85	360	PubChem, 2024b; Fisher Scientific, 2024a; Joelianingsih *et al*., 2014	92.05	81
linoleic acid (18:2)	355.4	354.85	360	Avantor Sciences, 2025	91.91	79
trilinolein	631.5	622.15	678.7	García *et al*., 2008	254.0	249
triolein	618.8	623.65	679.24	García *et al*., 2008	255.5	248.5
oleo-dilinolein	551.4	540.589	N/A	Sigma-Aldrich, 2025b; KM Pharma, 2025	254.4	251
palmito-dilinolein	557.1	534.189	N/A	Sigma-Aldrich, 2025a	248.2	245.5

The boiling points of the compounds at a pressure of 0.1 Pa were also calculated. It can be observed that the estimated boiling point values for certain free fatty acids differ by approximately 10°C compared to those retrieved from the Aspen Plus software. Consequently, this estimation method yields more accurate results under reduced pressure conditions, particularly for acylglycerols. The estimated boiling temperatures at atmospheric pressure for acylglycerols present a considerable difference from those found in the literature, but it should be mentioned that the literature data were obtained through group contributions and not experimentally determined.

The analysis of the results highlights the limitations of the Ceriani method in estimating the properties of acylglycerols. In the future, efforts will focus on identifying a method capable of providing conclusive results for these compounds.

5. Conclusions

Vegetable oil fractionation is a key process that enhances oil functionality across food, pharmaceutical, cosmetic, and industrial applications. Various techniques, including dry fractionation, solvent-based methods, and molecular distillation, enable the production of high-purity fractions with improved properties.

This paper presented potential methods for refining vegetable oils by removing compounds that adversely affect oil quality. The oil contains many groups of chemical compounds, and the goal of refining is to preserve the acylglycerols while eliminating components that reduce stability over time, impart undesirable flavors and odors during storage or heating, or may be valorized in other applications.

Two of the samples indicated a high content of free fatty acids, which leads to the need for a method to separate them from the oil mass. Comparing the methods presented in this work, it can be said that the method with the greatest potential for development at the industrial level is molecular distillation. Studies conducted to date have reached up to the pilot scale.

Among all the methods discussed above, this approach appears to be the most feasible for industrial implementation, given the limitations and disadvantages of the other techniques. Its applicability to a wide range of oils and fats, along with the high purity of the resulting products and the ability to recover thermally sensitive compounds, underscores its particular importance in this field. However, prior to industrial application, the molecular distillation unit must be properly designed within a process simulation environment- an endeavor that will undoubtedly present a significant challenge.

This method achieves the separation of unwanted compounds such as free fatty acids and tocopherols under high vacuum, which helps prevent oil degradation. The boiling temperatures of the components in the oil are high and heating to these temperatures can lead to oil degradation. Therefore, it is necessary to reduce the pressure until the boiling temperatures of the target compounds are sufficiently lowered.

In this regard, the boiling temperature was calculated at a pressure of 1 atm, the pressure will be reduced to a temperature that will not degrade the oil during separation by molecular distillation. The boiling temperature of the sunflower oil components was calculated at a pressure of 0.1 Pa. The Ceriani method led to results similar to those obtained from the Aspen Plus software at this pressure. While the Ceriani method performs well for free fatty acids, it exhibits notable inaccuracies when used for acylglycerols at atmospheric temperature.

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ABORDĂRI MODERNE ALE FRACȚIONĂRII ULEIURILOR VEGETALE

(Rezumat)

Acest studiu analizează fracționarea uleiurilor vegetale folosind metodele cunoscute până în prezent și examinează utilizarea acestor fracții în diverse industrii. Accentul a fost pus pe uleiul de floarea-soarelui datorită conținutului său ridicat de acid oleic, care are beneficii pentru sănătate. Fiind o metodă nouă de fracționare, lucrarea se concentrează în principal pe distilarea moleculară, o metodă care duce la purități ridicate, avantajoasă pentru substanțele sensibile la căldură sau ușor degradabile și care a fost studiată până în prezent la scară pilot. Trei probe de ulei de floarea-soarelui au fost supuse analizelor experimentale și empirice. Rezultatele au fost comparate cu datele disponibile în literatura de specialitate și cu rezultatele simulatoarelor de proces.