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DETERMINATION OF OXIDATIVE STABILITY OF CRUDE AND REFINED VEGETABLE OILS BY RANCIMAT

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Abstract: *The oxidative stability of vegetable oils has been introduced as a critical factor that affects on its quality, shelf life, and nutritional value. In this study, the Rancimat method was analyzed for investigation and comparing the oxidative stability of crude and refined vegetable oils. The induction period, representing the time taken for significant oxidative degradation to occur, has been used as a key parameter to evaluate the oxidative stability. The oxidative stability of different types of vegetable oils, including sunflower, rapeseed, soybean, and cottonseed oil, was studied at various stages of processing: water degummed and neutralized oil. The induction period (IP) and protection factor (PF) were used to assess the oils resistance to oxidation. The data showed that crude oil had the highest oxidative stability, with a PF of 1.89 for rapeseed, 2.13 sunflower, 2.3 for soybean and 1.95 for cottonseed oils, compared to water degummed oil. Neutralized oil showed improved oxidative stability, with a PF of 1.16 for rapeseed oil and 1.57 for soybean oil, but reduced stability with a PF of 0.85 for cottonseed oil comparing with degummed oils. Refining processes, such as neutralization and degumming, were shown to pose a potential decrease in oxidative stability due to the removal of minor components present in the crude oil.*

Keywords: *Oxidative stability, sunflower oil, rapeseed oil, soybean oil, cottonseed oil.*

Annotatsiya: *O'simlik moylarining oksidlanish barqarorligi muhim omillardan biri bo'lib, moylarning sifati, saqlash muddati va ozuqaviy qiymatiga ta'sir ko'rsatadi. Ushbu ishda rafinatsiyalangmagan va rafinatsiyalangan o'simlik moylarining oksidlanish barqarorligi Ransimat yordamida aniqlangan. Induksiya davri (ID) parametrlari o'simlik moylarining oksidlanishini boshlanish vaqtini ko'rsatib, moylar oksidlanishi baholashning asosiy mezonlardan biri hisoblanadi. Kungaboqar, raps, soya va paxta moylarining oksidlanish barqarorligi moylar rafinatsiyalashning turli bosqichlarida, ya'ni gidratatsiya va neytrallash jarayonlarida aniqlangan. Induksiya davri va proteksiya omillari o'simlik moylarining oksidlanishga qarshiligini baholash sifatida ishlatilgan. Natijalar shuni ko'rsatadiki, rafinatsiyalanmagan o'simlik moylari oksidlanishga qarshi eng barqaror bo'lib, proteksiya omillari kungaboqar moyida 2.13, raps moyida 1.89, soya moyida 2.3 va paxta moyida 1.95 ni tashkil etgan. Gidratlangan moylarga nisbatan neytralanngan moylar yuqori okisdalnish barqarorligini ko'rsatdi, raps moyi uchun PF 1.16, soya moyi uchun 1.57 ni tashkil etgan bo'lsa, paxta moyi uchun esa PF 0.85 ni tashkil etdi. Rafinatsiyalash jarayonlari: gidratatsiya, neytrallashda moylardagi hamroh moddalarning kamayishi hisobiga o'simlik moylarining oksidlanish barqarorligi tushib boradi.*

Tayanch so'zlar: *oksidlanish barqarorligi, kungaboqar moyi, raps moyi, soya moyi, paxta moyi.*

Аннотация: *Окислительная стабильность растительных масел - критический фактор, влияющий на их качество, срок хранения и питательную ценность. В данном исследовании был про анализирован метод Ранцимат для изучения и сравнения окислительной стабильности нерафинированных и рафинированных растительных масел. Индукционный период, представляющий время значительного окислительного разложения, использовался как ключевой параметр для оценки окислительной стабильности. Окислительная стабильность различных видов растительных масел, включая подсолнечное, рапсовое, соевое и хлопковое масло, оценивалась на различных стадиях обработки: гидратация и нейтрализация масла. Индукционный период (IP) и протекционный фактор (PF) использовались для оценки сопротивляемости масел окислению. Данные показали, что нерафинированное масло* *обладало наивысшей окислительной стабильностью, с PF, равным 1.89 для рапсового, 2.13 – для подсолнечного, 2.3 – для соевого и 1.95 – для хлопкового масел, по сравнению с гидратированными маслами. Нейтрализованное масло проявило улучшенную окислительную стабильность, с PF, равным 1.16 для рапсового масла и 1.57 – для соевого масла, но сниженную стабильность с PF равным 0.85 – для хлопкового масла по сравнению с методом гидратации. Процессы очистки (такие как гидратация и нейтрализация) могут привести к уменьшению окислительной стабильности из-за удаления сопутствующих веществ в нерафинированном в масле.*

Ключевые слова: *Окислительная стабильность, подсолнечное масло, рапсовое масло, соевое масло, хлопковое масло.*

Introduction

Vegetable oils are widely used in various food products and industrial applications due to their nutritional benefits, flavor profiles, and functional properties. However, the susceptibility of vegetable oils to oxidative deterioration is a major concern that affects their quality, shelf life, and safety. The formation of off-flavors, rancidity, and nutritional degradation resulting from lipid oxidation can significantly impact consumer acceptance and lead to economic losses for manufacturers. Therefore, accurate and efficient methods for assessing the oxidative stability of vegetable oils are of paramount importance in both the food industry and research fields. Over the years, numerous methods have been developed to evaluate the oxidative stability of vegetable oils. Among these, the Rancimat method has gained widespread recognition as a reliable and rapid technique for determining the resistance of oils to oxidation. The Rancimat method, also known as the "Rancimat test" or "accelerated oxidation test," was first introduced by W. M. Schultz in 1976 [1]. Since its inception, the Rancimat method has been further refined and standardized, making it a preferred choice for assessing the oxidative stability of vegetable oils.

In the Rancimat method, the oil sample is subjected to controlled heat and continuous airflow, simulating accelerated oxidation conditions. This exposure promotes the formation of volatile oxidation products, such as aldehydes and ketones, which are indicative of the oil's susceptibility to oxidation. The critical parameter in the Rancimat test is the induction period, which represents the time taken for the oil to reach a specified level of oxidative degradation.

Several researchers have investigated the oxidative stability of various crude and refined vegetable oils using the Rancimat method. For instance, studies have examined the oxidative stability of crude palm oil and its refined counterparts [2]. Others have explored the oxidative stability differences between crude and refined soybean oil [3], sunflower oil [4], and rapeseed oil [5].

Moreover, investigations into the impact of processing techniques on oxidative stability have been conducted for different vegetable oils. Research on the oxidative stability of crude and refined olive oil [6] and corn oil [7] has provided valuable insights into the effect of refining processes on oxidative stability.

Furthermore, the potential influence of natural antioxidants on the oxidative stability of crude and refined vegetable oils has been explored [8-10]. Studies have investigated the efficacy of incorporating antioxidant-rich extracts, such as rosemary [11] and green tea [12,13], to enhance the oxidative stability of these oils.

Despite the extensive research on the oxidative stability of vegetable oils, there is still a need to comprehensively compare the oxidative stability of crude and refined vegetable oils using the Rancimat method. Understanding the differences in oxidative stability between these oil types is crucial for both the food industry and consumers. Such knowledge can aid in the selection of suitable processing techniques, the optimization of storage conditions, and the development of antioxidant strategies to extend the shelf life and enhance the quality of vegetable oils.

The oxidative stability of both crude and refined vegetable oils has been the subject of investigation in several studies. Researchers have utilized various methods to assess and compare the oxidative behavior of these oils. The Rancimat method, which measures the induction period under accelerated oxidation conditions, has been widely applied to determine the oxidative stability of vegetable oils [14]. Studies have employed the Rancimat test to evaluate the oxidative stability of crude and refined sunflower oil [15], palm oil [16], soybean oil [17], and other vegetable oils.

The oxidative stability of crude and refined oils can be influenced by numerous factors, including the presence of natural antioxidants, such as tocopherols and phenolic compounds, as well as the effect of refining processes on the oil's chemical composition and antioxidant content. Understanding the impact of these factors is essential for optimizing the production and storage conditions of vegetable oils to maintain their oxidative stability.

This review aims to provide an overview of the current state of knowledge regarding the oxidative stability of crude and refined vegetable oils. By analyzing findings from various studies shows the differences in oxidative behavior between these two oil types and identify the key factors that contribute to their stability.

Experimental materials

Sunflower, rapeseed, soybean, cottonseed oils were processed from Uzbek, Slovak oilseed cultivars by industrial solvent extraction in “Kattakurgan yog moy” (Uzbekistan), Palma-Tumys Bratislava (Slovak Republic).

Apparatus

Magnetic stirrer (IKA Werk, Staufen im Breisgau, Germany), centrifuge (MPW-340, CHEMARGO, Blachownia, Poland) at 1300 x ***g*** and Rancimat (743, Metrohnm, Herisau, Switzerland) were used during the experiments.

Methods

Determining the oxidative stability of oils. To monitor the oxidation of vegetable oils, Rancimat (743, Metrohnm, Herisau, Switzerland) apparatus was used. The kinetics of oxidation was followed by the increase in conductivity at a constant volume under isothermal conditions at 110 °C. The oxidation medium was air, and the flow rate was 20 $l.h^{-1}$. The sample size was 3 grams. Three parallel measurements were carried out for each sample. Water degummed oils were analyzed as blanks and the oxidative stability was expressed as the protection factor: $PF = IP/IP_0$, where *IP* is an induction period of neutralized oils and IP_0 is an induction period of water degummed oils.

Water degumming. The process of water degumming was employed to treat crude rapeseed, sunflower, soyabean and cottonseed oils. This involved heating the oils to 80 ^{0}C and subsequently adding 5% water by volume. The mixture was stirred for 15 min. using a magnetic stirrer before mixture to centrifugation for 20 min. [18].

Neutralization. Crude rapeseed, sunflower, soybean, cottonseed oils were neutralized by heating the oils to 70 °C, adding water solution including caustic soda (10 % in weight) in a portion of 0.8 % by weight of the oil. The total reaction times are only 20 min. The formed soapstok are removed by centrifugation for 20 min.

Statistical analysis

All measurements were triplicate. The statistical analysis was carried out with the program Statgraphics Plus, Version 1.4 for Windows (Manugistic, Rockville, USA). The significance of differences between mean values was determined at the $p = 0.05$ (5%) level, using a one way analysis of the variance and the t-test.

Results and discussion

Table 1 shows the protection factor (PF) provides valuable information about the oxidative stability of sunflower oil at different stages of processing. Higher PF values suggest better protection against oxidation, and lower values indicate decreased oxidative stability.

From the data, we can observe the following trends:

Crude oil has the highest oxidative stability, with a PF of 2.13 compared to water degummed oil. Neutralized oil shows improved oxidative stability compared to water degummed oil, with a PF of 1.39.

The decrease in PF of crude oil to neutralized oil might be attributed to the refining process. While refining removes impurities and improves oil quality, it may also lead to the loss of natural antioxidants and minor components that contribute to oxidative stability. The data shows that crude oil has the highest oxidative stability, while neutralizing oil exhibits improved stability compared to water degummed oil.

Table 1.

Oxidative stability of sunflower oil

Sunflower oil				
Type of oil	Oxidative stability of extracted oil		Oxidative stability of pressed oil	
	IP (h)	PF	IP (h)	PF
Crude oil	$4.02 \pm 1.1*10^{-2}$	2.13	$4.21 \pm 1.2*10^{-2}$	2.01
Water degummed oil	$1.88 \pm 4.5*10^{-2}$	1.00	$2.09 \pm 3.2*10^{-2}$	1.00
Neutralized oil	$2.61 \pm 1.3*10^{-2}$	1.39	$2.77 \pm 2.4*10^{-2}$	1.32

In this discussion, we will analyze the oxidative stability of rapeseed oil at different stages of processing, including crude oil, water degummed oil, and neutralized oil. The induction period (IP) and Protection Factor (PF) are used to evaluate the oxidative stability of each type of oil.

The oxidative stability of crude rapeseed oil is represented by an induction period (IP) of 5.82 hours, and the corresponding Protection Factor (PF) is calculated to be 1.89 (table 2). This means that the crude oil has 1.89 times longer induction period compared to water degummed oil. A higher PF value indicates that the crude oil has better oxidative stability than water degummed oil. Water degummed rapeseed oil is used as the reference, and its induction period (IP) is given as 3.07 hours. The PF value for water degummed oil is considered as 1.00 since it is the baseline for calculating the PF. The oxidative stability of neutralized rapeseed oil is represented by an induction period (IP) of 3.56 hours, and the corresponding Protection Factor (PF) is calculated to be 1.16. This means that the neutralized oil has 1.16 times longer induction period compared to water degummed oil. Although the PF for neutralized oil is lower than for crude oil, it is still higher than 1.0 indicating that neutralized oil is more resistant to oxidation than water degummed oil.

Table 2.

Oxidative stability of rapeseed oil

Rapeseed oil				
Type of oil	Oxidative stability of extracted oil		Oxidative stability of pressed oil	
	IP (h)	PF	IP (h)	PF
Crude oil	$5.82 \pm 1.3*10^{-2}$	1.89	$6.32 \pm 2,1*10^{-2}$	1.84
Water degummed oil	$3.07 \pm 5.5*10^{-2}$	1.00	$3.43 \pm 1,6*10^{-2}$	1.00
Neutralized oil	$3.56 \pm 1.5*10^{-2}$	1.16	$3.92 \pm 2,2*10^{-2}$	1.14

The data reveals some important insights into the oxidative stability of rapeseed oil: Crude oil has the highest oxidative stability, with a PF of 1.89 compared to water degummed oil. Neutralized oil shows improved oxidative stability compared to water degummed oil, with a PF of 1.16. From the data provided, we can conclude that the crude rapeseed oil has the highest oxidative stability, followed by neutralized oil, and water degummed oil has the lowest oxidative stability among the three types. This suggests that the refining processes, such as neutralization and degumming, may lead to a decrease in oxidative stability due to the removal of natural antioxidants and minor components present in the crude oil.

Table 3 shows the oxidative stability of crude soybean oil is represented by an induction period (IP) of 3.62 hours, and the corresponding Protection Factor (PF) is calculated to be 2.3. This means that the crude oil has 2.3 times longer induction period compared to water degummed oil. A higher PF value indicates that the crude oil has better oxidative stability than water degummed oil.

Water degummed soybean oil is used as the reference, and its induction period (IP) is given as 1.57 hours. The PF value for water degummed oil is considered as 1.00 since it is the baseline for calculating the PF.

The oxidative stability of neutralized soybean oil is represented by an induction period (IP) of 2.47 hours, and the corresponding Protection Factor (PF) is calculated to be 1.57. This means that the neutralized oil has 1.57 times longer induction period compared to water degummed oil. Although the PF for neutralized oil is lower than for crude oil, it is still higher than 1.0, indicating that neutralized oil is more resistant to oxidation than water degummed oil.

Table 3.

Oxidative stability of soybean oil

Soybean oil				
Type of oil	Oxidative stability of extracted oil		Oxidative stability of pressed oil	
	IP (h)	PF	IP (h)	PF
Crude oil	$3.62 \pm 1.2*10^{-2}$	2.30	$3.96 \pm 1,1*10^{-2}$	2.13
Water degummed oil	$1.57 \pm 2.4*10^{-2}$	1.00	$1.86 \pm 1,1*10^{-2}$	1.00
Neutralized oil	$2.47 \pm 2.2*10^{-2}$	1.57	$2.77 \pm 1,4*10^{-2}$	1.49

Table 4.

Oxidative stability of cottonseed oil

Cottonseed oil				
Type of oil	Oxidative stability of extracted oil		Oxidative stability of pressed oil	
	IP (h)	PF	IP (h)	PF
Crude oil	$8,27 \pm 1,4*10^{-2}$	1,95	$6,67 \pm 1,3*10^{-2}$	1,64
Water degummed oil	$4,24 \pm 2,4*10^{-2}$	1,00	$4,06 \pm 2,6*10^{-2}$	1,00
Neutralized oil	$3,61 \pm 1,3*10^{-2}$	0.85	$3,37 \pm 1,2*10^{-2}$	0.38

Crude soybean oil has the highest oxidative stability, followed by neutralized oil, and water degummed oil has the lowest oxidative stability among the three types.

The oxidative stability of crude cottonseed oil is determined by an induction period (IP) of 8.27 hours, resulting in a corresponding Protection Factor (PF) of 1.95. The substantial IP value and PF indicate that the crude oil exhibits a relatively extended induction period, making it 1.95 times more resistant to oxidation compared to water degummed oil (table 4).

Water degummed cottonseed oil is used as the reference, with an induction period (IP) of 4.24 hours. The PF value for water degummed oil is considered as 1.00, serving as the baseline for calculating the PF. Water degumming is a refining process aimed at eliminating impurities, including phospholipids, to enhance the oil's quality and stability. The oxidative stability of neutralized cottonseed oil is characterized by an induction period (IP) of 3.61 hours, resulting in a corresponding Protection Factor (PF) of 0.85. The lower PF value for neutralized oil indicates reduced oxidative stability in comparison to water degummed oil. Neutralization is a refining step that removes free fatty acids and acidic components, but it may also lead to the loss of natural antioxidants and minor components present in the crude oil, which can impact the oil's oxidative stability. The data reveals that crude cottonseed oil demonstrates the highest oxidative stability, with a PF of 1.95 compared to water degummed oil. Conversely, neutralized oil exhibits significantly reduced oxidative stability, with a PF of 0.85 in comparison to water degummed oil.

These findings underscore the importance of refining processes in influencing the oxidative stability of cottonseed oil. To maintain desired oxidative stability, it is essential to carefully manage the refining process to preserve natural antioxidants and minor components that contribute to the oil's resistance to oxidation.

Conclusion

The oxidative stability of oils plays a crucial role in determining their quality and shelf life. The Protection Factor (PF) provides valuable information about an oil's resistance to oxidation at different stages of processing. Higher PF values indicate better protection against oxidation, while lower values suggest decreased oxidative stability. From the data presented, we can observe several trends in the oxidative stability of different types of oils: Crude oils generally exhibit the highest oxidative stability compared to water degummed oils and neutralized oils. This is evident in sunflower, rapeseed, soybean and cottonseed oils. Neutralization, a refining process aimed at removing free fatty acids and acidic components, may lead to a decrease in oxidative stability due to the potential loss of natural antioxidants and minor components. Water degumming, a refining process that removes impurities like phospholipids, serves as a baseline for calculating PF, with a value of 1.00.

To maintain desired oxidative stability, it is essential to carefully balance the refining process, preserving natural antioxidants and minor components that contribute to the oil's resistance to oxidation. Proper storage conditions and the use of antioxidants can further enhance the oxidative stability and prolong the shelf life of oils.

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