The Effect of Temperature and Wax Content on the Appearance of Turbidity in Sunflowerseed Oil

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Turbidity in refined sunflowerseed oil, caused by the presence of waxes, is a frequent occurrence. As such, it is a special problem in a number of countries where clear packaging is used for this oil. The application of cold test for the determination of sunflowerseed oil clarity is not always satisfactory, as the negative cold test is not a guarantee that the waxes are completely removed and that the oil will remain clear for a longer period. In this study, the threshold value for wax content which would cause turbidity in refined sunflowerseed oil was determined. At the same time, the influence of cooling temperature and wax content on the visible turbidity appearance rate was investigated. The results show that the turbidity threshold for the cold test is 80 mg wax/kg oil, and that the rate of the visible turbidity appearance of the oil depends both on wax content and cooling temperature.

The aim of winterization, a thermomechanical operation, is to obtain an oil which will remain clear at refrigeration temperatures (1).

The oil components causing oil turbidity are high molecular weight compounds such as saturated triglycerides, waxes, free fatty acids and, to a lesser extent, hydrocarbons, sterols and their esters, as well as the fatty alcohols (2-4). The content of these components in the oil is usually very low, aggravating their removal (3,5,6). Some investigators have found that these components probably are bound to the nonhydratable phospholipids of the oil (7), which explains the well-known fact that phospholipids hinder the winterization of sunflowerseed oil (8,9).

During winterization of sunflowerseed, grape seed and corn oil, primarily waxes are removed. In the case of cottonseed oil and hydrogenated soybean oil, high melting triglycerides, the so-called stearin, also are removed (1).

Lately, the problem of obtaining clear sunflowerseed oil has been rather pronounced. New high-oil hybrid sunflowerseeds contribute to this due to the increased wax content of the hull, about 3.5 to 5 times greater than in earlier varieties (9-12).

A very simple method, the so-called cold test (13) prescribed by the AOCS, is most frequently used for the control of the winterization process. This method has been criticized, mainly because of the long time needed for the test. A more important reason is that a great number of oils, primarily sunflowerseed oil, will have a satisfactory cold test, but later will become turbid again. This is a special problem in a number of countries, such as Yugoslavia, where sunflowerseed oil is packed in translucent packaging.

For the above reasons certain modifications of the cold test were performed, referring mostly to the prolonged crystallization (14,15). However, this is not a satisfactory solution for continuous refining.

Lately, Brimberg and Wretensjö (15), Caupeil (2) and Morrison (16) have proposed faster instrumental methods for the determination of the content of waxes separated during cooling. Morrison's method is simple and thus very interesting for broader use. It seems that Caupeil's method will solve the wax analysis problem; however, the apparatus is very complicated and time will be needed before the method is widely applied in the industry (2).

Because the cold test is not satisfactory, the aim of our work was to investigate the application of this test for the evaluation of refined sunflowerseed oil clarity, with known wax content, in order to determine the lowest wax content which causes oil turbidity during the performance of the cold test.

To better understand the behavior of waxes at different temperatures, the visible oil turbidity appearance rate was investigated by evaluating the dependence of wax concentration and cooling temperature using prepared solutions of known concentrations of pure sunflowerseed waxes in dewaxed oil.

The results will ensure better and more effective winterization, as well as the possibility of precise evaluation of wax content in the refined sunflowerseed oil.

MATERIALS AND METHODS

The sunflowerseed oil used for these investigations was refined by a continuous process, under industrial conditions. The oil investigated had a fatty acid composition of 6.5% palmitic acid, 4.1% stearic acid, 19.4% oleic acid, 68.7% linoleic acid, 0.6% linolenic acid and 0.6% arachidic acid. The iodine value, determined by the Wijs method (17), was 138 g I_2/100 g.

Although the oil was processed under industrial conditions, using classical winterization, it became turbid at refrigerator temperature (8 C). This indicated that a certain amount of wax remained in the oil. To obtain clear, wax-free oil, winterization was repeated in the laboratory. After storing at 5 C for 10 days, the oil was filtered through blue ribbon filter paper (Schleicher and Schüll No. 589). After this treatment, the oil remained clear both during cold test and at all temperatures during investigation.

Pure waxes, used for the investigation, were isolated from the layer formed on the filter cloth when filtering the oil during the winterization of sunflowerseed oil in industrial conditions.

The method of Popov and Stefanov was used for the isolation (18). The characteristics of the waxes were as follows: melting point, 74.0 C; dropping point, 74.8 C; iodine value (Hanush method), (mg I_2/100 g) 12.3, and saponification value (mg KOH/1 g), 104.

Determination of turbidity threshold during the cold test. For turbidity threshold determination, model solutions were prepared using pure sunflowerseed waxes added to clear sunflowerseed oil, in concentrations from 6 to 250 mg/kg.

The clarity evaluation of the oil stored at 0 C for 5.5 hr was performed by cold test, using a three-member

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TABLE 1

Turbidity Appearance in Sunflowerseed Oil Depending on Wax Concentration and Storage Time at 0 C

No.	Wax content of the oil (mg/kg)	Cold test[a]	Storage time at 0 C (days) 1	2	3	4	8	
1	6	−	−	−	−	−	−	Poorly visible flakes
2	8	−	−	−	−	−	+	Large flakes in groups
3	10	−	−	−	−	+	++	
4	20	−	−	−	−	++	++	
5	30	−	−	+	++	++	++	
6	40	−	−	+	++	++	++	
7	50	−	−	+	++	++	++	
8	60	−	−	+	++	++	++	
9	70	−	+	+	++	++	++	
10	80[b]	+	+	+	++	++	++	
11	90	+	++					Dense flakes
12	110	+	++					
13	130	+	++					Layer at the bottom
14	150	+	++					
15	170	++	++					
16	200	++	++					
17	250	++	++					

[a]−, clear oil; +, visible turbidity of the oil, and ++, more pronounced visible turbidity of the oil.
[b]Turbidity threshold.

panel (13).

Determination of the turbidity appearance rate at different temperatures depending on the wax content. The same series of samples with the known wax concentration was used for these investigations, and the appearance of turbidity was observed at 0, 5, 13 and 16 C. The oil samples were heated to 130 C, cooled to 0 C and further tempered at 0, 5, 13 and 16 C until the appearance of turbidity. The time needed for the turbidity appearance was recorded. All analyses were run in triplicate.

RESULTS AND DISCUSSION

The results of the cold test and turbidity appearance investigation in refined sunflowerseed oil as a function of added wax concentration and storage time at 0 C are shown in Table 1.

The results show that samples containing more than 70 mg/kg of waxes became turbid during the cold test. The lowest wax concentration causing turbidity of the oil during the cold test can be considered the turbidity threshold. According to our results, the turbidity threshold is 80 mg/kg of oil.

If the wax concentration is lower, the oil remains clear for a longer period of time. In our case, the sample containing the lowest wax content, 6 mg/kg, became turbid after 10 days at 0 C.

There are different data in the literature on the lowest wax concentration causing visible turbidity in sunflowerseed oil. Caupeil (2) states that sunflowerseed oil containing 25 mg of wax/kg of oil will remain clear for at least eight days at 0 C. According to Brimberg and Wretensjö (15), visible turbidity in sunflowerseed oil will appear at 6–8 C when the wax content is higher than 10 mg/kg.

In a second series of investigations, we investigated the influence of cooling method on rate of crystallization causing turbidity. The samples which satisfied the cold test (less than 70 mg wax/kg) were investigated in these experiments.

The dependence between the wax content and time needed for the appearance of visible oil turbidity at the investigated temperatures is shown in Figure 1.

Comparing these results, it can be seen that the increase of the tempering temperature to 13 increases the turbidity appearance rate. That is more obvious in Figure 2. The wax crystallization rate is the highest at 13 C; that is, the time needed for the appearance of visible oil turbidity is the shortest at this temperature compared to the other temperatures.

It is known that crystallization includes two processes which take place practically at the same time: (i) the formation of submicroscopic crystallization nuclei, and (ii) the growth of nuclei by settling from the solution.

The crystallization nuclei formation rate depends largely on the cooling temperature and, at a certain temperature, reaches a maximum. On the other hand, the microcrystal growth is a process which needs a certain activation, and also depends on the temperature. Our results, the earlier appearance of oil turbidity at 13 compared to 5 and 0 C, can be explained by this fact.

The working conditions applied to the turbidity appearance investigations at 13 C were more convenient for the formation of a greater number of crystal nuclei, as well as for the faster growth of microcrystals. This resulted in the shortest time needed for the formation of visible turbidity caused by the separated wax molecules, compared to 0 and 5 C. At higher temperatures the oil is less viscous, thus enabling the faster diffusion of wax molecules promoting crystallization.

The further increase of the keeping temperature decreases the crystallization rate. It is possible that certain wax crystals dissolve at 16 C. This can be supported

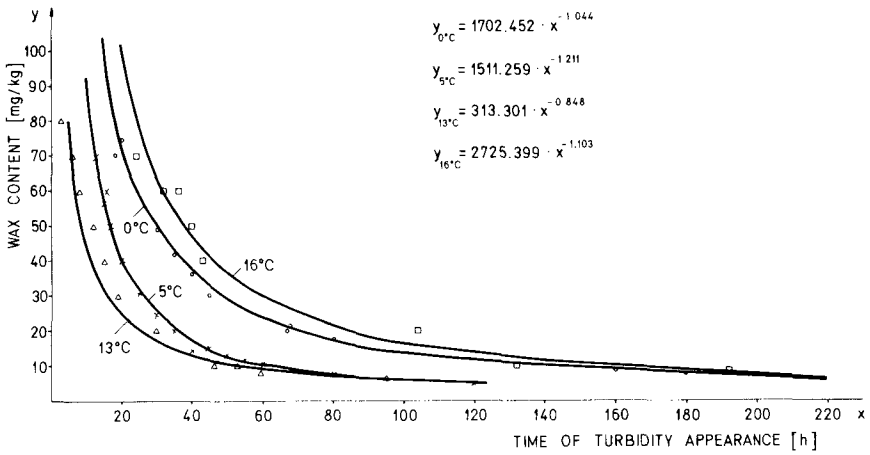

FIG. 1. The effect of wax content and cooling temperature on the turbidity appearance of edible sunflowerseed oil.

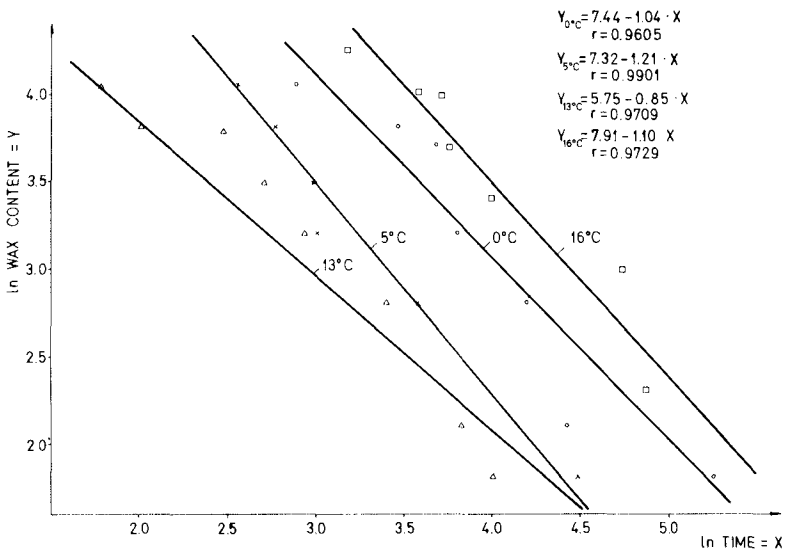

FIG. 2. ln - ln dependence between the time needed for the appearance of visible turbidity and wax content at different temperatures.

by the fact that oil samples with the wax content 6 and 8 mg/kg of oil remained clear during 10 days at 16 C.

On the basis of the experimental data, the functional dependence between the wax content and cooling time, that is, the equation of wax separation rate at all the mentioned temperatures, was calculated (Figs. 1 and 2).

It can be concluded that both wax concentration and cooling temperature have a large influence on the oil turbidity appearance. Higher wax content causes oil to become turbid much faster at a certain temperature. On the other hand, turbidity will appear in the oil at a certain concentration, depending on the cooling temperature. Rivarola et al. investigated the influence of cooling temperature on the formation and size of wax crystals (19).

According to our visual observations, wax crystals separated at different temperatures in the form of tiny flakes. After a short time (24 to 48 hr) they began grouping, forming larger flakes. After that, a sediment was formed.

The visible sediment formed by the separation of wax remained in the oil for long periods (more than a month), even at room temperature (23 C). However, when the temperature was somewhat higher (31 C), the samples with wax concentrations from 6 to 60 mg/kg became clear in a short time, while the sediment remained in the samples containing more than 70 mg of wax/kg of oil. This suggests that oil turbidity at higher temperatures is caused by the wax content, as waxes having the same composition were added to the oil samples.

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A Technique for Monitoring the Quality of Used Frying Oils

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The objective of this work was to develop a practical method for monitoring the quality of oils during the frying process. A special effort was made to find a technique that would not be affected by dilution, since replenishment with fresh oil to varying degrees is a frequent necessity. Nine analytical methods, i.e., measurements of viscosity, polymers, change in dielectric constant, polar compounds, dimers, free fatty acids, smoke point, carbonyls and cyclic monomers, as well as certain combinations of these measurements were evaluated. Since each single method was influenced by replenishment with fresh oil, combinations of two methods were studied in an attempt to produce a single value unaffected by dilution. The ratio polymer/FOS (polymers according to Peled's technique of methylation and extraction and change in dielectric constant by Foodoil Sensor readings) proved not only to be adequate for monitoring the quality of the used oil, but also was affected minimally by replenishment.

Deep-fat frying is one of the most commonly used procedures for the preparation of foods. Desirable texture and flavor can be generated during the frying operation; however, when the oil is used repeatedly at elevated temperatures in the presence of air, thermal oxidation occurs and the oil deteriorates. Severe decomposition of frying oils not only compromises the quality of the food being fried, but also poses a potential hazard to human health and nutrition. The importance of establishing simple, objective methods for quality evaluation of used frying oil cannot be overemphasized.

The purpose of the present work was to develop such methodology. A special effort was made to find a technique whose applicability would not be affected by dilution, since replenishment with fresh oil to varying degrees is a frequent necessity.

MATERIALS AND METHODS

Nine analytical methods were chosen to evaluate the quality of used oils. These were measurements of viscos-

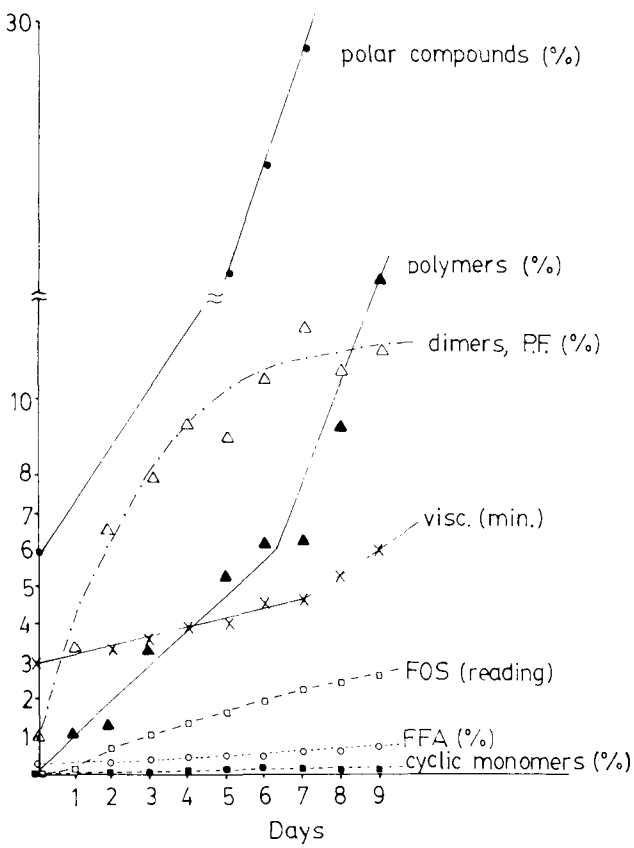

FIG. 1. Monitoring corn oil heated at 185 C by different methods.

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