*Crystallization of Waxes During Sunflowerseed Oil Refining

G. RIVAROLA, M.C. AÑÓN and **A. CALVELO**, Centro de Investigación y Desarrollo
en Criotecnología de Alimentos CIDCA, UNLP-CIC-CONICET, Facultad de Ciencias
Exactas, Calle 47 y 116 (1900) La Plata, Argentina

ABSTRACT

Cooling conditions and wax content in oil determine the morphologies adopted by crystals. At high cooling rates (K) and low temperatures of the refrigerant (T_f), nucleation temperatures are low. This induces the formation of a great number of small nuclei. However, at low K and high T_f, nucleation temperatures are high, producing a few large nuclei. The wax/oil equilibrium curve was determined; it allows the evaluation of the wax remaining in the oil after a given treatment. In addition, experiments were performed to evaluate crystal separation from oil. The increase of temperature from 10 to 25 C and the presence of soaps in the oil facilitate wax separation. These results give additional information that can improve operating conditions and make the choice of technological alternatives in wax separation easier.

INTRODUCTION

The introduction of new varieties of sunflowerseeds with high oil yields has brought about the need to increase the efficiency of the wax separation process in order to avoid turbidity of the refined oil.

Waxes are found mainly in the seed hull and are incorporated into the oil during the pressing and extraction procedures.

There are several technical alternatives for the separation of waxes during the refining process, all of which involve different crystallization conditions (temperatures, residence times, presence or absence of soaps, phospholipids, etc.). Furthermore, one of the quality specifications requires oil to remain clear for 24 hr at 0 C (1). Consequently, good separation of waxes has to be ensured through the formation of crystals which can be filtered or centrifuged easily with a minimum retention of oil so as to maintain high yields. Crystallization conditions are greatly affected by the degumming and neutralization processes, because of economic or energy saving considerations that lead to different flow sheet positions for the wax separation step. Therefore, it is necessary to have data which allow for selection of technical alternatives on the basis of a better knowledge of the variables which control the size and morphology of wax crystals.

The purpose of this work was to study the crystallization characteristics of waxes in sunflower oil under different cooling conditions and wax content. Descriptions of the morphology adopted by the crystals and an evaluation of the wax/oil equilibrium curve were made. The crystal size distribution as a function of the parameters which describe the thermal history of the oil during the cooling process, the hydrophilic characteristic of crystals and the separation in presence of surfactants also were determined.

MATERIALS AND METHODS

Samples

Crude and refined sunflowerseed oils were used for this study.

Crude oil was obtained from an oil processing plant. Its fatty acid content and the qualitative evaluation of phospholipids were carried out by gas liquid chromatography (GLC) (2) and thin layer chromatography (TLC) techniques (3), respectively. The phosphorous content (4) was 150 ppm (4500 ppm expressed as lecithin) and the wax concentration was 0.15%. The wax ester fraction was obtained according to the method described by Bianchi et al. (5). The determination of its fatty acids and alcohols were carried out by the procedure of Kleiman et al. (6).

The refined oil had a wax content of 0.005% and 10 ppm phospholipids expressed as phosphorus (300 ppm expressed as lecithin).

Microscopy

A Leitz microscope with a controlled temperature plate was used for observations of the crystal morphology, determinations of temperature and crystal formation times, melting point temperatures, crystal size and growth determinations.

The temperature was controlled through a programmable Lauda UK 30 cryostat. Ethylene glycol in water (3:1) was used as refrigerant fluid.

The sample and 0.05 mm diameter Copper-Constantan thermocouple connected to a potentiometric recorder were placed between a slide and the slide cover. Moisture condensation was avoided by circulating a very light dry air current over the slide cover.

Crystals formed were microphotographed using polarized light.

Isolation of Oil-Free Waxes

In order to obtain oil-free wax crystals, crude oil was filtered through a Buchner filter. The solid residue was washed several times with petroleum ether at 0 C and dried at room temperature.

Wax/Oil Equilibrium Conditions

Refined oil which passed the cold test (1) with a 300 ppm lecithin content was cooled at 0 C for 24 hr to eliminate any remaining waxes.

Under these conditions no crystals were detected visually, but they were found under the microscope at sizes close to 3 μm. These crystals were separated by centrifugation (20,400 x g for 20 min) and the remaining oil subjected to additional cooling (-5 C for several hours) with negative results. Consequently, this oil was considered free of waxes and was used to prepare different solutions with known quantities of wax. Solution concentrations ranged from 0.005% to 0.2% of waxes in oil. Crystallization and solubilization temperatures were determined by means of the controlled temperature-plate microscope already described.

In the crystallization tests the sample placed in the slide first was heated to 80 C and then cooled slowly at a rate of 0.1 C/min, until wax crystals formed (the minimum detectable size was 2 μm). The temperature was measured by a 0.05 diameter Copper-Constantan thermocouple which was immersed in the sample.

For the melting point determination, the previously melted sample (80 C) was kept in a thermostatic container at 4 C for 3 hr to allow the formation of the wax crystals. Afterwards, an aliquot was placed in the microscope plate and heated at 0.25 C/min while oil and crystals were mixed through slow movements of the slide cover. The solubilization temperature was considered to be the temperature at which the last portion of wax disappeared. The thermal history was recorded in a way similar to that used for cooling.

Heat Exchangers Cooling

Experiments were carried out in an attempt to simulate cooling conditions similar to those used in industrial refining plants.

Twenty l of crude oil were placed in a 60 C thermostatized container.

Once the oil reached this temperature, it was circulated through a 3 m × 0.75 cm internal diameter long copper coil immersed in a cryostat at a constant temperature, T_f. The circulated flow rates simulated residence times similar to those existing in plate coolers used in industrial plants (45-60 sec). The cooled oil flowed continuously into a thermally isolated container thermostatized at the same outflow temperature as the exchanger. The cylindrical shaped container (6 cm diameter, 17 cm high), had a six-blade agitator distributed along its height. The blades produced vertical currents which avoided sedimentation of crystals. Experiments were made at 40 rpm without agitation. Samples were taken after 1 and 24 hr of residence in the tank. Crystal size distributions were determined.

Viscosity Determination

A sample of crude oil free of suspension particles was used to determine viscosity. Accordingly, the oil was settled and filtered in a 9 C chamber. A Haake rotative viscosimeter was used to determine viscosity at temperatures ranging from 3 to 30 C.

RESULTS AND DISCUSSION

Sample Characterization

Table I shows the percentage of fatty acids of crude sunflowerseed oil and fatty acids and alcohols present in the ester fraction of the waxes used.

C18:1 and C18:2 represent 94.7% of the fatty acids in the oil. C20:0, C22:0, C24:0 constitute 81.3% of the fatty acid content in the waxes and C24, C26 and C27 are the main components of the alcohol fraction in the waxes (90.7%).

Phosphatidylcholine (lecithin) was the main component of phospholipids present in sunflowerseed oil. Phosphatidylethanolamine, phosphatidylserine, phosphatidylinositol and lysophosphatidylcholine were the minor components.

Morphology

Depending on the cooling conditions and the wax concentration in the oil, different morphologies were detected.

For wax concentrations found in crude oils (approx. 0.15%), the crystals initially were visible in the polarized light microscope with the shape of elongated rods close to 2 μm long.

As the crystals grew, they clustered in irregular shapes which could be assimilated nearly to a sphere. Larger crystals were obtained in runs carried out with higher concentration of waxes. Thus, for concentrations of 1% wax in slow-cooled samples (0.1 C/min), sizes close to 50 μm were obtained. Above such concentrations, branched-off crystals that reached 100 μm were found. Although these concentrations are excessive compared to those existing in crude oils, this information might be useful when considering the conditions prevailing at the bottom of winterization tanks.

Wax/Oil Equilibrium Conditions

In order to obtain equilibrium conditions between waxes and sunflowerseed oil, known wax concentration solutions were prepared as described above to evaluate the solubilization and crystallization temperatures, respectively. The results obtained are shown in Figure 1. A continuous increase in the solubilization temperature (T_e) was observed as a function of the percent wax content (Y). The experimental values were interpreted by means of the following equation:

$$T_e = T_R + a\,(Y - Y_R)^b \qquad [1]$$

where a = 42.49 C and b = 0.1761. Least square method was applied to the logarithmic form of eq. [1]. The correlation coefficient was r = 0.991. The temperature T_R and the wax content Y_R were reference values taken as T_R = 21 C and Y_R = 0.005%.

Figure 1 also shows supercoolings from 15 to 18 C for the crystal formation temperatures, obtained at a cooling rate of 0.1 C/min.

In order to verify that the lower curve had its origin in the necessary supercooling for the nucleation of crystals, crystallization and solubilization tests were performed on two samples of refined oil with 0.10% wax content. Both were maintained at a selected temperature of 42 C for 48 hr. After this time the cooled sample showed wax crystals according to the previously mentioned supercooling effect (this sample originally was clear).

The melting point of the isolated waxes also was determined by microscopy (73 C). Such value was checked by the capillary method. It was within the order reported by Leibovitz and Ruckenstein (7), who found a range of melting points within 76-77 C for the crystals of pure sunflowerseed waxes.

The wax/oil equilibrium curve (solubility curve) allows the evaluation of the content of wax remaining in the oil after a given treatment. It should be emphasized that with temperatures as high as 21 C the content of wax remaining in the oil once the crystals were separated would comply with the cold test. In such a case the crystals formed during the cold test could only be seen through the microscope.

This curve also supplies a precise method to evaluate the wax content in a given oil by determination of the solubilization temperature of the crystals.

Cooling Conditions

Cooling conditions of the oil in the winterization processes of industrial plants involve heat exchangers or agitation

TABLE I

Fatty Acid and Alcohol Percentages of Crude Sunflowerseed Oil and Waxes

	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:0	C22:0	C24:0	C26:0	C28:0	Others
Fatty acids												
Oil	0.4	6.3	1.5	20.4	71.3	0.1	–	–	–	–	–	–
Wax (ester fraction)	–	–	0.8	–	–	–	45.7	28.1	7.5	5.5	8.2	4.2
	C20	C22	C24	C26	C27	C28	C30 (%)					
Alcohol												
Wax (ester fraction)	0.2	9.4	40.8	33.6	16.3	0.4	0.7					

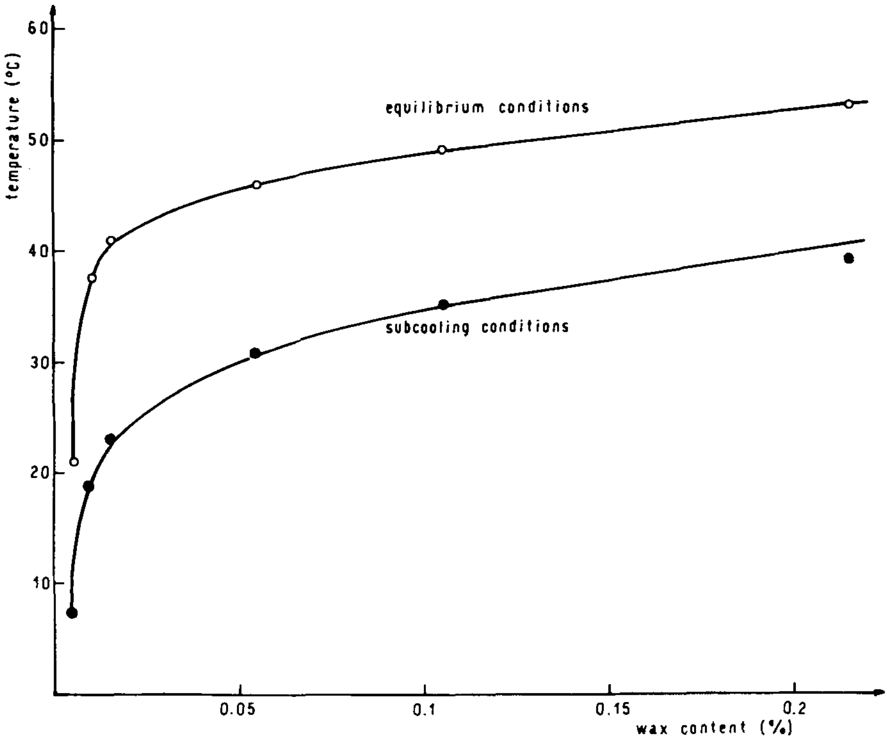

FIG. 1. Oil/wax equilibrium conditions.

tanks with coils. In either case the thermal history of the oil can be approximated by exponential cooling. In order to simulate these conditions, laboratory samples were cooled with thermal histories following the equation:

$$T = T_f + (T_i - T_f)\, e^{-Kt} \qquad [2]$$

where T_f is the temperature of the coolant, T_i is the initial temperature of the sample and K is a constant which represents the heat transfer from the coolant to the sample. Thus, for different cooling alternatives in industrial plants, knowing the thermal history of the oil, it is possible to assimilate a T_f and a K to the respective process.

In the microscope crystallization studies the samples were cooled according to equation [2]; K was calculated from the slope of the line obtained by the graphic representation of ln $(T - T_f)/(T_i - T_f)$ as a function of t.

Consequently, accepting that samples began to cool down from the same temperature T_i, the thermal histories were fully characterized in terms of parameters K and T_f.

Crystal Formation Times

An initial temperature T_i = 60 C was used for simulation of the exponential cooling in the microscope plate. The crystal formation times were thus determined (the smallest detectable size in the order of 2 μm).

Figure 2 shows the crystal formation times t_n for different temperatures of the plate coolant T_f, maintaining K as a parameter. Crude oil containing 0.15% wax was used. As can be seen, for a constant K, a decrease in the coolant temperature produces a shorter crystal formation time. On the other hand, an increase in K with a constant T_f (higher cooling rate) also reduces the crystal formation time.

Once T_f and K values are known for a given industrial process Figure 2 allows evaluation of the residence times for the formation of crystals close to 2 μm.

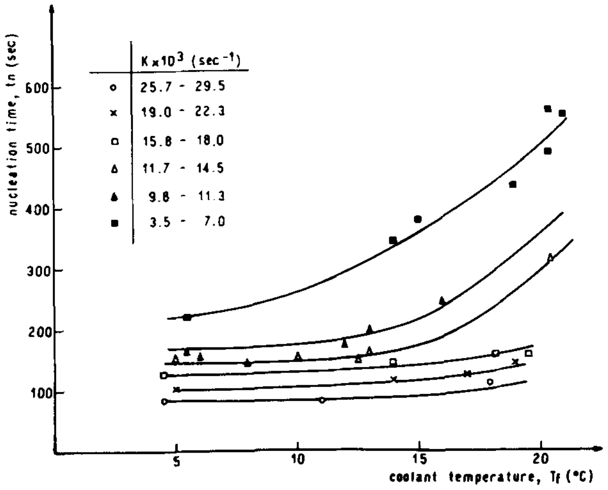

FIG. 2. Crystal formation times, t_n, for different coolant temperatures, T_f, maintaining K as a parameter.

Crystal Formation Temperature

Figure 3 shows the temperature at which 2 μm crystals form as a function of the parameters which characterize the thermal history. It is interesting to observe the significant supercooling that the oil attains before crystals are formed (supercoolings between 23 and 42 C were detected according to the cooling conditions tested). It is worthwhile to compare these data with the smaller values of supercooling detected in the determination of the equilibrium curve in which far slower rates were used.

It is also possible to observe that the lower the coolant temperatures the lower the temperatures for crystal formation. This can be interpreted as a need for larger supercooling so as to compensate for the shorter time that the sample remains supercooled.

A similar interpretation can be performed with respect to the parameter K. When K increases, cooling takes place faster and the sample remains supercooled for less time. Consequently, lower temperatures should be attained in order to begin nucleation. It should be mentioned that results of Figure 3 are related to those of Figure 1 through equation [2].

Time and temperature required for the formation of crystals as determined by conditions similar to industrial plant cooling allow evaluation of the sectors of equipment where nucleation and growth of crystals are taking place as well as their dependency on operative conditions.

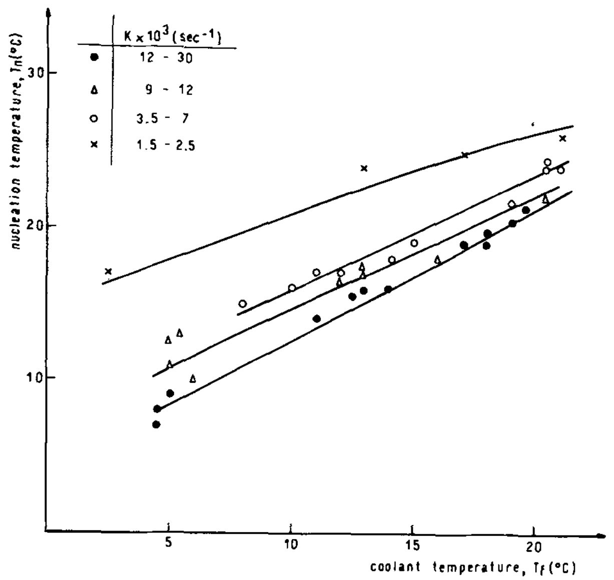

FIG. 3. Crystal formation temperature, T_n, for different coolant temperatures, T_f, maintaining K as a parameter.

Crystal Sizes

Taking into account that for usual wax concentrations in sunflowerseed oil the morphology of the crystals does not undergo great modifications, the possibilities of separation are strongly linked to the size of the crystals formed. Consequently, controlled cooling experiments were carried out measuring the distribution of crystal sizes one hr after their formation. After this period of time practically no growth took place, and it was estimated that total crystallization of waxes had taken place for the temperature reached (this temperature was in all cases close to T_f).

The crystal size was arbitrarily adopted as the largest dimension of the crystal or cluster formed. This requirement was needed mostly for the small rods of 2 μm rather than for larger size clusters which, in general, easily adopted the spherical shape.

Always beginning with samples melted at T_i = 60 C, different temperatures were analyzed for the coolant T_f and different heat transfer conditions K. Figure 4 represents typical normalized crystal size distributions obtained with close values of parameter K. It is clearly seen that the mode (size of the most numerous fraction) is a function of the temperature of the coolant T_f. The higher T_f, the larger the crystal size. The parameter K produces a less pronounced effect and it was detected that for values of $K > 4.5 \times 10^{-3}$ sec^{-1} it has no practical influence.

Figure 5 shows the mode of the crystal distributions as a function of T_f for $K > 4.5 \times 10^{-3}$ sec^{-1}. The experimental data were subjected to a regression analysis, and the following equation was obtained:

$$\bar{D} = \alpha\, e^{\beta T_f} \qquad [3]$$

α = 2.60 and β = 0.071 were obtained by applying the least square method to the logarithmic expression of equation [3]. The correlation coefficient was r = 0.993.

As can be readily seen, for high values of K (good heat transfer systems), the crystals formed do not exceed modes

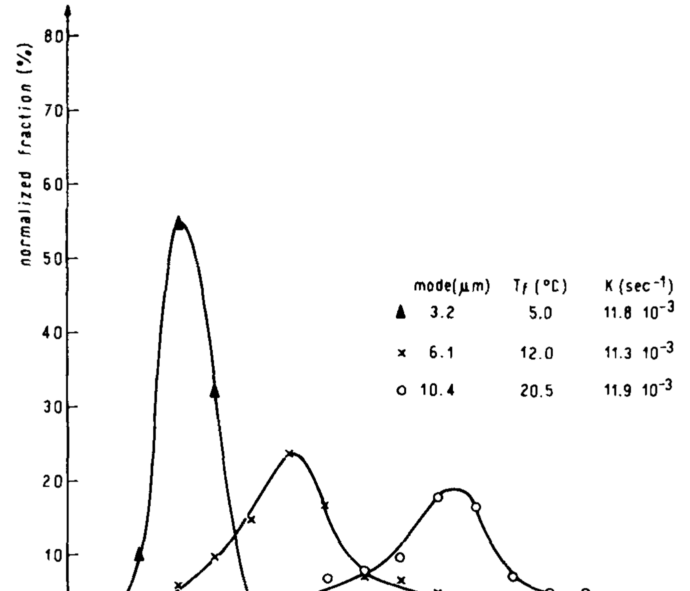

FIG. 4. Typical crystal size distribution.

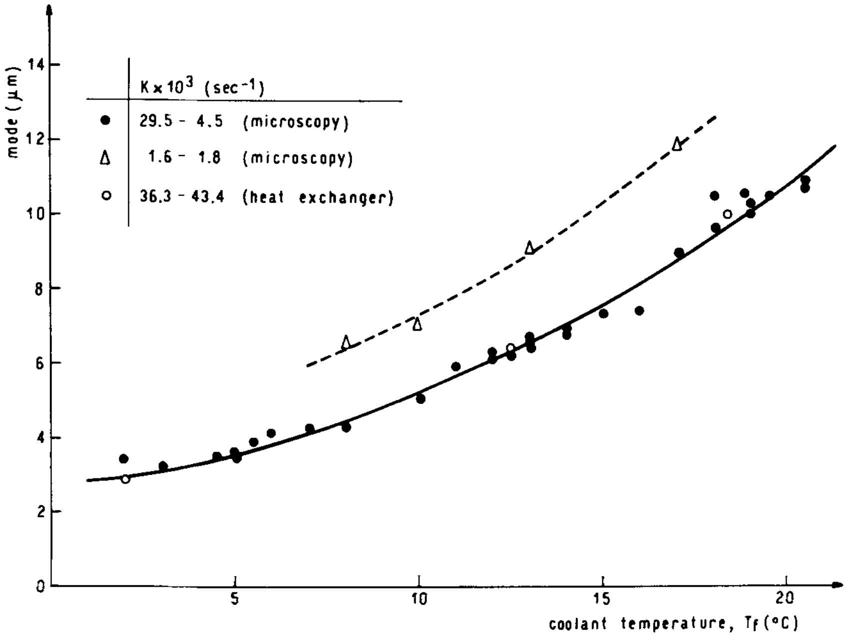

FIG. 5. Mode of the crystal distributions for different coolant temperatures, T_f, maintaining K as a parameter.

larger than 13 μm (Obviously the distribution includes larger sizes; 20 μm crystals have been detected.). For values of K smaller than 4.5×10^{-3} sec^{-1} this parameter also has an influence, and the trend is that the lower the K value the larger the crystal size. Figure 6 shows this effect with α = 3.625 and β = 0.070 for the dashed line (r = 0.997).

The behavior reported is consistent with the temperature and formation times required by crystals. Thus, for high K values and low T_f the nucleation temperatures are low, generating many nuclei that develop only in small sizes. For low K values and high T_f temperatures, nucleation temperatures are high (low supercooling), generating a small number of nuclei which reach considerable sizes.

Cooling in the Heat Exchanger

In order to verify to what extent the experiments performed on the microscope plate were transferable to larger scale equipment, the size of crystals was studied in a system representative of the cooling conditions existing in industrial plants. The equipment, described in the Materials and Methods section, simulated through its residence times the heat exchangers and the crystallization tanks used in refining plants.

Table II shows the operative conditions for the heat exchanger and the crystal size distribution modes obtained after remaining in the crystallization tank one hour.

It is observed that the lower the temperature of the coolant, the smaller the size of the crystals. These sizes were not changed even with residence times of 24 hr in the crystallization tank. No differences were detected with or without agitation.

As in the exchanger K ≅ 37×10^{-3} sec^{-1}, the sizes obtained also have been included in Figure 5 and fit quite well the runs carried out in the microscope plate. Therefore, it may be concluded that the experiments with the microscope do satisfactorily represent larger scales systems even with cooling of the oil in a circulating condition.

Crystal Separation

Since the purpose of this paper is to supply information which would allow higher efficiency in the separation of wax, experiments were carried out trying to clarify the separation characteristics of crystals in sunflowerseed oil.

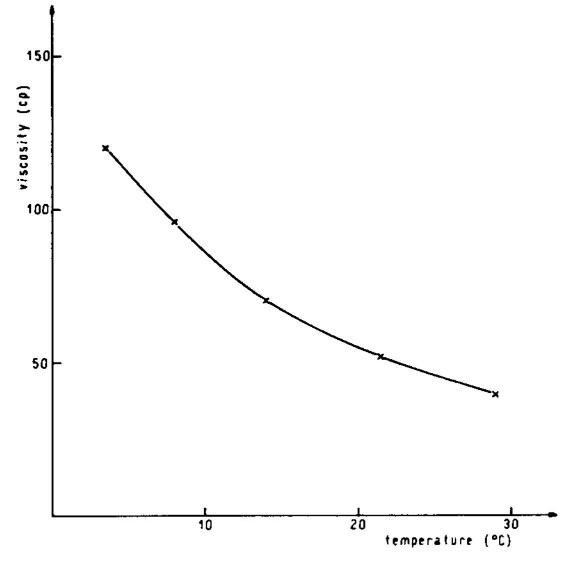

FIG. 6. Sunflowerseed oil viscosity for different temperatures.

It is important to mention the hydrophilic nature of the crystals, as reported by Rac (8). In order to verify this effect, microscope observations were made on crude oils cooled in the presence of water droplets and dodecyl sodium sulphate droplets (surfactant, at 1% concentration). With water wax crystals tend to locate at the water/oil interface; this phenomenon was enhanced with the addition of surfactant.

In order to evaluate the advantages of an eventual separation in the presence of soaps, degummed and neutralized samples of oil were centrifuged with a 2400 ppm soap content (expressed as sodium oleate) and 0.15% wax which had been crystallized at 1 C/min.

In parallel, refined oil was tested with the same wax content but without soaps. Prior to centrifugation 25% water

TABLE II

Simulation of the Operative Conditions of the Industrial Heat Exchanger

	Entrance temperature (C)	Exit temperature (C)	Coolant temperature (C)	Flow rate (m/sec)	Residence time (sec)	K × 10^3 (sec)	Mode μm
A	60	8.5	2.0	2.30	58	37.7	2.9
	60	18.5	12.5	2.33	57	36.3	6.4
	60	23.0	18.5	2.15	61	36.4	10.0
B	60	9.5	2.0	2.44	54	37.8	2.9
	60	22.0	18.5	2.32	57	43.4	10.0

was added to both samples for better visualization of the oil/water interface.

After 15 min centrifugation at 1500 × g and 16 C it was observed that in the sample with soaps, most of the crystals had passed to the water phase while in the one without soaps the wax crystals remained totally in the oil phase. This behavior can be explained by the presence of the ester group which produces a hydrophilic effect which in turn is emphasized by the presence of soaps up to the point of separating them in the water phase. These results open up interesting possibilities for wax separation in the water phase.

Temperature is another important factor for separation. Figure 6 shows the viscosity of clear oil as a function of temperature. It can be shown that an increase of temperature from 10 to 25 C involves a reduction of the viscosity of one-half, with the corresponding improving in the separation of waxes during the centrifugation or filtration stage.

In view of the several refining alternatives in sunflowerseed oil plants, the results obtained supply information for a better handling of the operative conditions and for an easier selection of the technical alternatives for the separation of waxes.

REFERENCES

1. Official and Tentative Methods, American Oil Chemists' Society, 3rd edn., AOCS, Champaign, IL, 1981. Method Cc 11-53.
2. Official Method of Analysis, Association of Official Analytical Chemists, Horwitz, W., ed. 13th ed., AOAC, Washington, D.C., 1980, Method 20.053.
3. Wagner, H., L. Horhammer and P. Wolff. Biochem. Z. 334:175 (1961).
4. Official and Tentative Methods, American Oil Chemists' Society, 3rd edn., AOCS, Champaign, IL, 1981. Method Ca 12-55.
5. Bianchi, G., P. Avato and F. Salami. Cereal Chem. 61:45 (1984).
6. Kleiman, R., F.E. Earle and I.A. Wolff. JAOCS 46:505 (1969).
7. Leibovitz, Z., and C. Ruckenstein, H.L.S. Ltd. Petah Tikua, Israel, Rev. Fr. Corps Gras 81:23 (1981).
8. Rac, M. Proceeding of 5th International Sunflower Conference, Clermont-Ferrand, France, July 1972, p. 365.

[Received January 29, 1985]