Winterization of Oils and Fats[1]

PUSHPINDER S. PURI[2], Best Foods Research and Engineering Center, Union, NJ 07083

ABSTRACT

The process of winterization consists of fractional crystallization of oils and fats followed by the separation of solids to make high quality salad oils. To design a winterization process, the rate of cooling of oil, the temperature of crystallization and the mobility of triglyceride molecules in the oil mass are crucial. These variables play a significant role both in separating the solid fats as distinct crystals and facilitating their filtration from the oil. Thus, the main emphasis in this paper is on the effect of the above variables on the performance of the winterization process.

INTRODUCTION

The process of winterization involves a partial crystallization followed by separation of the solids from the liquid portion; the liquid fraction is used to make high-quality salad oils whereas the solid fraction is used in shortening or margarine formulations. Technically, the winterization process involves 2 component fractional crystallizations in terms of solid and liquid fractions. The solid fraction consists mainly of higher melting triglycerides whereas the liquid fraction is dominant in low-melting components. Distinction must be made between this process and the process used to remove waxes from vegetable oils. The waxes in oil are primarily caused by esters of fatty acids and alcohols; the mechanisms for their removal from oils is totally different from the one used in the winterization process.

In the winterization process, the oil is cooled from room temperature to a predetermined temperature of crystallization. The cooled oil is kept at this temperature for a certain period of time prior to the separation of solid phase from the liquid oil by filtration of the oil-solid fat slurry. Commercially, several variations of this process are used; in some processes crystal modifiers are used (1) and in others, the winterization is carried out in solution of oil in an appropriate solvent (2-4).

In this paper, the basic principles of the winterization process will be discussed. Concepts also will be evolved for the design of winterizers and the effect of different process variables on winterization.

PRINCIPLE OF WINTERIZATION

Winterization is a thermomechanical separation process where component triglycerides of fats and oils are crystallized from a melt. The fractionation is accomplished via partial solidification of certain triglyceride components which are separated from the oil by filtration. The triglycerides found in oils and fats have a complex nature because a single triglyceride may have one, 2 or all 3 fatty acids either the same or different in any of the possible configurations. Most of the triglycerides tend to assume the average characteristics of their constitutent fatty acids. Hence, removal of a certain phase by fractional crystallization becomes a difficult process.

The fat crystallization occurs in 2 steps. The first is the crystal formation process called nucleation. The second is crystal growth. The driving potential for both steps is supersaturation, and neither nucleation nor growth will occur in a nonsupersaturated solution. In physical terms, a supersaturated solution is one which contains more solute than would dissolve under equilibrium conditions. For fats and oils, a supersaturated solution can be obtained only by reducing the temperature of the melt. The saturation-supersaturation curve can be determined experimentally as a function of temperature.

The concept of saturation-supersaturation curves was first proposed by Miers (5,6). According to Mier's theory, the saturation-supersaturation curves (see Fig. 1) define 3 regions in the concentration-temperature field: the unsaturation region where a crystal of solute will dissolve, the metastable region between the saturation and supersaturation curve where crystal growth can occur and the labile (or supersaturated) region where nucleation occurs instantaneously. Nucleation also is stimulated by input of mechanical energy. The action of agitators, pumps and impact against the solid walls may initiate nucleation (7). The other factors which affect nucleation are crystal surface area and the rate of cooling (8).

Nucleation also can occur when foreign matter acts as a nucleus on which solute can start to build a lattice. The presence of such foreign matter which may be dust or nucleation by the solid phase allows the nucleation and growth at lesser degrees of supersaturation.

Once the nucleation has occurred in the supersaturated region from the solid phase formation, the solute concentration of the solution will drop. If this concentration is then kept between the saturation and supersaturation zone, the nucleus will grow to form crystals. Crystal growth can be either diffusion-controlled or particle-integration-controlled, depending on the type of crystallizer used. For the quiescent crystallizers, the crystal growth is diffusion-controlled and the rate of growth becomes crystal-size-dependent. However, in a well mixed crystallizer, the growth rate is generally particle-integration-controlled, and therefore, independent of size (9).

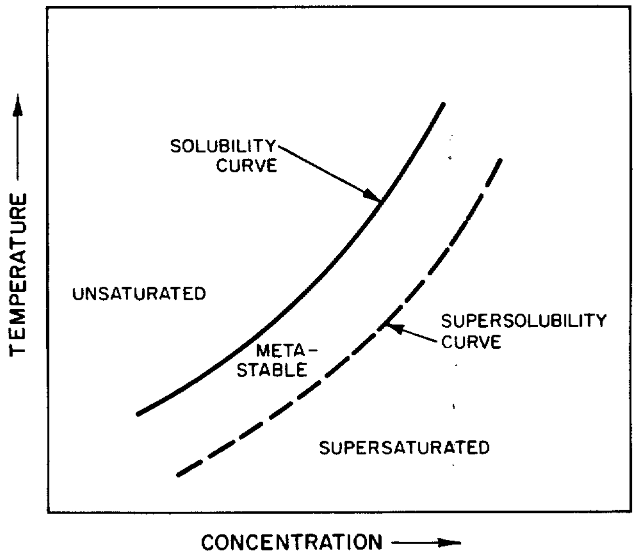

FIG. 1. Saturation and supersaturation curves for a fat melt.

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[2] Present Address: Consultant, 4911 S.W. 101st Ave., Cooper City, FL 33328.

In summary, the rate of nucleation depends on the triglyceride composition of oil being winterized, the rate of cooling of the oil, the temperature of nucleation and the mechanical power input. The growth rate, on the other hand, is dependent on the temperature of crystallization, time of crystallization and the mechanical power input.

FACTORS AFFECTING THE WINTERIZATION PROCESS

A careful selection of process variables for the winterization of a given oil is very important. In commercial processes, the aim is to produce a small number of nuclei around which the crystals grow larger in size as cooling continues. If a vast number of nuclei are formed, then a large mass of small crystals is developed which is difficult to filter. On the other hand, if the crystals group together in clumps, the liquid phase will be occluded, the result being poor separation and yield.

The effect of major processing variables on the performance of a winterization process is briefly discussed here.

Composition of Glyceride Oil

The saturation-supersaturation curve which governs the nucleation and crystal growth mechanism depends on the composition of the oil being winterized. In general, the various triglycerides in a given oil will fractionate in the following order: trisaturates, disaturates monounsaturate, monosaturate diunsaturates and triunsaturates. As opposed to common belief, some linoleic glycerides crystallize to a greater degree at a given temperature than the corresponding oleic glycerides (10). For example:

$$\text{PLP} > \text{POP},\ \text{OLP} > \text{LOP} > \text{OOP}$$

Here, P, O and L stand for palmitic, oleic and linoleic acid groups on the triglyceride. The behavior of several binary mixtures of glycerides has been reported by Russell (11). He observed that the difference in the melting points of the 2 components govern their melting behavior in the binary mixture. Thus, in a complex mixture of triglycerides, a portion of the higher melting glycerides will be found with the lower melting liquid oils resulting from eutectic formation and equilibrium solubility. Deroanne (10) pointed out that the other factor which makes prediction of crystal behavior of oils and fats difficult is their compatibility for each other. For example, a greater compatibility exists between PPP/SOS than between PPP/POP. Here again, P, S and O represent palmitic, stearic and oleic acid groups, respectively. The compatibility/incompatibility behavior in the crystallization of fats and oils results from the polymorphic nature of the fat crystals.

Several crystalline modifications of fat crystals have been observed by X-ray and other techniques (12); 3 main modifications are α, β' and β. The transformation of one form into the other occurs with increasing energy from α to β' to β. The best crystals are formed when β'-form is used as seeds. These crystals grow larger, stay in suspension in the liquid oil and are easy to filter. Since the transformation of β' to β cannot be suppressed totally, β-form crystals also are formed during winterization. They cling to the heat transfer surfaces which makes a scrape surface agitator essential to maintain a constant temperature and composition of oil in the crystallizer and to keep the heat transfer surfaces clean.

For partially hydrogenated oils, the composition of the oil will depend to a greater extent on the selectivity of the hydrogenation process. Since the mixture of triglycerides of an oil is too complex to predict their phase behavior, a given set of winterization conditions are true only for a fixed set of hydrogenation conditions or composition of feed oil.

Rate of Cooling of Oil

In a winterization process, extreme care is required to obtain a supersaturated solution. If the supercooling of an oil is carried out too quickly, rapid crystallization of α-form crystals occurs, resulting in a mass of very small crystals. Also, in rapid supercooling, the rate of nucleation is very high, resulting in high viscosity which leads to little or no crystal growth. By controlling the supercooling, the more stable crystal forms (i.e., β' and β) are formed, and, in addition, the viscosity remains low enough to permit the movement of these nucleii thus allowing the condition for growth. The typical rate of cooling of oil reported in *Bailey* (13) are 1-3 C/hr, but for certain partially hydrogenated oils, cooling rates as high as 13-17 C/hr have been used.

Temperature of Crystallization

The temperature of crystallization is important from the crystal growth rate standpoint. It is normally determined from the saturation-supersaturation plot. Too low a temperature will result in high viscosity and reduced crystal growth rate. The crystal modification form of the fat crystals also is very much dependent on the temperature of crystallization. Since crystallization is an exothermic process (a slight increase in temperature of crystallization mass occurs after crystal growth starts), control of this temperature is important for the transformation of crystal form from α to β'. If the process is not properly controlled at this stage, the tendency will be toward the formation of β crystals.

Agitation Rate

Proper agitation of the oil during nucleation and crystal growth will minimize mass and heat transfer gradients because of localized nucleation. The agitation rate should be such that it can keep the temperature and composition uniform in the bulk oil; it should provide a gentle motion to the crystals to enhance their growth rate by increasing their impact on each other. The agitator design and the rate of agitation under no circumstances should provide shear to break the crystals.

Agitation rate also has interaction with other properties, e.g., an increased agitation rate will require lower temperatures of crystallization or a slightly higher supersaturation to result in the same quality of winterized oil.

Since lower temperatures and higher agitation rates will require more energy, it is recommended that lower agitation and higher crystallization temperatures be used.

As already mentioned, the agitation of the oil mass encourages both nucleation and crystal growth and therefore is very much desirable. In general, a mild agitation is recommended because high agitation rates can fragment the crystals during their growth stage. In certain applications, scrape surface heat exchangers are desirable. These agitators, in addition to providing uniformity in the crystallizers, also renew the heat transfer surfaces, thereby keeping high heat transfer coefficients.

Time of Crystallization

Referring again to the saturation-supersaturation curve, one would find that for a given temperature of crystallization, after crystal growth has occurred for a certain period of time, the concentration of the solute in the oil will approach the saturation concentration. Since at this concentration no further nucleation or crystal growth occurs, the time required to approach the saturation concentration from a supersaturated solution in the liquid oil determines the time for crystal growth.

Bailey's Industrial Oils and Fat Products recommends a crystal growth time of 48-60 hr. In certain well designed systems, the crystal growth time for the same oil can be reduced to 6-10 hr.

From this discussion it is clear that, for the design of a winterization process, the rate of cooling of the oil, the temperature of crystallization and the agitation of the oil are crucial and play a significant role both in separation of solid fats as distinct crystals and in helping separate them from the liquid oil. Thus, under the general objective of obtaining data to develop a more efficient winterization process, the main emphasis should be in studying the effect of these variables on the performance of the winterization process.

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Hydrogenation of Oils and Fats[1]

PUSHPINDER S. PURI[2], Best Foods Research and Engineer Center, Union, NJ 07083

ABSTRACT

Hydrogenation is a complex 3-phase reaction, and the end result depends largely on transport and chemical resistances. Control of these factors is of critical importance to a predictable end product and this control is possible if a fundamental understanding of the process is achieved. The basic transport steps involved to bring the hydrogen and oil together in the presence of catalyst and the effect of different process variables on the course of the chemical reaction will be the major subjects of discussion in this presentation.

NOMENCLATURE

a = Bubble area/unit volume of reactor, cm^2/cm^3; A_P = particle surface/unit volume of catalyst, cm^2/cm^3; C^* = saturation concentration of hydrogen in oil, mol/l; C_L = hydrogen concentration in oil at any time, mol/l; C_P = hydrogen concentration on catalyst surface, mol/l; C_r = reactant concentration on catalyst; mol/l; C_{r_1} = concentration of fatty acids with one double bond, mol/l; $C_{r>1}$ = concentration of fatty acids with more than one double bond, mol/l; H = Henry's law constant, mol/1-atm.; k_L = mass transfer coefficient, cm/min; k_P = oil-catalyst mass transfer coefficient, cm/min; k_r = kinetic rate constant, 1-cm/mol/min; k'_r = pseudo kinetic rate constant; k'_{r_1} = pseudo rate constant for fatty acids containing one double bond; $k'_{r>1}$ = pseudo rate constant for fatty acids containing more than one double bond; P_{H_2} = hydrogen partial pressure, atm.; R = reaction rate, mol/min-liter; S_p = particle active surface/unit volume of catalyst, cm^2/cm^3.

INTRODUCTION

Hydrogenation is a unit process whereby hydrogen is added directly to unsaturated oils in order to increase their stability to oxidative changes (rancidity). Also, it is widely used to convert liquid oils to semisolid fats for their use in margarines and shortenings. Hydrogenation processes in combination with interesterification and/or fractionation processes are used to make confectionery fats. In today's world of increasing population and limited resources, hydrogenation processes play a vital role in providing food products both in quality and quantity. Soybean oil, e.g., which is inherently vulnerable to oxidative changes, can attain a desired stability by partial hydrogenation.

In hydrogenation, edible oil is reacted with hydrogen gas in the presence of an active metal catalyst. The hydrogenation reaction is exothermic with heat of reaction of ca. 25 Kcal/mol/double bond of hydrogenation, in the usual range of commercial conditions of 130-200 C and 5-20 psig pressure (1). The degree of hydrogenation of an oil is directly related to iodine value (IV), the addition of 1 mol of hydrogen corresponding to the absorption of 1 mol of iodine. It can be calculated that ca. 14.1 cu ft (at 0 C and 760 mm Hg) of hydrogen is required to reduce the IV of 1000 lb of oil by 1 unit. The heat generated during this reduction (by 1 unit IV) is enough to raise the oil temperature by 1.6-1.7 C. Commercially, hydrogenation reaction is conducted in stirred batch reactors, although some installations use continuous processes as well. After the reaction has occurred to a desired extent, the metal catalyst is separated from the oil by filtration. At some installations, oil is posttreated to reduce the residual metal content in oil to <0.5 ppm.

GENERAL NATURE OF THE REACTION

Oils or fats are triglycerides of fatty acids; when they are hydrogenated, the hydrogenation process reduces the number of double bonds on the various unsaturated fatty acid molecules. Also, hydrogenation alters the location of double bonds (positional isomerization) by migration along the fatty acid chain (2-4) and transforms some of the naturally occurring *cis* bonds into *trans* (geometric isomerization) configuration (5). All these changes alter the physical and chemical properties of the fat.

Since fats and oils contain a spectrum of fatty acids with different numbers of double bonds, for a given set of reaction conditions, they react differently. This preferential nature of reaction for one kind of fatty acid group over the

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[2] Present address: Consultant, 4911 S.W. 101st Ave., Cooper City, Florida 33328.