A Novel Approach to Process Crude Oil Membrane Concentrate Using a Centrifuge

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ABSTRACT: The present work discusses an alternative process to handle crude oil membrane concentrate during a degumming process. In this process, the membrane concentrate, which typically consists of 15–30% phospholipids (PL) by weight of oil, is first stripped of hexane and then centrifuged to produce two phases—supernatant (PL < 0.6%) and lecithin concentrate (PL > 62%). The main advantages of this method are limited oil loss, potential lecithin by-product, and a supposedly simpler process. In this work, we first show that the phase behavior of an oil–PL–hexane system can be exploited to identify the various steps of the process. The steps include membrane degumming, hexane evaporation, and centrifugation. Although much knowledge already exists on these unit operations for miscella degumming, it is the combination and sequence of these steps that is proposed here. Since the novelty of this process lies in using a centrifuge after the membrane separations, we focus on this step. Here, we evaluate the dependence of hexane removal, moisture, temperature, hexane amount, residence time, centrifuge *g*-force, and nonhydratable PL on the phase separations.

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KEY WORDS: Centrifuge, degumming, membrane, miscella, phospholipid, soybean oil.

Crude vegetable oil processing typically involves, among other things, solvent extraction, distillation, and degumming steps. In the solvent extraction procedure, solvent, such as hexane, is added to the flaked oilseeds, and oil is extracted out of the flakes. During this step, while oil is extracted from the oilseeds, some undesired components, such as phospholipids (PL), are also removed, and this results in a hexane–oil–PL mixture (miscella). Hexane is removed by distillation, resulting in a crude oil containing PL. In order to achieve a desired quality of oil, these PL are removed in the degumming step. The presence of substantial amounts of PL may otherwise lead to an undesirable flavor and color and lead to a low-grade finished product (1). Water degumming, combined with acid degumming, is a commonly used method to remove these PL. In the water degumming step, PL are hydrated with the help of additional water and are subsequently removed by a centrifugation process. In the acid degumming step, hydratability of the remaining PL is enhanced by addition of either phosphoric or citric acid, and the PL concentration is brought down to levels that typically are lower than 1500 mg/kg of oil (2). Superdegumming, a patented process, produces oil with a maximal PL content of 900 mg/kg (3). Although this method is widely used in the industry, it remains subject to oil loss, energy-intensive steps, waste acid streams, and a possibility of degradation of recovered TG and PL. To overcome these limitations, alternative methods using membrane separations have also been reported. Principal advantages of this method over the conventional method include low energy consumption, ambient temperature operation, minimal wastewater treatment, no addition of chemicals, and retention of nutrients and other desirable components (4).

Various researchers have examined membrane usage to refine vegetable oils (5–10). Essentially, most of the previous work has shown that since PL self-aggregate to form reverse micelles having molecular sizes of 20,000 or more, they could be removed by using appropriate ultrafiltration membranes. Reported PL rejections in these works are typically >90%, and in most cases PL levels achieved are lower than those obtained from the conventional degumming steps. However, to have a successful commercial application one also needs to obtain good permeate fluxes (especially at high PL concentration) and oil recoveries greater than the traditional process. This issue has been a major focus since the conceptualization of the idea in 1977 (5), but to date there have been limited successes—most notably by scientists at Archer Daniels Midland Company (11). Major challenges come from the facts that the allowable oil loss is typically a few tenths of a percent and that membranes should have good sustainability. To achieve minimal oil loss, concentrate from the membrane process can be processed successively. However, under such conditions PL concentrations build up in the process loop and result in a considerable loss of permeate fluxes. This may be handled by a usual approach of diafiltration (adding hexane), but in doing so, one also needs to consider the economic factors involved.

In this work, we present an alternative approach of using a hybrid combination of membrane, evaporator, and centrifuge. PL are first concentrated in the retentate stream using membranes, followed by a hexane removal using an evaporator and separation of resulting lecithin and oil using a centrifuge. It must be noted that this method is different from the previous reported work on centrifugation. Here, we first concentrate PL and then centrifuge the mixture into two dominant phases. The top phase is PL-lean and the bottom phase is >62% PL (lecithin) on a dry basis. The main advantage of this method is that both of these two resulting phases are salable

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products. Hexane stripping does not amount to an additional cost, as this step is inherent to the whole degumming process. Since all streams coming out of the process have a market value equal to or greater than the vegetable oil, oil loss is reduced to negligible amounts. Other benefits include possible ambient temperature operation, which may result in a better product quality. In this work we discuss the details of this approach and focus on the centrifugation part of the process. In particular, we present a study to evaluate the dependence of hexane removal, moisture, temperature, hexane amount, residence time, centrifuge *g*-force, and nonhydratable PL on centrifugal separations of the oil–PL–hexane mixture.

EXPERIMENTAL PROCEDURES

Samples. Soybean oil miscella from Cargill oil processing plants was the basis for all sample preparation. PL and hexane concentration in this miscella varied from 0.5–1% (w/w) and 60–75% (w/w), respectively. Miscella was processed using membrane separations, which resulted in a clear permeate and PL-rich retentate (10–15% PL). Hexane from retentate was removed either completely or partially, and this resulted in a crude concentrate having 20–30% PL. As hexane is removed, some water may also escape the system, but this can be avoided in the actual process. A typical chemical analysis of mixtures so produced is presented in Table 1. After the preparation of crude concentrate, deionized water was added to the samples. The resulting mixtures were then mixed for 1 h and centrifuged. Duplicates of each test were done. In most cases, repetitive results, within ±3%, were obtained. Data presented in the Results and Discussion section are averages of these results.

Chemical analysis. Feed samples, top and bottom phases were typically analyzed for total phosphorus, Ca, Mg, moisture, hexane, and weight fraction of each phase. Moisture analysis was performed using a Karl Fischer apparatus, and phosphorus was measured using AOCS method Ca12-55 (12). Some selected samples were sent to an outside laboratory for a more detailed analysis on P, Ca, and Mg by an inductively coupled plasma–atomic emission spectroscopy method. The total phospholipid content was determined by multiplying phosphorus content by 30.1. All data reported are on a weight basis, unless otherwise mentioned.

Apparatus. The main apparatus used in this study consisted of batch centrifuges. Two centrifuges were used: Beckman J-21C with a JA-12 fixed-angle rotor (Fullerton, CA) and IEC Clinical (Needham Heights, MA). Maximum speed for the Beckman model is 12,000 rpm. The Beckman model also has the capability of maintaining the desired temperatures. Centrifuge type turned out to have a negligible effect on the separations.

In addition, Osmonics, Inc. (Minnetonka, MN) provided polymeric ultrafiltration membranes used in this study, which had a M.W. cutoff between 50,000 and 100,000. Membrane chemistry was found to have a negligible impact on the separations (13). The modules used were spiral wound, and all the experiments were performed at 70 ± 1 psi trans-membrane pressure and 25 ± 0.5°C.

TABLE 1
Chemical Composition of Various Miscella Mixtures Used[a]

Description	Hexane (%)	Oil (%)	PL (%)	Water (%)
Miscella	70.0	29.34	0.6	0.06
Retentate	63.7	27.3	8	1
Crude	0	77.4	22.5	0.1

[a]Overall recovery of permeate: 93%. PL, phospholipids.

RESULTS AND DISCUSSION

Approach. To understand the approach and results, let us first discuss some of our previous work on phase behavior of oil–PL–hexane systems that form the basis of this study.

As shown in Figure 1a, three principal regions (micellar solution, two-phase dispersion, and dense micellar phase) exist in an oil–PL–hexane system (with limited water content). A micellar phase consists of uniformly distributed reverse micelles in the bulk phase of hexane and oil. As the concentration of PL is increased, a smooth transition to dense micellar phase is observed for the mixtures with a hexane-to-oil ratio greater than unity. Both micellar phase and dense micellar phase exist as single phases. However, a phase transition to a two-phase region from micellar phase is observed with an increase in PL concentration for mixtures with a hexane-to-oil ratio less than unity. The two-phase region forms as large as micrometer-sized PL structures dispersed in a continuous phase. These dispersed structures aggregate over time, resulting in two equilibrium phases (micellar and dense micellar phases). Details of this work are discussed elsewhere (14).

During membrane degumming, feed miscella (typically 0.5–1.5% PL) results in a concentrate and a permeate stream. On the phase diagram, this corresponds to streams moving in the opposite directions (as shown in Fig. 1a). PL concentration of retentate increases and of permeate decreases, but both streams remain in the micellar region. Even when the process is designed for high concentration factor operation (high PL concentration in retentate), the retentate stream remains in the micellar region and no significant change in micellar structures is expected. However, as is known, fluxes drop considerably here, and there is a trade-off between fluxes obtained and oil recovery. At this point, instead of achieving a very high concentration factor, we instead desolventize the stream through a solvent removal step (e.g., stripper column) to reduce the hexane-to-oil ratio such that the concentrate stream reaches the two-phase region of the oil–hexane–PL phase diagram. Once the concentrate is in the two-phase region, some settling of the PL takes place, while the supernatant, after settling, tends to reach the micellar phase. Thus, using a gravity separation step (e.g., settler, centrifuge, decanter, etc.) we can accomplish PL separation from the concentrate. A schematic of this process is shown in Figure 1b.

Hexane removal. For the initial stage of study, we wanted to understand if complete or partial hexane removal is

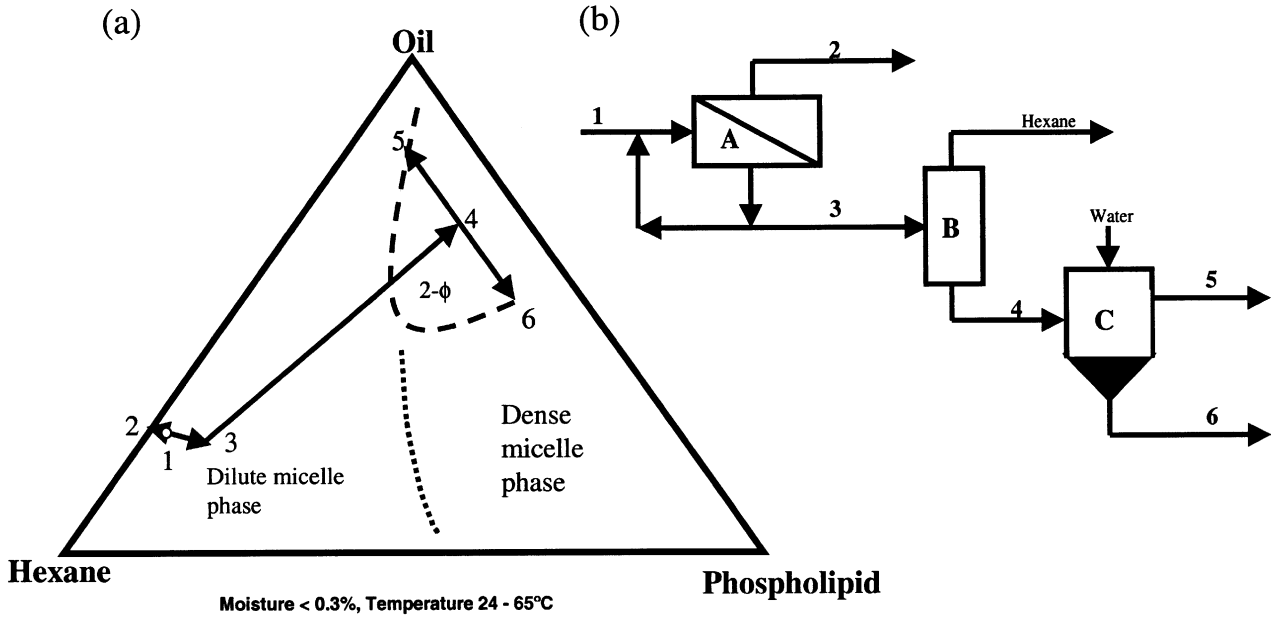

FIG. 1. Phase diagram and process schematic showing location of various mixtures during membrane processing (1 → 2,3), hexane evaporation (3 → 4), and centrifugal separation (4 → 5,6). 1: Feed miscella, 2: permeate, 3: retentate, 4: crude concentrate, 5: supernatant, 6: lecithin concentrate, A: membrane, B: evaporator, C: centrifuge. ϕ, phase.

required from the membrane retentate. Here, our focus was on achieving (i) clear upper phase or supernatant with minimal PL, possibly 50 mg/g or less, and (ii) lower phase (lecithin concentrate) with PL > 62% (dry basis). For an insufficient separation, most PL remain in the upper phase, resulting in an undesired low-weight fraction of the lower phase. Table 2 shows separation as a function of hexane removal for a retentate feed as in Table 1. From these preliminary experiments we found that a complete hexane removal is necessary to achieve the desired separations. Our next step was to minimize phosphorus levels in the supernatant. For this purpose, we studied the effect of water, temperature, centrifuge time, and *g*-forces on the separations.

Effect of water. Effects of water on phosphorus in supernatant and lecithin concentrate for a crude concentrate feed of Table 1 (referred to as "feed" hereon) are shown in Figure 2. Clearly, an increase in water results in a significant drop in phosphorus levels in the supernatant. For the system studied, a minimum of 5 wt% water is apparently required to achieve low phosphorus levels in the supernatant. Further, from Figure 2 we see that in order to achieve a lecithin concentrate of 62% acetone-insolubles (AI) or more, we need to have a minimum of 7.5% water. What is sold in the marketplace is 62% AI lecithin. For further experiments, we considered water levels of 7.5 and 12.5%.

TABLE 2
Separation as a Function of Hexane Removal

Sample	Hexane removal (%)	Fraction wt% (lower phase)
A	75	10
B	90	42
C	100	50

For this approach, water addition, as in a conventional water degumming process, is necessary. It is interesting to note that, whereas we deal with levels of PL 15–25 times greater than in the water degumming process, water levels required in this case are just 3–4 times greater. The typical water amount necessary in the water degumming process ranges from 1–3%. Further, in the water degumming process, the quantity of water added is critical. Too little water can lead to insufficient removal of PL, and too much can lead to undesired three phases during the centrifugation. With the proper amount of water and adequate hydration of the PL, the centrifuge can then deliver a clear degummed oil and a brown compacted gums phase, whose volume is about 4% of the total mixture (15). In general, in water degumming, the proper amount of water is normally about 75% of the oil's PL content (16). However, in our case, we found that the use of more water leads to better separations. The compacted lecithin concentrate phase is 45–55 wt% of the total mixture, and 25–30%

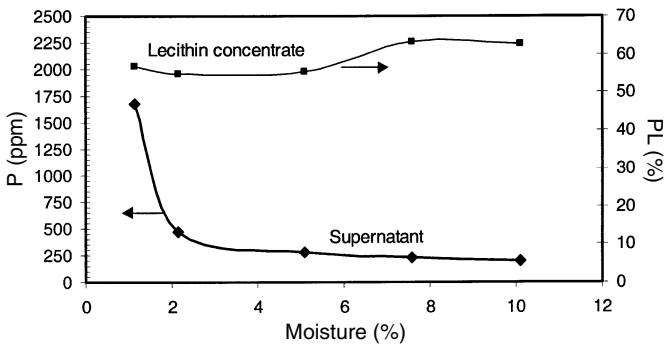

FIG. 2. Phosphorus in the supernatant and lower phase (lecithin concentrate) as a function of moisture. Crude concentrate feed as in Table 1. Temperature: 20°C.

water of PL content is sufficient to achieve the desired separations.

The next question to address is how much water addition would be required in this process. It must be noted that some water is inherently in the centrifuge feed. Depending on the PL concentration in retentate and other factors, water already present in the feed could be 2–5%. The higher the starting phosphorus concentration is in the retentate, the higher the water concentration in it. Water addition would correspond to the difference of water required and water already present in the feed.

Effect of temperature. Experiments discussed above were reported for low room temperatures (20°C). To evaluate the temperature dependence, experiments were performed at 60°C as well. Table 3 shows that temperature has a negligible effect on the phosphorus levels in the supernatant. This result also suggests that there is a flexibility in choosing the desired temperature of an actual operation. High temperatures may be chosen for a low mixture viscosity, whereas low temperatures may be desired for possible better product characteristics.

Centrifuge time. As shown in Table 3, centrifugation time has only a marginal effect on the phosphorus levels, and the levels remain in the range of 175–210 ppm. The separation is reasonably fast, and the residence time required in the actual operation is of the order of minutes or less. Further work can provide data for shorter residence times. It must also be mentioned that density difference between the two phases is in the range of 0.08–0.12 g/cc.

Centrifugal force. It is also important to evaluate the *g*-forces for the required separation. Table 3 again shows that the separation remains essentially independent over a wide range of *g*-forces.

From these experiments, it is apparent that, in the ranges studied, temperature, time, and *g*-forces have a negligible impact on separations. Another interesting aspect is that we repeatedly get phosphorus levels in the supernatant in the range of 175–210 ppm. This may be due to the presence of nonhydratables in the feed mixture.

TABLE 3
Effects of Various Variables on Supernatants' Phosphorus

Variable		P (ppm) at moisture level of	
		7.5%	12.5%
Temperature (°C)	20	180.0	184.1
	60	175.4	168.6
Time (min)	1	180.6	177.5
	2	180.0	184.1
	5	181.6	189.5
	10	183.6	178.2
	15	206.4	191.8
	30	209.7	191.5
	45	202.7	203.0
g-Force	1250	207.9	199.3
	2700	198.6	191.4
	5000	206.4	191.8

Nonhydratable PL. We hypothesized that the PL removed by the water addition were hydratable PL, and those that remained in the supernatant were nonhydratable PL. To confirm this, we analyzed the magnesium and calcium contents in the feed, supernatant, and lecithin concentrate. Typically, nonhydratables are associated with Ca and Mg. Some published papers (e.g., 17) have shown that the greater part of the nonhydratable PL in oil is composed of magnesium and calcium salts of PA and PE. The hydratable PL in vegetable oils contain strongly polar groups such as choline, serine, or inositol.

Thus, based on this understanding, the P/Ca or P/Mg ratio in our case should reflect the following trend: supernatant < feed mixture < lecithin concentrate. In other words, the supernatant should have a higher Ca or Mg content than lecithin concentrate or feed mixture on the total phosphorus basis. This is exactly what we have found in our analysis. Figure 3 shows that ratios of P/Ca and P/Mg in supernatant are lower than the ratios in feed and lecithin concentrate for all water levels considered. Thus, PL in the supernatant are indeed predominantly nonhydratable PL.

Further, from Figure 3, it is clear that with increasing water concentration, P/Ca and P/Mg ratios in supernatant decrease, but in the lecithin concentrate these ratios remain almost constant. The decrease in supernatants' ratios is most significant

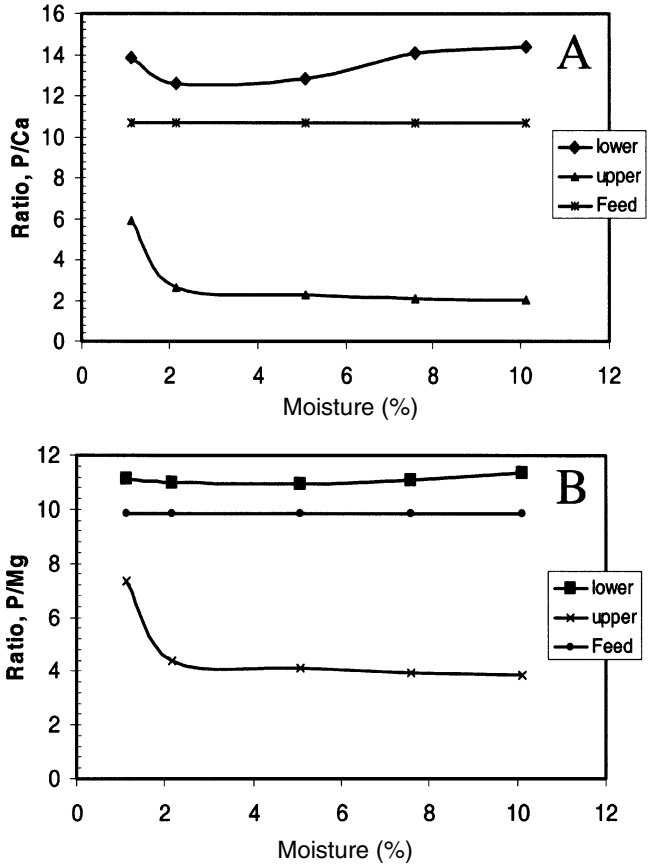

FIG. 3. Change in P/Ca (A) and P/Mg (B) ratios for feed (crude concentrate), lower phase (lecithin concentrate),and upper phase (supernatant). Figure also shows effects of moisture on these ratios.

TABLE 4
Effects of Moisture on Ca and Mg in Supernatant and Lower Phase (lecithin concentrate)[a]

		Moisture (%)				
		1.1	2.2	5.1	7.6	10.1
P, ppm	Ca, concentrate	1313.5	1355	1266.5	1239.5	1157
	Mg, concentrate	1634.5	1559	1483	1574	1465
	Ca, supernatant	284.65	180.6	122.4	111.35	101.8
	Mg, supernatant	228.7	107.9	67.1	58.8	54.2

[a]Feed: Mg, 753 ppm; Ca, 692 ppm.

up to 2% water, and after that the change is negligible. This observation implies that a considerable portion of PL is hydrated within a couple of percent of water, and after that the relative amount of nonhydratables in the supernatant remains constant. It is also important to realize that after a certain water level, the amount of nonhydratables dictates the phosphorus level in the supernatant, and thus the minimum achievable supernatant concentration depends on the nonhydratables in the feed. This surely will depend on the starting quality of the miscella; a nonhydratable lean miscella is expected to result into a much cleaner supernatant.

Figure 3 further suggests that although P/Ca and P/Mg ratios in the feed are almost the same, there is a considerable difference in these ratios for supernatant (at water > 2%). The P/Mg ratio is approximately two times greater than the P/Ca ratio. Further, on comparing the absolute amounts of supernatant and lecithin concentrate, as shown in Table 4, it is clear that in the concentrate, magnesium content is always more than the calcium content and in the supernatant it is always less. This suggests that magnesium salts of nonhydratable PL are more easily hydrated than the calcium salts.

These laboratory experiments indicate that using a centrifuge to handle membrane concentrate may be a viable alternative to present approaches, especially to minimize the oil loss. Further work is needed to optimize the process and take the technology to commercialization.

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