Continuous Ultrasonic Degumming of Crude Soybean Oil

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Ultrasonic energy has been applied to continuous degumming for the efficient removal of phospholipids from crude soybean oil. The crude oil and water (2.0% by weight) were pumped through an ultrasonic processing cell, oil and hydrated gums were separated by centrifugation, and the recovered oil was vacuum bleached. The degummed and bleached oil had a residual phosphorus content of less than 10 ppm and was subsequently deacidified-deodorized in all-glass laboratory deodorization equipment. Odor and flavor evaluation indicated that the salad oil produced by the process of ultrasonic degumming/deodorization-deacidification was equivalent in quality and stability to a conventionally processed salad oil.

The replacement of chemical refining with a physical refining process for purification of soybean oil is a likely response of the food oils industry to increasing energy costs and growing sensitivity to environmental problems. Implementation of a combined deacidification-deodorization process depends on efficient pretreatment for removal of phospholipids. Early attempts to apply this technology with soybean oil failed due to inconsistent quality of the crude oil and inadequate pretreatment to overcome these inconsistencies.

For more than 40 years, basic processing of vegetable oils, called the "chemical refining process", has involved six steps—degumming, alkali refining, water washing, vacuum drying, bleaching and deodorizing. Often, oils are not degummed prior to alkali refining and the gums, primarily phosphatides, are recovered in the foots (or soapstock).

In "chemical refining", free fatty acids and phosphatides are reduced by treating crude soybean oil with NaOH (1). The oil and caustic mixture is agitated at controlled elevated temperature for a pre-determined time, either in batch tanks or with an in-line mixer, and then centrifuged to separate refined oil from soapstock. The refined oil is washed and dried, and subsequently bleached and deodorized to give a salad or cooking oil. The soapstock is usually acidulated, washed and dried to produce a low-value acid oil. Waste water from washing the neutralized oil and waste water from soapstock acidulation must be treated and disposed without stream or land pollution. High losses of neutral oil in the soapstock and from saponification of the crude soybean oil often result during chemical refining.

The alkali refining step has the additional drawback of high operating expenses due to substantial energy and water consumption.

Therefore, there is a need for alternative methods to produce an oil free of impurities and suitable for human consumption. One method is deacidification of a bleached oil by steam deodorization at high temperature under vacuum. In the 1970's, Sullivan (2), Mag (3), List (4) and Gavin (5) demonstrated that soybean oil, when specially treated, could be degummed, bleached and steam deodorized/deacidified, a process called "physical refining". An acceptable oil feedstock for the physical refining process requires nearly complete removal of phosphorus, iron and magnesium. For this process, the oil is first pre-treated with phosphoric acid at a controlled, elevated temperature to condition phosphatides in the crude oil. The treated crude oil is then degummed with water or other degumming agent at an elevated temperature for a time sufficient to hydrate the gums. The oil-water mixture is centrifuged to separate the gums. Phosphoric acid pretreatment gives more efficient separation in the centrifuge and reduces the level of non-hydratable phosphatides in the degummed oil (6). The degummed oil is finally washed to remove residual phosphoric acid, heated, vacuum dried, bleached and deodorized/deacidified to give a salad or cooking oil. The acid wash water must be treated and disposed without polluting streams or land. According to Balicer (7), the opponents of physical refining of soft oils present two main claims against it—the system requires an uneconomical pretreatment procedure, and high-quality finished oils cannot be assured. Bailey (8) and Forster (9) reported that for physical refining to be successful, the oils must be low in phosphatides. A "melon" flavor develops in the finished oil if H_3PO_4 is left in the oil.

Traces of phosphorus in refined oil are blamed for darkening the oil during deodorization (10), and also for interfering with the catalyst during hydrogenation (11). Crude soybean oils are reported to contain 600–800 ppm P (11). Balicer (7) recommends a maximum limit of 700 ppm P in soft oils.

Ultrasonic action, called acoustical cavitation, results when a liquid, subjected to alternate expansion and compression sound waves, develops minute vapor-filled bubbles which collapse rapidly. Acoustical cavitation of a liquid can generate extreme localized heat and pressure and produce intimate contact of reactants without substantially raising the temperature of the final product. Pre-heating the reactants may not be necessary to initiate a chemical reaction.

Reported here are the results of investigations to determine the feasibility of a continuous ultrasonic degumming process as an alternative to chemical refining and to the current pretreatment-degumming of soybean oil in the physical refining process.

METHODS AND MATERIALS

Several lots of hexane-extracted crude soybean oils from commercial sources were used to develop procedures for continuous degumming, oils A-E, shown in Table 1. After operations were optimized, single lots of crude soybean oils from two commercial sources [oil A (528 ppm P) and oil B (800 ppm P)] were used for replicate comparative experiments. Degumming agents

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TABLE 1

Analysis of Commercial Crude Soybean Oil

Oil	P (*ppm*)	Phospholipid (%)[a]
A	528	1.67
B	800	2.54
C	500	1.59
D	664	2.10
E	446	1.41

[a]% Phospholipid = % P × 31.70 (12).

used were distilled water and 20% aqueous citric acid.

The ultrasonic degumming system is shown in Figure 1 and consists of a 750 watt (continuous rating) power supply (Model 184V), converter, 1:0.5 booster horn, 1-inch diameter titanium processing horn and stainless steel high-pressure processing cell (Branson Ultrasonics Corp., Danbury, CT). The high-pressure processing cell (Fig. 2) was also used for our previous research on ultrasonic hydrogenation (13,14). Crude soybean oil is pumped by a McCannameter pump (Hills-McCanna Co., Chicago, IL) at a rate of 7400 g/hr. Degumming agent is pumped by a variable speed laboratory pump (Fluid Metering, Inc., Oyster Bay, NY) at a rate of 160 g/hr.

Crude oil and degumming agent are combined just before entering the processing cell. Temperature of the entering oil and exiting oil-gums are measured by thermocouples in the lines (Fig. 1) and displayed on a recorder. Reaction temperature of the oil-water mixture is measured immediately beneath the horn. Volume of the reaction zone beneath the horn measured 2.4 cc. At our flow rates, the oil-water mixture is subjected to ultrasonic vibration for 0.8 second. Overflowing the orifice adapter ensures that ultrasonic vibrations are translated to all the reactants. The discharge oil-gums are then sent to a centrifuge for separation.

The 1:0.5 booster horn, connected between the converter and processing horn, reduces the mechanical amplitude of the horn. By reducing the amplitude, we found that the ultrasonic action is continuous and controlled. Since ultrasonic energy raises the temperature of the reactants slightly (30–35°C), we found it unnecessary to heat the oil. If an inert atmosphere is required, nitrogen may be introduced coaxially with the reactants.

Power to the horn is varied from 20 to 100% (full power) by regulating the power supply rheostat. Changing the input power from 20% to 100% increases the power to the processing horn from 20 to 150 watts, depending on the type of oil and oil temperature.

As a control, 1,000 gm of each crude soybean oil was batch degummed in the laboratory at conditions usually practiced by industry (15), i.e., mechanically agitated for 30 min at about 70°C, and then cooled prior to centrifugation.

Gums were separated from the degummed oils immediately after continuous ultrasonic or batch degumming by batch centrifugation (250-ml bottle) at 2,000 rpm for 45 min (model UV, International Centrifuge, International Equipment Co., Needham, MA). Clear degummed oil was decanted from the settled gums and analyzed for phosphorus, iron, magnesium and free fatty acid (FFA).

Phosphorus was measured by the turbidity method of Sinram (16), and selected samples were verified by AOCS Method Ca 12-55 (17). Iron in the oils was determined by AOCS Method Ca 15-75 (17). Magnesium in the oils was determined in oil matrix using atomic adsorption spectrophotometry (18), by comparing measured values with values of prepared magnesium stock standards (Morton Thiokol, Inc., Alfa Products, Danvers, MA) at the wavelength for magnesium, 2852

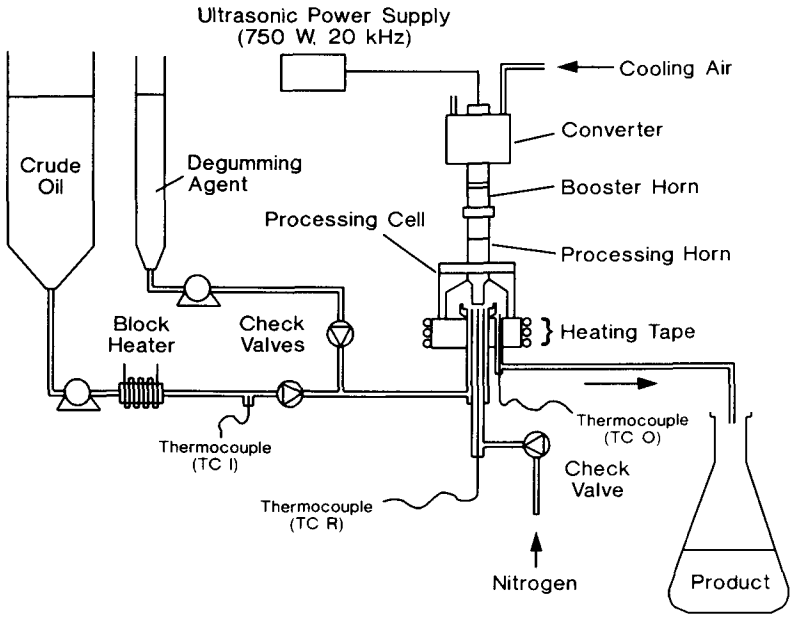

FIG. 1. Flow diagram showing equipment used for continuous ultrasonic degumming of soybean oil.

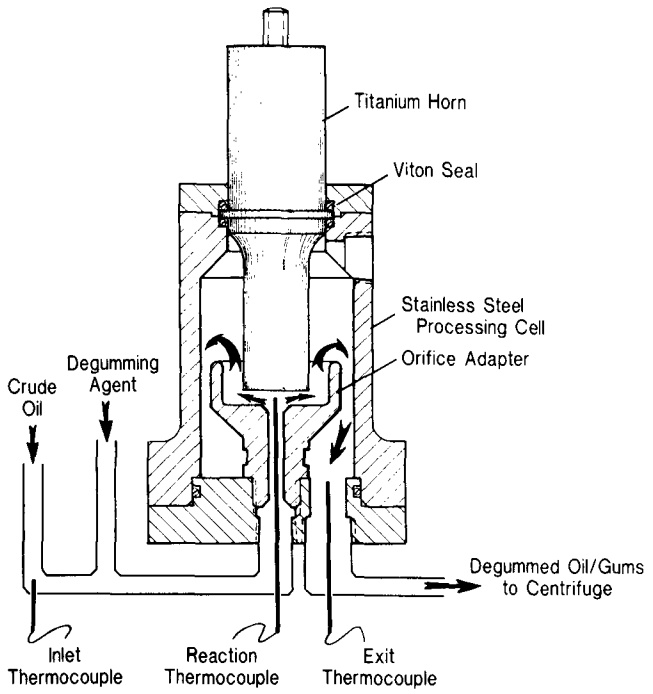

FIG. 2. Schematic of ultrasonic processing cell.

A. FFA determinations were made according to AOCS Method Ca 5a-40 (17). Selected degummed oil samples were analyzed for headspace volatiles according to the method of Snyder *et al.* (19) to determine if different or more volatiles were produced by continuous ultrasonic-degumming than by batch degumming.

Continuous ultrasonic degummed and batch degummed soybean oils were bleached and deodorized. 100 ppm citric acid was added to all deodorized oils at 100°C during the cooling stage in the deodorizer. Finished oils were evaluated for flavor quality and stability by a 15-member, experienced taste panel (20).

RESULTS AND DISCUSSION

The efficacy of sonic energy for enhanced degumming of crude soybean oil is demonstrated by the results presented in Table 2. The test oil was pumped continuously through the processing cell with the selected degumming agent. With oil D, the degummed product was collected with the power to the horn turned on, and subsequently, with it turned off. With oil E the sequence of operation was reversed. Sonification improved degumming with both crude oils, as indicated by the lower phosphorus content of the ultrasonic-degummed oil. Oil E was more easily degummed than oil D, as shown by the lowering of the phosphorus content of oil E even when the power to the horn was turned off. This difference was confirmed by batch degummings conducted on the same oils.

Degumming oil continuously with ultrasonic sound was five times faster than batch degumming (not considering the time to charge and discharge the batch vessel) to achieve the same degree of phosphorus removal.

TABLE 2

Continuous Ultrasonic Degumming of Crude Soybean Oils[a]

			Phosphorus content (ppm)		
				Degummed	
				Sonic Energy	
Oil	Temp	Agent	Crude	W	W/O
A	33C	1.6% Water	528	11	—
A	33C	1.6% Water	528	8	—
B	30C	1.5% Water	800	35	—
B	30C	1.6% Water	800	46	—
C	33C	2.5% Citric acid	500	7	119
D	33C	2.5% Citric acid	664	12	342
D	33C	2.5% Citric acid	664	17	379
D	33C	2.5% Water	664	54	405
E	30C	2.5% Water	446	38	52
E	30C	2.5% Water	446	30	49

[a]All degumming experiments at 200 watts power.

For oil A, batch degumming with 20% citric acid or with water was effective to lower phosphorous content. Degumming with water was more effective than with citric acid to lower iron and magnesium in the oil (Table 3). Since batch degumming of oil A with citric acid was less effective than with water at optimum conditions, the comparison was not repeated for batch degumming of oil B nor for continuous ultrasonic degumming (which was found to be effective with water alone at low temperature).

The effect of ultrasonic power at various levels was correlated to the percent phosphorus removed during processing (Fig. 3). The temperature rose slightly, from 33 to 40°C, for this series of processing conditions. With oil A (528 ppm P), 99% of the original phosphorus was removed in 0.8 second using 22 watts. With oil B (800 ppm P), 90% of the original phosphorous was removed using 21 watts; 93% phosphorus was removed using 143 watts. While low power was effective to lower the phosphorus in the oil, more power appeared to increase the weight of gums recovered, possibly due to greater entrainment of neutral oil. For purposes of comparison, full power was applied to the processing horn in all our experiments.

As shown in Table 3, nearly 100% phosphorus was removed from oil A by either batch degumming at 60°C or continuous ultrasonic degumming at 33°C. For oil B, 88% phosphorus was removed during conventional batch degumming at 60°C; and 96% during continuous ultrasonic degumming at 33°C. Bleaching of degummed oils from oil B removed 7% more phosphorus from the batch degummed oil, and 2% more from ultrasonic degummed oil. Although oils with greater than 10 ppm P are reported to darken an oil and such oils deodorize with difficulty, the bleached oils in this study containing 38 ppm and 19 ppm P did not darken and they deodorized satisfactorily.

Iron in an edible oil is a strong pro-oxidant and contributes to inferior stability of a finished oil. Good crude soybean oils may contain 3 ppm iron; oils from damaged beans may contain up to 9 ppm iron (21,10). Iron contents of oils A (5.8 ppm) and B (6.2 ppm) were somewhat higher than would be expected for good qual-

TABLE 3

Continuous Ultrasonic Degumming vs Batch Degumming of Crude Soybean Oils[a]

	Crude & degummed				Degummed/bleached	
	FFA %	P ppm	Fe ppm	Mg ppm	FFA %	P ppm
Oil A	0.5	528	5.8	65.6	—	—
Batch citric acid degum @ 60C	0.4	13	2.4	2.6	0.3	5
Batch water degum @ 60C	0.5	11	0.8	0.7	0.3	6
Continuous ultrasonic water degum @ 33C	0.3	11	2.1	0.1	0.3	6
Oil B	0.8	800	6.2	73.1		
Batch water degum @ 60C	0.6	94	3.0	21.2	0.5	38
Continuous ultrasonic water degum @ 33C	0.6	35	2.1	13.8	0.5	19

[a]Representative analyses for comparative purposes.

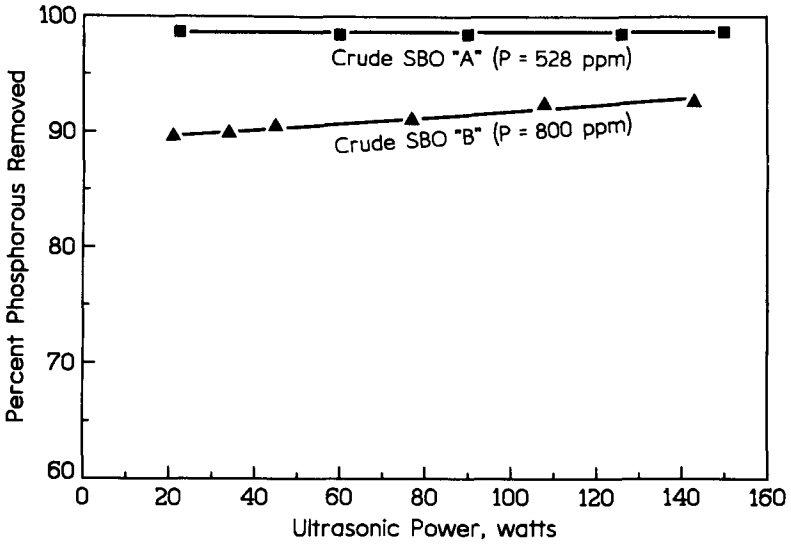

FIG. 3. Effect of ultrasonic power to the horn on percent phosphorous removed from crude soybean oil at 33°C.

ity crude oil. For both oils, batch and continuous ultrasonic water degumming reduced the iron by more than 50% (to less than 3 ppm iron). 50% iron removal by degumming has been reported to be usual and customary (22).

Magnesium and calcium have been reported to combine with phosphatides in crude soybean oil to form non-hydratable phosphatides (6). Oils A and B contained approximately the same amount of magnesium—65.6 and 73.1 ppm. For oil A, batch degumming or ultrasonic degumming with water, removed 99% of the magnesium. For oil B, 71% magnesium was removed by conventional batch degumming and 81% by continuous ultrasonic degumming. Such magnesium values are still quite high.

Flowsheets of existing "chemical refining process" and "physical refining process" are compared in Figure 4 with the "continuous ultrasonic degumming process." In the "continuous ultrasonic degumming process" phosphatides in the crude oil are hydrated with a small amount of degumming agent, without an acid pre-treatment or the heating of the oil. Lower oil temperature was found to increase the ultrasonic cavitation. The oil-water mixture is then centrifuged without cooling to separate the degummed oil from gums. Water-washing ultrasonic-degummed oil is not required since no acid pre-treatment of the oil is required. The small amount of water added to the oil for degumming essentially ends up in the gums and, therefore, drying the oil further is not necessary. The degummed oil is finally bleached and deodorized to give a salad or cooking oil.

For soybean oil in particular, the deodorizer will not produce good quality oil from poor quality refined, washed and bleached oil sent to the deodorizer (5). The final judgement of a good deodorized oil is the flavor evaluation of the oil by an experienced taste panel in a proven statistical process as described by Mounts and Warner (20).

Finished oils from degummed oils A and B, both fresh from the deodorizer and after atmospheric storage for four days at 60°C were tasted and compared (Table 4). An experienced panel tasted the oils in pairs and rated the flavors on a scale of one to ten—where one is strongly objectionable and ten is bland. In previous studies, oils stored for four days at 60°C scored similarly to oils stored at ambient temperature for three months (23). Measured peroxide values of 1.3 and 1.4 me/kg after four-day storage at 60°C indicated little difference in oxidative deterioration of the oils.

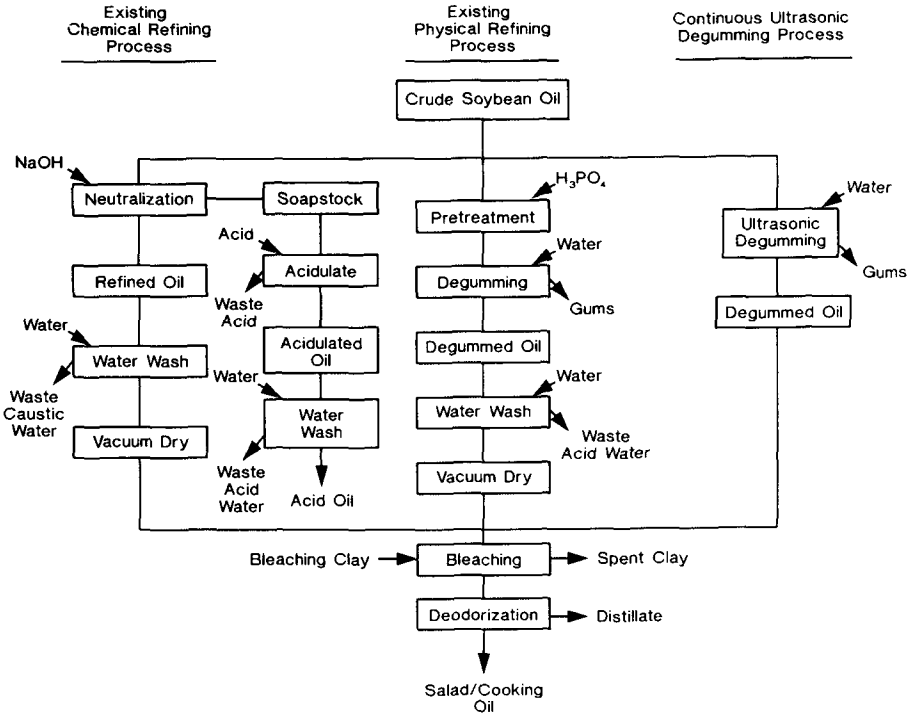

FIG. 4. Comparison of diagrams for existing chemical refining process, existing physical refining process, and proposed continuous ultrasonic degumming process.

TABLE 4

Flavor Evaluation of Physically Refined SBO[a]

	Oil A		Oil B	
	Initial	Four days @ 60C	Initial	Four days @ 60C
Batch citric acid degum @ 60C	8.4(0.1)[b]	7.1(1.3)		
Batch water degum @ 60	8.2(0.1)	7.2(1.3)	7.3(0.1)	6.1(1.3)
Continuous ultrasonic water degum @ 33C	8.4(0.1)	6.9(1.4)	7.3(0.1)[c]	5.0(1.3)
Flavor description	Buttery	Buttery Grassy	Buttery	Grassy Rancid

[a]Based on 10-point scoring scale; 1 = strong, 10 = bland.
[b]Peroxide value (me/kg) at time of tasting.
[c]Indicates significantly different scores at 95% confidence level.

Flavor descriptions of "nutty" or "buttery" reflect a good oil; "grassy", "rancid" or "fishy" indicate that an oil has been oxidized to some extent.

Finished oils from oil A showed no significant difference in flavor scores between batch and ultrasonic degummed oils, initially or after accelerated storage. From previous experience, a score of 8 is the score of a very good fresh deodorized oil. Flavor description by the panel for initial oils was "buttery" and for stored oils, predominately "buttery," with a low intensity of "grassy."

With the finished oils from oil B, the batch and ultrasonic degummed oils initially scored the same (7.3). In our experience, 7.3 is a satisfactory score for a fresh deodorized oil. The score of 6.1 for stored, batch degummed, finished oil is significantly better than 5.0 for stored, ultrasonic degummed, finished oil. Oil B appears to be a damaged bean oil based on a higher value of FFA in the crude oil, possibly due to action of hydrolytic enzymes, and the higher content of magnesium and phosphorus retained in the degummed oils, indicating the presence of non-hydratable phospholipids. Damaged bean oils often exhibit satisfactory flavor scores initially, but flavor stability during storage is poor (24).

There were no unusual flavors detected in either finished oil. "Grassy" flavor, detected in stored finished oils from oil B, was also detected in stored finished oils from oil A.

Snyder *et al.* (19) reported a method to measure and identify critical volatiles in the headspace above heated soybean oil. Using this method, headspace vola-

tiles were measured and compared for continuous ultrasonic degummed and batch degummed oils. Although the total amount of volatiles in the headspace above ultrasonic degummed oil was slightly greater than above batch degummed oil, there was no outstanding difference between composition of the volatiles and the peaks for the individual volatiles were of the same magnitude. Continuous ultrasonic degumming does not produce more nor different volatiles than conventional batch degumming.

These laboratory experiments indicate that continuous ultrasonic degumming of soybean oil may be a viable alternative to present commercial practice, especially to minimize potential environmental pollution. Optimization of the technique will be required for commercial application.

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