

☛ Degumming Soybean Oil from Fresh and Damaged Beans with Surface-Active Compounds

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ABSTRACT

Oils from both properly stored and damaged soybeans were degummed with a series of 4 nonionic, 2 cationic and 5 anionic surfactants and with lecithins as amphoteric emulsifiers. Efficiency of phosphatide removal in the presence or absence of citric acid was determined by colorimetric analysis of phosphorus in the degummed oils. For normal oils, efficiency of citric acid degumming was improved by the addition of fatty alkyl oxazoline, polymeric sulfonate, alkyl sulfate and crude or purified lecithin. Success in degumming of oils from partially damaged soybeans was limited; however, the average phosphorus content was lowest for those solutions degummed with alkyl sulfate. Aqueous citric acid degumming of oils from severely damaged soybeans indicated high levels of nonhydratable phosphatides (NHP). When added to the oil from severely damaged beans, several nonionic and anionic surfactants showed statistically significant improvements in degumming efficiency. However, the nonhydratable phosphorus contents of the degummed oils were still too high, indicating the need for special processing of damaged oils. Crude lecithin was effective in removing NHP from oil of fresh soybeans, but was ineffective on oils of stored and severely damaged beans.

INTRODUCTION

In current soybean processing, degumming is applied as a separate stage to one-third of extracted crude oil to meet soy lecithin market requirements (1). Crude soybean oil contains ca. 2% phospholipid, of which more than 90% is removed by hydration. However, if beans are damaged by storage or early frost, the phospholipids are poorly recovered by hydration, and the resulting degummed oils have high levels of phosphorus-containing compounds (2). These oils are difficult to process into finished products.

Phospholipids in whole soybeans (by analysis of chloroform-methanol extracts) include 39-45% phosphatidylcholine (PC), 14-21% phosphatidyl inositol (PI), 5-8% phosphatidic acid (PA) and 23-28% phosphatidylethanolamine (PE) (3-5). Only one-sixth of these phosphatides occurs in the crude oil extracted from soybean flakes with hexane (5), and their composition varies with bean storage time and condition. The typical range of phosphatide components in normal soybean oil before degumming is 29-33% PC, 14% PI, 17-28% PA, 25-29% PE and 0-10% other components (5,6). The phosphatide composition in degummed oils from sound, undamaged soybeans includes 11-15% PC, 10-11% PI, 10-75% PA, 0-20% PE and 0-49% unknown and other compounds (5,6). Analysis of degummed oil after storage of beans showed the absence of PC after 4 months, and only PA after 6 months (5).

Many patents have appeared on improved methods to degum soybean oil by hydration. Schonfeld (7) cited early patents on the use of calcium sulfate, sodium sulfites and boric, hydrochloric and tannic acids as degumming aids. Later patents, summarized by Norris (8), described as degumming aids the use of sodium chloride, phosphoric acid, alkaline phosphates and polyphosphates in combination with neutralization, refining and bleaching. Citric acid (9) or acetic anhydride (10) have been applied as degumm-

ing aids. Nonionic, cationic and anionic surfactants have also been patented as degumming agents (11). Anionic surfactants were recently reported for dewaxing oil (12). Crude lecithin was patented recently (13) as an agent to complex nonhydratable phosphatides (NHP) of incompletely degummed soybean oil.

Hvolby (14) washed NHP from degummed oil with sodium citrate, sulfate, tartrate, carbonate, fluoride, oxalate or phosphate in concentrated aqueous solution, Ca⁺⁺ and Mg⁺⁺ precipitants. He applied surfactants in the washing of soybean oil following aqueous degumming. In support of his proposed structure of NHP as Ca⁺⁺ and Mg⁺⁺ salts of PA, he indicated that alkaline earth and phosphorus contents were closely correlated before and after washing.

A poor recovery of gums and a high residual level of phosphorus were noted when degumming was attempted on oils extracted from soybeans exported to Europe (15, 16) and on oils from beans grown or stored under adverse conditions (17). When soybeans in this country and elsewhere are in surplus supply, processors tend to increase use of beans that have been stored for prolonged periods. Therefore, further knowledge is needed on improved methods to remove the phosphatides in crude oils from beans with different storage histories.

This paper reports a study aimed at determining how surface-active compounds affect the degumming process with oil from fresh and storage-damaged soybeans.

EXPERIMENTAL

Materials

Crude soybean oil from properly stored or fresh soybeans (normal oil) was obtained commercially (Lauhoff Grain Co., Danville, IL) and stored at 1 C. A second batch of crude oil (stored 8 yr at 4C and 2 yr at 25 C), obtained in bulk from a processor in the southeastern US, represented damaged soybeans from the 1971 crop year (damaged oil). To prepare partially damaged soybeans, local samples were hydrated to 16.8% moisture, stored in constant humidity chambers over saturated dibasic sodium phosphate solution (95% relative humidity) and heated adiabatically (54-55 C in 15 days) in a forced-draft oven. Samples were stirred and aerated 3 times a week. After air drying, soybeans were cracked and dehulled, and the meats were steam-tempered (86 C and 18% moisture) and flaked in 250 g batches. The flakes were extracted with petroleum ether (b.p. 35-60 C) at room temperature in a 3 L glass Soxhlet extractor (partially damaged oil).

The phosphorus concentrations of the crude oils from normal, partially damaged and severely damaged beans were 631, 581 and 223 ppm. The respective FFA contents were 0.69, 1.15 and 7.0% (as % oleic acid). Peroxide values varied from 1.5-2.6 meq/kg of oil and appeared to have no relationship to the degree of damage.

Nonionic (GAF Corp., New York, NY; Akzo Chemie USA, Chicago, IL; ICI Americas, Inc., Wilmington, DE; Rohm and Haas, Philadelphia, PA), cationic (Onyx Chem Co., Jersey City, NJ and International Minerals and Chemical Corp., Terre Haute, IN), and anionic (Witco Chemical

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Co., New York, NY; Rohm and Haas, ICI Americas, Inc.; DuPont Co., Deepwater, NJ) surfactants were obtained commercially. The levels of surfactant used were one-tenth and one-twentieth molar ratios (based on estimated formula weights) of the phospholipid content of normal soybean oil (2% and formula weight as lecithin = 770). Commercial food-grade soy lecithin (15% PC) and purified egg lecithin (100% PC) were used as representatives of amphoteric emulsifiers (Riceland Foods Co., Stuttgart, AK; American Lecithin Co., Woodside, NY; Sigma Chemical Co., St. Louis, MO). Citric acid was reagent grade (J.L. Baker Chemical Co., Phillipsburg, NJ).

Procedures

Degumming was done with 30 g batches of crude oil at 60 C by adding 2% of an aqueous surfactant solution containing 0 mg, 10 mg or 40 mg citric acid per mL and by stirring mechanically for 15 min. Surfactants that were incompatible with citric acid solution or insoluble in water were weighed and added directly to the oil. After standing for 1 hr, slurries were centrifuged at room temperature ($2,000 \times g$ for 20 min), and the degummed oils were analyzed for phosphorus colorimetrically (18).

RESULTS AND DISCUSSION

The experimental design involved tests of each surfactant at 2 concentrations without added citric acid and in combination with 2 levels of citric acid. The total phosphorus concentration in oils after degumming was measured. Control degummings without surfactant were done with water and citric acid solutions. The design was applied to crude oils from normally stored soybeans and from storage-damaged soybeans at 2 levels. Residual phosphorus contents were determined after surfactant degummings of 84 normal, 24 partially damaged and 72 severely damaged soybean oils (Table I). Surfactants selected as degumming aids to hydrate the phosphatide gums include representatives of the major classes and subclasses of detergents. The 2 control degummings of normal oil with citric acid solutions were more efficient for reducing residual phosphorus than the degumming with water. This effect of citric acid was noted also in the presence of most surfactants. Polyoxyethylated vegetable oil, when used to degum partially damaged oil, was required in high concentration to achieve the same residual phosphorus levels obtained with low concentration of either alkyl sulfate or crude lecithin. In degumming oil from severely damaged beans with surfactants, increasing the level of citric acid improved the efficiency slightly, but not to the extent noted with normal oils.

Because residual phosphorus contents varied over a 7-fold range after the most efficient degummings of normal oils, analyses of variance were based on the logarithms of the values. Dunnett's test (19) was used to compare phosphorus content after application of each surfactant with the phosphorus content of the control. Least significant ratios (LSR) of control over sample are shown in Table I. A significant decrease in phosphorus resulting from use of the surfactant is indicated when the control/sample ratio of phosphorus content is greater than the LSR value.

With oils from normal soybeans, addition of a high concentration of crude lecithin without citric acid was found to improve aqueous degumming. Although adding low-level citric acid improved degumming of normal oil, this was further improved by adding high concentration of either crude lecithin or alkyl aryl sulfonate to the system. The degum-

ming was more efficient with a high level than with a low level of citric acid.

This degumming was further improved by adding either low or high concentration of crude or pure lecithin, and by high concentrations of fatty alkyl oxazoline, polymeric sulfonate or alkyl sulfate. The amount of crude lecithin (15% PC) added to degum is 13-fold higher than that added as purified egg lecithin. Also, anionic surfactants of lowest and highest molecular weight and cationic oxazoline are among the effective agents. Thus, the mass and ionic form of these additives seem to be of secondary importance in degumming normal oils.

Polymeric carboxylate, an anionic surfactant, aided degumming of oils from severely damaged soybeans at low concentration with water and at high concentration with low-level citric acid. Nonionic surfactants of high molecular weight that improved the degumming efficiency at a low level of citric acid were polyoxyethylated vegetable oil at either low or high concentration and polyoxyethylated glycol acid ester at high concentration. Also, the addition of alkyl aryl sulfonate at high concentration improved the degumming of this oil at a high level of citric acid. Both high and low molecular weight anionic and high molecular weight nonionic surfactants are among effective agents for degumming oil from damaged beans.

Averaged phosphorus contents of the 6 conditions of surfactant application and 3 of control can be compared on partially damaged and severely damaged oils. Averaged values from normal oil degumming with and without surfactant gave less meaningful comparisons because residual phosphorus contents varied greatly with citric acid concentration. Comparison of these latter averages to average of control degummings supported the finding that degumming of normal soybean oil with crude soy lecithin was very efficient. Average of phosphorus contents of partially damaged oil after degumming with alkyl sulfate indicated the general effectiveness of this agent, because it was also an effective degumming aid for severely damaged oil.

Other effective surfactants for degumming severely damaged oil were the polyoxyethylated derivatives of vegetable oil and glycol acid ester. Polyoxyethylated alkyl ether and polymeric sulfonate, as with alkyl sulfate, were shown to be effective for degumming severely damaged oils, based on averages for these surfactants. Conversely, alkyl aryl sulfonate was only marginally efficient, despite its good performance with high citric acid noted earlier. Polymeric carboxylate was generally efficient for degumming damaged oil.

In a patent by Segers (13) was the first mention that lecithin complexes with phosphatides of water-degummed soybean oil and removes them from the oil dispersion on washing. At concentrations paralleling those of Segers, Kanamoto et al. (20) established the degree at which PA (representative of NHP) and PC react in a model system to form a complex that is subsequently hydrated and removed. Our finding of improved degumming of crude soybean oil by addition of commercial soy lecithin (Table I) confirms their results. However, residual PC and PA in their system represented ca. 80 ppm P, which was high compared with our average residual phosphorus concentration, 19 ppm in normal oils degummed with lecithin. Our higher degumming efficiency apparently resulted from a higher concentration of PC in the system.

Although this study shows positive effects of some surfactants in oils from damaged soybeans, the phosphorus levels in the degummed oils were still too high for optimum processing. More work is needed to identify specific compounds in NHP if processing problems are to be minimized when oils are extracted from soybeans damaged in storage.

DEGUMMING SOYBEAN OIL

TABLE I

Degumming of Soybean Oils with Surfactants [Phosphorus Content of Degummed Oils (ppm P)]

Surfactants	Oil from fresh soybeans ^a (citric acid concentration, %)							Oils from storage-damaged soybeans ^{c,d} (citric acid concentration, %)						
	None		0.018		0.072		Average	None		0.018		0.072		Average
	L ^b	H	L	H	L	H		L	H	L	H	L	H	
Control (no surfactant added)	53		32		15		33	218 ^c 168 ^d		266 172		227 151		237 164
Nonionic														
Polyoxyethylated vegetable oil	58	35	46	50	34	44	45	251 ^c 127 ^d	213 217	251 118 ^f	231 114 ^f	276 117	184 106	234 133 ^f
Polyoxyethylated glycol acid ester	58	63	52	44	34	42	49	146 ^d	119	134	97 ^f	107	120	121 ^f
Polyoxyethylated sorbitan monooleate	56	52	33	42	9	16	35	151 ^d	148	170	160	143	130	150
Polyoxyethylated isooctylphenyl ether	46	102	25	28	9	13	37	148 ^d	125	141	123	124	113	129 ^f
Cationic														
Quaternary ammonium chloride	53	50	31	20	15	16	31	150 ^d	161	145	139	131	144	145
Fatty alkyl oxazoline	50	52	40	46	11	6 ^f	34	165 ^d	180	180	171	147	141	164
Anionic														
Phosphated mono and diglycerides	55	53	36	36	12	14	34	227 ^c 164 ^d	258 171	303 166	324 199	252 170	279 177	274 175
Polymeric carboxylate	52	51	43	46	9	12	36	113 ^{d,f}	120	128	95 ^f	136	122	119 ^f
Alkyl aryl sulfonate	49	60	29	14 ^f	15	11	30	166 ^d	169	138	154	161	75 ^f	144
Polymeric sulfonate	49	47	29	24	12	6 ^f	28	145 ^d	141	132	124	143	123	135 ^f
Alkyl sulfate	57	49	28	31	9	8 ^f	30	215 ^c 134 ^d	204 126	216 139	240 128	184 128	214 115	212 ^f 128 ^f
Amphoteric														
Crude soy lecithin I	37	29 ^f	22	11 ^f	6 ^f	6 ^f	19 ^f	231 ^c 322 ^d	220 458	216 317	235 386	238 299	187 407	222 365
Crude soy lecithin II	46	44	21	21	3 ^f	7 ^f	24 ^f							
Purified egg lecithin	51	51	18	25	6 ^f	9	27							
Least significant ratio of control/sample	1.85		1.85		1.85		1.28	1.27 ^c 1.44 ^d		1.27 1.44		1.27 1.44		1.10 1.16

^aContained 613 ppm P.^bSurfactant conc.: L=1.3 mM and H=2.6 mM.^cOil from partially damaged soybeans 581 ppm P (see Experimental).^dOil from severely damaged soybeans 223 ppm P (see Experimental).^eAccording to Dunnett's test (19).^fSignificantly lower than control (0.05 level).

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