Oilseed Pretreatment in Connection with Physical Refining

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ABSTRACT

Tests have shown that the nonhydratable phosphatides (NHP) arising by the action of phospholipases are not present in significant quantities in commercial soybeans, but that they are formed predominantly only during extraction. By a moisture-heat treatment of the soy flakes prior to the extraction, this enzyme activity can be almost completely eliminated so that, during the subsequent extraction, an enzymatic change of the oil no longer occurs. In comparison with the extraction of untreated soy flakes, the yield of soy lecithin is doubled; the lecithin has a higher content of phosphatidylcholine; the crude, degummed soy oil has extraordinarily low NHP contents; and the soy meal tastes less bitter.

INTRODUCTION

The commercial crude, degummed soy oil produced according to today's state of technology contains, apart from other impurities, a 0.2-0.6% portion of nonhydratable phosphatides (NHP), which corresponds to a P-content of 70-200 ppm (1,2). The presence of these NHP forces the crude oil processor, when producing edible oils or hydrogenated products, to use refining processes which lead to an almost complete removal of the NHP (1,3,4). A phosphatide content of 0.015% corresponding to 5 ppm P is aimed at as an upper limit prior to deodorization (5). Although attempts are made more or less successfully today in many refining plants to use other refining methods with a simplified and environmentally compatible technology (5) instead of the customary alkali refining, no one has yet been successful in developing a refining process by which the phosphatides can be removed from all oils and fats economically with consistently good results as by the alkali refining method. Such processes include a treatment of the oil by acids and bleaching earth and subsequent deodorization with a simultaneous deacidification by distillation. These processes are successful in general only with crude oils that already contain very small quantities of phosphatides. Palm oil and coconut oil are typical examples. There are considerable differences in the phosphatide content of crude soy oils (2). Every soybean extraction plant produces a crude, degummed oil that seems to have a phosphatide content which is typical for that plant.

In many cases, difficulties with the oil quality (e.g., high contents of phosphatides) in extraction plants are explained by the quality of the soybeans and accepted as an unchangeable property of the beans themselves. Varying qualities of beans lead to different oil qualities (6-8) in today's manner of operation of extraction plants. Various factors can considerably affect the oil quality during extraction. By appropriate pretreatment of the soy flakes prior to èxtraction, it is possible to produce crude, degummed oils with very low phosphatide contents suitable for physical refining. A bleaching earth treatment will reduce the phosphatide content to 0.01%, and the soy oil can then be deodorized directly.

Factors Affecting the Quality of Oil

Retention time of soy flakes. Ong (2) showed that considerable deterioration of the oil quality is caused by storing flaked soybeans for more than 24 hr before extraction. The contents of NHP and free fatty acid (FFA) as well as the An (anisidine) number and the POV (peroxide value) rise considerably. Ong traces this effect to enzyme reaction of lipoxygenases and phospholipases of soybeans in the flaked condition. Although flaked beans are not stored for such a long time in any extraction plant, there are certainly considerable differences in the seed's retention time between the flaking rollers and the extraction. If the broken beans are flaked at relatively high temperatures, this factor alone may lead to considerable differences in the oil quality from various extraction plants.

Water content. To visualize the effect the water content of the soybeans has on the phosphatide content of the crude, degummed oil during extraction, we have first run some laboratory tests with dried and undried beans of identical quality.

Test 1. A sample of "US No. 2" quality beans was divided into two parts in the sample divider. One half of the sample was dried in the drying cabinet at 90 C. After flaking, under identical conditions, the crude, degummed oil was then recovered from both samples and analyzed.

Test 2. A sample was taken during unloading of an ocean freighter. One part of the load was dried immediately by hot air on a production scale via a drying plant and again sampled. As in the case of Test 1, the crude, degummed oil was produced from both samples on laboratory scale. Table I shows the characteristic numbers of the oils.

TABLE I

Soybean Drying Tests

	% H_2O of the soybeans	Characteristics of the oil after degumming with water: % Phosphatides	Acid number
Test 1	10.8	0.16	0.55
	8.0	0.11	0.43
Test 2	11.8	0.32	0.88
	9.3	0.10	0.56

These results show that the extracted beans have lower NHP content and lower acid numbers in the dry state than upon extraction of the same beans with a higher moisture content.

It is known that enzymatic reactions are accelerated by moisture (9,10). From these results it may thus be derived that the phospholipases are active during the extraction, and the lower the content of water, the lower the enzyme activity. It remains unsolved as to which portion of the NHP present in the oil already existed in the beans prior to their processing and which portion was formed during the extraction. It has been proven, however, that at least the specific differences (0.05% in Test 1 and 0.22% in Test 2) were formed during the extraction.

To determine whether this effect also takes place in an extraction plant, we have compared daily the phosphatide contents of crude, degummed oil with the water content of the beans processed on that day over a period of ca. 100 consecutive production days.

Figure 1 shows the result of this comparison. Despite a considerable scattering range, the tendency can clearly be seen: that the content of NHP increases in the crude, degummed soya oil with an increased moisture content of the beans. This confirmed the result of the laboratory tests.

The extraction temperature. Samples were taken frðm the flaked soybeans in the extraction plant to see the effect of the extraction temperature on the NHP content in the oil. The sample was divided into three parts and extracted in the laboratory with hexane under otherwise identical conditions at 40, 50 and 60 C. To exclude any effects that a varying storage time may have on the flakes, the extractions were always performed at the same time in 3 identical devices at the 3 different temperatures. After degumming with water, the phosphatide content was determined from the oils thus produced. Table II shows results of 3 tests run on different days.

These results show that a rise of the extraction temperature leads to a strong increase of the phosphatide content in the oils.

To compare these laboratory test results with the results obtained on a production scale, soy oil was sampled in the extraction plant after degumming with water and the miscella temperature simultaneously taken in the extractor.

It was agreed with production management to operate the extractor daily with a different miscella temperature. In this way temperatures ranging from 40 to 57 C could be examined. Figure 2 shows the phosphatide contents of the degummed oils obtained during the various extraction temperatures.

This figure shows that, in excellent agreement with the results of the laboratory tests, the NHP content in the degummed oil increases with a rising extraction temperature. Assuming that the NHP formation is only caused by the enzymatic reaction of the phospholipases, it can again

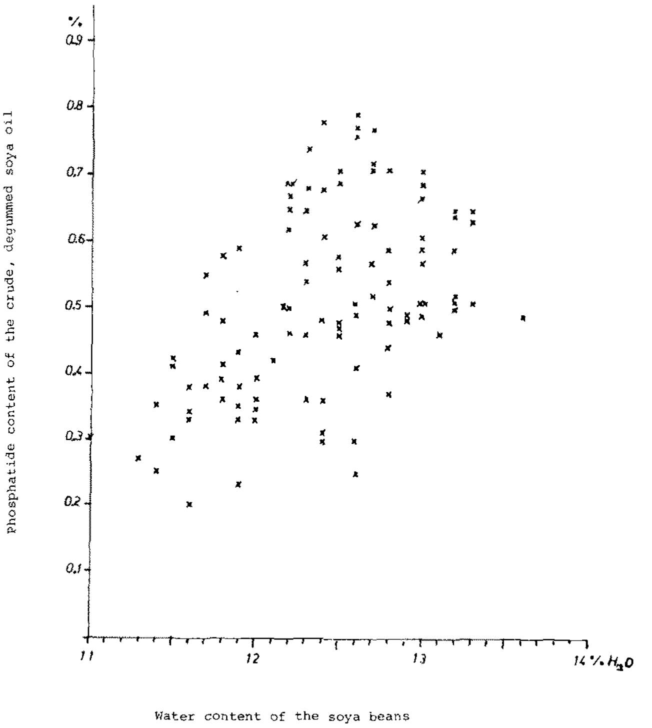

FIG. 1. Influence of water content of the soybeans on the NHP content of the oil (production scale).

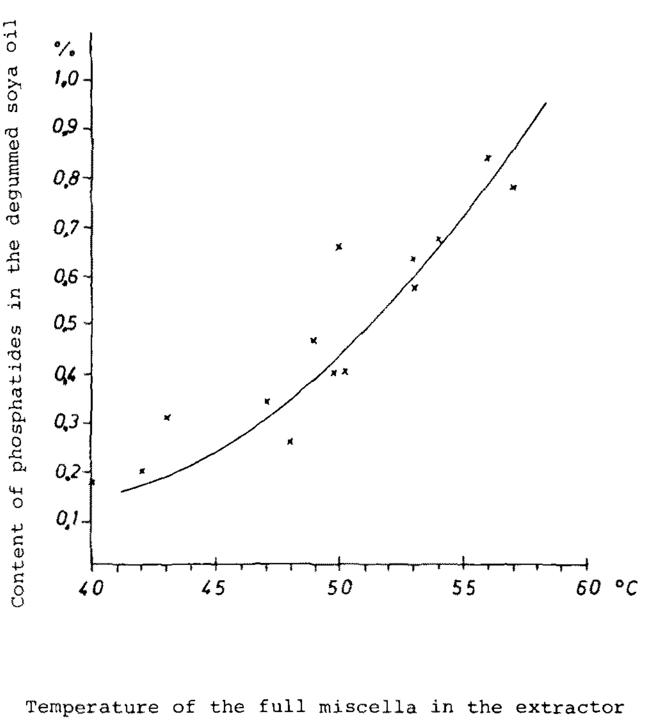

FIG. 2. Influence of extraction temperature on the NHP content of the oil (production scale).

TABLE II

Effect of Extraction Temperature on the Phosphatide Content of the Soy Oil

Sample	H_2O content of flakes (%)	Extraction temperature (C)	Phosphatides after degumming (%)
1	12.4	40	0.43
		50	0.70
		60	1.05
2	12.3	40	0.50
		50	0.85
		60	1.21
3	13.0	40	0.44
		50	0.91
		60	1.10

be concluded that a considerable part of these reactions takes place only during the extraction.

Accordingly, if you are successful, prior to extraction, in inactivating the enzymes that are responsible for the formation of NHP so that these are no longer able to develop their activity during the extraction proper, it should be possible to obtain soy oils with a very low content of NHP (11).

Moisture-Heat Treatment on a Technical Production Scale

In 1971, we started to subject flaked soybeans to a moisture-heat treatment on a technical production scale, thereby causing an inactivation of the phospholipases with the result of a pronounced decrease of the phosphatide content in the crude, degummed soy oil. Recently, we were able to develop the process further to such an extent that crude, degummed soy oils were obtained with a phosphatide content of 0.03% which corresponds to 10 ppm P. This result is achieved by a number of treatments whose effect on the quality of oil can be shown by the results of the test described in the following.

Beginning with the flaked beans, all treatment steps up to immediately before the addition of solvent were sampled in the production plant. On a laboratory scale, these samples were extracted under standardized conditions, with the phosphatide content determined on the oil before and after degumming with water.

Figure 3 shows the phosphatide contents of the oils extracted from the pretreated flakes before and after the degumming with water. Two opposite effects occur by the pretreatment: (a) increase of the phosphatide amount extracted from the soybeans together with the oil; and (b) decrease of the NHP content in the degummed oil.

These test results agree perfrectly with the practical results obtained in our extraction plant. Thus, the annual yield of soy lecithin in our extraction plant averages 1.2% of the soybeans processed. Normally, i.e., without pretreatment of the flakes, the yield of lecithin is only ca. 0.6% (10) of the beans processed.

The low phosphatide content of the oil after the degumming has also been confirmed completely in practice. The average characteristics of this oil are 0.6 acid number, 0.03% phosphatides (10 ppm P) and anisidine number of 0.5.

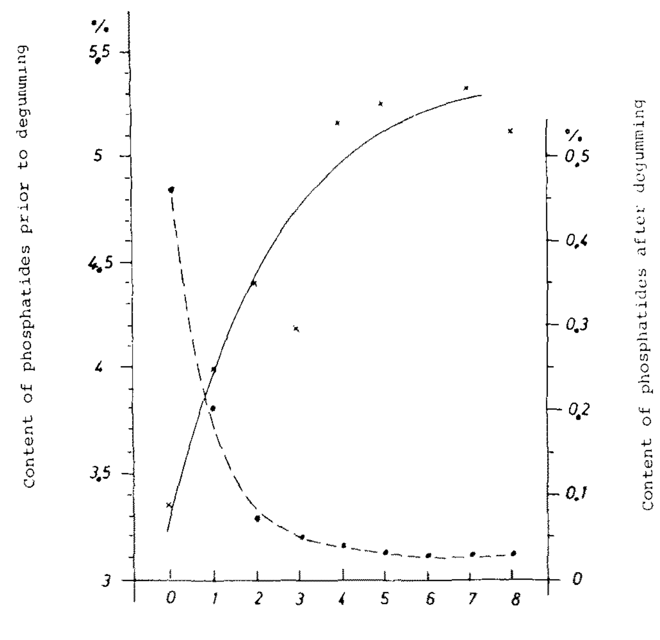

FIG. 3. Content of phosphatides in the crude soy oil: x——x prior to the degumming; ------ after the degumming.

Processing of Damaged Soybeans

We had the opportunity to evaluate the inactivation process on damaged soybeans when we recevied a supply of beans that had already been exposed to temperatures between 35 and 38 C in the ship. These beans contained a high portion of splits, damaged, kernels, heat-damaged kernels, bicoloured and purple mottled beans. The classification according to US Standards resulted in the quality designation "US No. 4" and "sample grade."

Phosphatide contents, acid and anisidine number of oils extracted during the period in which these heat-damaged beans were processed partly alone and partly mixed with sound beans showed that there is a distinct correlation between the content of nonhydratable phosphatides on the one hand and the acid and anisidine numbers on the other. If the NHP content increases, the acid number and the anisidine number also rise distinctly.

The phosphatide contents of oils produced from these damaged beans increased only as high as 0.2%, with acid numbers of almost 4 and anisidine numbers of 2 being reached.

It was of interest to know what oil qualities would be achieved if the identical quality beans had been extracted without previous moisture-heat treatment under otherwise identical conditions. As corresponding tests could not be run on a production scale, we tried to answer this question with laboratory tests. During the processing of the poor-grade soybeans mentioned above, samples were taken behind the flaking rollers and following the moisture-heat treatment in the extraction plant, with the crude, degummed soya oil produced from them on a laboratory scale. Table III shows the characteristics of these oils.

These results show that the phosphatide content of the degummed oil from nonpretreated flakes is ca. 10 times higher than that from pretreated flakes. A clear difference, even if less significant, exists in the case of the acid and the anisidine numbers.

In a further laboratory test we first cracked and flaked soybeans of poor quality. One portion of these flakes was directly extracted, the other was subjected to a moisture-heat treatment on a laboratory scale and then extracted in the same way. The soybean sample processed during these tests obtained was designated "sample grade" acording to the classification of US Standards, with 1.0% foreign material, 6.9% splits, 13.3% damaged kernels, 1.0% heat-damaged beans, and 3.1% bicolored and purple mottled beans. Table IV shows the quality of oils produced from the sample.

This case also shows that the phosphatide content of the oil from pretreated beans is only one tenth of that from nonpretreated beans.

TABLE III

Crude, Degummed Soy Oil from Pretreated and Untreated Flakes

	% Phosphatides	Acid no.	Anisidine no.
From untreated flakes	0.55	3.3	3.8
From pretreated flakes	0.06	2.1	2.1

It can be concluded that, also on processing heavily damaged soybeans, a moisture-heat treatment of the flakes prior to the extraction leads to a distinct lowering of the phosphatide content in the degummed oil. Acid and anisidine numbers are, however, considerably higher in both cases.

Further Removal of Phosphatides by Treatment with Bleaching Earth

Samples of degummed oils recovered on a production scale in the forementioned manner have been treated with different quantities of bleaching earth and then phosphatide contents determined in order to note the further removal of phosphatides by bleaching.

The results in Table V indicate that, under completely normal bleaching conditions, phosphatide contents of < 0.01%, corresponding to between 3 and 4 ppm P can be achieved. Such oils are best suited for the deacidification by distillation and deodorization.

On processing good-quality beans, crude, degummed oils are often obtained containing between 4 and 5 ppm P. In such cases only 0.2% bleaching earth suffices to reach the goal that has been set. On processing soybeans of inferior quality, the phosphatide content will increase, and larger quantities of bleaching earth will have to be used.

Change of the Phosphatide Composition

The fact that the extracted quantity of phosphatides increases ca. 100% by inactivation of the enzymes in soyflakes prior to extraction, let us presume that the soy lecithin, produced in this way, has another phosphatide composition than that of nontreated flakes.

Thin-layer chromatographic analyses of lecithin produced from nonpretreated flakes and from pretreated flakes are shown in Table VI.

The moisture-heat treatment prior to the extraction accordingly leads to a distinct change of the phosphatide composition. At this point, we would like to mention, in particular, the increase of the phosphatidylcholine content.

Flavor Properties of Soy Meal

It is known that by short-term heating of the soybeans with steam a debittering takes place (9,13).. This process is applied, e.g., in the production of whole soy flours. According to expectations, the soy flakes treated by our moisture-heat process are free from bitter flavors in contrast to the nontreated flakes. Also the meal, obtained after the extraction, tastes less bitter. This was the result of a taste test carried out with appropriate meal samples which, finely ground, were tested as a watery mash by several tasters.

Corresponding results were also received by R.D. Rice, Steinberg and staff who have proven very clearly that soy meal obtained after a moisture-heat treatment of soybeans is virtually free from bitter flavors (14).

TABLE IV

Crude, Degummed Oil from Soybeans of "Sample Grade" Quality

	Without pretreatment	With pretreatment
Phosphatides	0.77%	0.07%
Acid number	4.1	4.1
Anisidine number	2.4	2.5
$E^{1\%}_{1cm}$ 232	6.47	6.34
$E^{1\%}_{1cm}$ 268	0.66	0.78

TABLE V

Content of Phosphatides from Soy Oils Before and After Treatment with Bleaching Earth

Phosphatides in starting product (%)	0.5%	1.0%	1.5%
0.0	Residual phosphatides (%)		
0.05	0.024	0.020	0.104
0.04	0.011	0.008	0.005
0.03	0.013	0.009	0.007
0.02	0.010	0.005	0.005
0.01	0.005	0.004	0.004

TABLE VI

Composition of Soy Lecithin by Thin Layer Chromatographic Analysis

	From normal soy flakes (%)	From pretreated soy flakes (%)
Phosphatidylcholine	33	46
Phosphatidylethanolamine	30	23
Lysophosphatidylcholine	2	2
Monophosphatidylinosite	14	8
Phosphatide acid	17	19
Other phosphatides	4	2

DISCUSSION

Deactivation of the phospholipases obviously occurring during this treatment explains the low content of NHP. It does not, however, explain the fact that the amount of phosphatides extracted from the beans rises by ca. 100%. To explain this, we refer to the published results of tests carried out by other laboratories.

Baker and Mustakas showed that, of all soybean enzymes, the lipoxygenases are the easiest to inactivate by heat. We may, therefore, assume that by conditions under which the phospholipases are inactivated, the lipoxygenases are inactivated aswell (15).

Sessa has established that soy lipoxygenases type 1 is able to oxidize the unsaturated fatty acids combined with phosphatidylcholine (16). Rackis and staff reported that oxydized phosphatidylcholine is to be considred as the most important bitter flavor component in soybean meal (17). Finally, we mention the work of Nielsen from the Arhus University (18) who reported on the existence of covalent combinations between peroxidized phosphatides and protein.

Our test results and the knowledge of the above cited studies of work lead to the following thesis. The effect of the lipoxygenases leads to an oxidation of phospholipids during the extraction to a much larger extent than previously assumed. These oxidized phospholipids, during the extraction, form complex combinations with the soy protein which remain in the meal as hexane insoluble constituents, thus reducing the lecithin yield. If the lipoxygenase is inactivated prior to the extraction, an oxidation of the phospholipids and the formation of phosphatide-protein complexes connected therewith cannot take place. Consequently, the phosphatides will remain in their original form and can be extracted from the soybeans together with the oil.

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