Comparison of Oxalic Acid and Phosphoric Acid as Degumming Agents for Vegetable Oils

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ABSTRACT

For many years, phosphoric acid has been used for degumming vegetable oils with high phosphatide content prior to alkali refining. One disadvantage of this technique is the resulting undesirable phosphate waste in streams, a problem which has increased substantially in importance in recent times. We have investigated an alternative degumming technique using oxalic acid that alleviates the pollution problem in cases where water purification by means of a chemical treatment process is not possible.

INTRODUCTION

Lecithins and other gums are often removed at the end of the extraction process of a vegetable oil. Nevertheless, there are still some mucilaginous components in the oils, mainly phosphatides, which can be measured by the amount of phosphorus present. The presence of phosphatides will increase the risk of losses due to the formation of emulsions during the alkali treatment, and a disagreeable flavor may occur after deodorization.

Various methods for degumming oils have been suggested, e.g., treatment with acetic, citric, oxalic, boric (1), and nitric acids (2,3).

A common way to degum edible fats is to treat the oil with 0.02-0.2% of phosphoric acid (85% technical grade) followed directly by alkali treatment according to the Alfa-Laval Short-Mix process (4), or to treat the oil at a temperature of 80 C with 0.025-0.3% by volume of 85% phosphoric acid for 5-30 min under vacuum and then separate the precipitates by centrifugation according to the Zenith process (5).

One present disadvantage of this technique is the waste of phosphates to water streams. We have therefore investigated different chemicals as degumming agents and found oxalic acid suitable. This will alleviate the pollution problem in cases where water purification by means of a chemical treatment process cannot be carried out.

EXPERIMENTAL PROCEDURES

Laboratory Experiments

Rapeseed oil was degummed with different agents—such as acetic, citric, oxalic, nitric, and boric acids—and phosphoric acid was used as a reference. The best of these degumming agents, phosphoric acid and oxalic acid, were then used to degum soybean oil. The conditions for rapeseed oil are shown in Table I and those for soybean oil in Table II. The treatment was performed in laboratory batch equipment, and the oils were protected with nitrogen during processing.

After degumming, the oils were neutralized with 4 M sodium hydroxide and the soapstock was permitted to sediment. If this did not work properly, the oil was centrifuged. After separation of the soapstock, the oil was washed with deionized water and dried. The rapeseed oils were bleached with 0.8% Tonsil LFF 80 (Süd-Chemie A.G., Munich, W. Germany) and the soybean oils with 0.5% Tonsil LFF 80. The bleaching conditions were 90 C, 5 torr (mm Hg), for 30 min. The oils were deodorized at 3 torr for 2 hr at 220 C. Finally, 0.012% of 50% citric acid in ethanol was added to the rapeseed oils and 0.024% to the soybean oils.

Full Scale Experiments

Phosphoric acid and oxalic acid have been compared as degumming agents in full scale Alfa-Laval Short-Mix re-

TABLE I

Degumming Conditions for Rapeseed Oil

Degumming agent	Concentration of added acid weight (%)	Added amount oil (ml/1000 g)	Temperature (C)	Contact time (min)
Phosphoric acid	85	1	90	5
Acetic acid	98 - 100	1	80	15
Acetic acid	5	50	80	15
Citric acid	5	50	90	5
Oxalic acid	5	50	90	5
Oxalic acid	10[a]	10	90	5
Nitric acid	5	50	90	5
Boric acid	5	50	90	5

[a]$C_2H_2O_4$ x $2H_2O$; saturated water solution at 20 C consisting of 10.2 parts of water free oxalic acid.

TABLE II

Degumming Conditions for Soybean Oil

Degumming agent	Concentration of added acid weight (%)	Added amount oil (ml/1000 g)	Temperature (%)	Contact time (%)
Phosphoric acid	85	1	90	5
Oxalic acid	10[a]	10	90	5

[a]$C_2H_2O_4$ x $2H_2O$; saturated water solution at 20 C consisting of 10.2 parts of water free oxalic acid.

TABLE III

Degumming Conditions for Rapeseed Oil and Soybean Oil

Degumming agent	Concentration of added acid weight (%)	Added amount (1/ton)	Temperature (C)
Rapeseed Oil			
Oxalic acid	5	36	90
Oxalic acid	5	20	90
Phosphoric acid	85	1.8	90
Soybean Oil			
Oxalic acid	6.5	32	90
Oxalic acid	6.5	16	90
Phosphoric acid	85	2.1	90

TABLE IV

Analytical Figures for Neutralized and Bleached Rapeseed Oil

		Neutralized oil		Bleached oil			
					Lovibond color 5¼ in. cell		
Degumming agent	Concentration of added acid weight (%)	Soap (ppm)	Phosphorus (ppm)	Soap (ppm)	Yellow	Red	Total[a]
Phosphoric acid	85	13	2	0	30	2.0	50
Acetic acid	98-- 100	760	52	210	55	1.7	72
Acetic acid	5	500	53	150	55	1.9	74
Citric acid	5	220	38	24	30	1.2	42
Oxalic acid	5	0	4	0	40	1.1	51
Oxalic acid	10	13	3	0	24	1.2	36
Nitric acid	5	34	14	0	50	4.0	90
Boric acid	5	480	23	23	30	1.2	42

[a]Yellow + 10 x red = total.

TABLE V

Analytical Figures for Deodorized Rapeseed Oils

						Lovibond color 5¼ in. cell				
Degumming agent	Concentration of added acid weight (%)	BV[a]	PV[a]	FFA[a] (%)	Trans fatty (%)	Yellow	Red	Blue	Total[b]	Flavor[c]
Phosphoric acid	85	1.7	0.0	0.03	3.2	3.0	0.2		5.0	Normal (2.4)
Acetic acid	98 - 100	1.5	0.0	0.06	2.0	8.4	0.6	0.6	20.4	Bad (1.8)
Acetic acid	5	2.6	0.0	0.07	3.7	14.0	0.7	1.0	31.0	Bad (1.1)
Citric acid	5	1.2	0.0	0.03	3.1	4.5	0.3		7.5	Bad (1.8)
Oxalic acid	5	1.0	0.0	0.03	2.6	2.4	0.2		4.4	Normal (2.5)
Oxalic acid	10	1.7	0.0	0.03	2.0	3.5	0.3		6.5	Normal (2.2)
Nitric acid	5	3.1	0.0	0.06	15.6	40.0	5.6		96.0	Bad (1.0)
Boric acid	5	1.7	0.0	0.04	2.5	3.4	0	0.5	8.4	Normal (2.4)

[a]BV = Biological value; PV = peroxide value; see Ref. 7. FFA = Free fatty acid.
[b]Yellow + 10 x red + 10 x blue = total.
[c]The oils were checked by a 5-person taste panel.

fining (4) in a number of experiments. Phosphoric acid was mixed into the oil with a paddle mixer before lye was added, but this type of blending was not sufficient when oxalic acid was used. The paddle mixer had to be changed to a static mixer to get a very intimate blending.

In these experiments, mainly rapeseed oils and soybean oils were used, but cottonseed oil, peanut oil, and sunflower oil were also tested. Phosphoric acid and 2 different amounts of oxalic acid were tested in each trial. The degumming conditions for rapeseed and soybean oils are shown in Table III.

After degumming, the oils were neutralized with 4 M sodium hydroxide, and following separation of the soap stock, the oils were washed and dried. Before being bleached and deodorized, the rapeseed oils, degummed with different amounts of oxalic acid, were blended; the same was done for soybean oil. The rapeseed oils were bleached with 0.8% Tonsil LFF 80 and the soybean oils with 1.0% Tonsil LFF 80. They were deodorized, and 0.012% of 50% citric acid in water was added as antioxidant in the cooling step.

RESULTS AND DISCUSSION

Laboratory Experiments

Rapeseed oil: Different analytical figures for neutralized and bleached rapeseed oils are shown in Table IV. A comparison of the different degumming agents shows that phosphoric acid and oxalic acid give the best degumming effects, i.e., the lowest content of phosphorus in the oil. 10 ml of 10% oxalic acid solution in 1000 g of oil is the smallest amount that will give a degumming result for rapeseed oil comparable to that of 1 ml/1000 g oil of 85% phosphoric acid. Parallel to the lower phosphorus content in the neutralized oil is a lower soap content. Soap content decreased during bleaching and reached its lowest value for oils degummed with phosphoric acid, oxalic acid, and nitric acid. The highest color is obtained for oil degummed with nitric acid.

The analytical figures for deodorized rapeseed oils are shown in Table V. The highest benzidine values are obtained for oils degummed with acetic acid and nitric acid.

TABLE VI

Analytical Figures for Neutralized and Bleached Soybean Oils

Degumming agent	Neutralized oil Soap (ppm)	Neutralized oil Phosphorus (ppm)	Bleached oil Soap (ppm)	Bleached oil Lovibond color 5¼ in. cell Yellow	Red	Total[a]
Phosphoric acid	0	30	0	30	9.0	120
Oxalic acid	25	3	0	40	5.0	90

[a]Yellow + 10 x red = total.

TABLE VII

Analytical Figures for Deodorized Soybean Oil

Degumming agent	BV[a]	PV[a]	FFA[a] (%)	Trans fatty acids (%)	Lovibond color 5¼ in. cell Yellow	Red	Total[b]	Flavor[c]
Phosphoric acid	4.4	0.0	0.07	2.0	10	0.8	18	Normal (2.2)
Oxalic acid	3.2	0.0	0.03	2.8	5	0.3	8	Normal (2.1)

[a]BV = Biological value; PV = peroxide value; see Ref. 7. FFA = Free fatty acid.
[b]Yellow + 10 x red = total.
[c]The oils were checked by a 5-person taste panel.

TABLE VIII

Analytical Figures for Neutralized and Bleached Rapeseed Oil and Soybean Oil

Degumming agent	Added amount (1/ton)	Neutralized oil Soap (ppm)	Neutralized oil Phosphorus (ppm)	Bleached oil Soap (ppm)	Bleached oil Lovibond color 5¼ in. cell Yellow	Red	Total[a]
Rapeseed oil							
Oxalic acid	36	60	3.8	0			
Oxalic acid	20	65	4.3		22	1.5	37.0
Phosphoric acid	1.8	30	3.9	0	30	2.0	50.0
Soybean oil							
Oxalic acid	32	75	5.0				
Oxalic acid	16	75	4.4	0	30	1.7	47.0
Phosphoric acid	2.1	30	7.7	0	30	3.0	60.0

[a]Yellow + 10 x red = total.

TABLE IX

Analytical Figures for Deodorized Rapeseed Oil and Soybean Oil

Degumming agent	BV[a]	PV[a]	FFA[a] (%)	Trans fatty acids (%)	Lovibond color 5¼ in. cell Yellow	Red	Total[b]	AOM[c] stability (hr to PV 100)	Flavor[d]
Rapeseed oil									
Oxalic acid	1.9	0	0.05	2.2	3.5	0.5	8.5	19.5	Normal (2.8)
Phosphoric acid	2.3	0	0.04	2.1	4.0	0.5	9.0	20	Normal (2.7)
Soybean oil									
Oxalic acid	2.9	0.0	0.03	3.0	4.5	0.6	10.5	16.0	Normal (2.7)
Phosphoric acid	3.0	0.0	0.04	2.8	4.5	0.9	13.5	16.0	Normal (2.9)

[a]BV = Biological value; PV = peroxide value; see Ref. 7. FFA = Free fatty acid.
[b]Yellow + 10 x red = total.
[c]AOM = Active oxygen method.
[d]The oils were checked by a 5-person taste panel.

After deodorization, oils degummed with these acids also show the highest color. For acetic acid, this may be due to the low degumming effect and the fact that phosphatides remain in the bleached oil, which will darken the oil during deodorization. The nitric acid treated oil even raised its color index, perhaps due to nitration (c.f. sulfonation) of the oil. The highest trans fatty acid content is obtained with nitric acid (6). The best flavors are obtained with phosphoric, oxalic, and boric acids.

Soybean oils: The analytical figures for neutralized and bleached soybean oil are shown in Table VI. Oxalic acid gives the lowest phosphorus content in the neutralized oil. Oil degummed with phosphoric acid shows a high content of residual phosphorus but, remarkably, no soap, although a high soap content normally accompanies a high phosphorus content. This may, however, be due to inadequate determination of the soap content. Degumming of soybean oil is difficult to perform with phosphoric acid in our laboratory batch equipment, but there are no such difficulties with oxalic acid. Oil treated with phosphoric acid has the highest color index.

In Table VII, the analytical figures for deodorized soybean oil are shown. No substantial difference exists between the oxidation values for different degumming techniques. The color index is substantially reduced in both trials, and it is still higher in the oil treated with phosphoric acid. There is no difference in flavor between oils degummed with oxalic acid and phosphoric acid.

Full Scale Experiments

Analytical figures for neutralized and bleached rapeseed oils and soybean oils are shown in Table XIII. The phosphorus content of neutralized oils shows that the degumming effect of oxalic acid and phosphoric acid is the same. Wolff's method indicated a higher soap content in the oxalic acid degummed oils, although no sign of a high soap content was noticed in refining. This response could be due to alkaline products other than soap, or to a lower residual acid content in the case of oxalic acid treatment. Oxalic acid degummed oils also show a higher green and lower red pigmentation than phosphoric acid degummed oils. This was expected, as phosphoric acid converts chlorophylls to pheophytins.

In Table IX, analytical figures for deodorized rapeseed oil and soybean oil are shown. After deodorizing, there is no difference between oils treated with phosphoric acid and oxalic acid.

Corresponding trials were made for sunflower oil, peanut oil, and cottonseed oil, with the same results.

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