Chemical Degumming of Canola Oils

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ABSTRACT

Crude oil produced from 2 varieties of canola (low thioglucoside rapeseed), i.e., Candle and Tower, were chemically degummed using 54 reagents. Phosphorus, iron, calcium and free fatty acid levels, and Lovibond colors were measured. Inorganic and organic acids or their anhydrides gave the best results in terms of phosphorus removal. Phosphoric, nitric and citric acids, and maleic anhydride were used in laboratory refining tests to determine the effects of chemical degumming on the refining process and on refined oil quality. Citric acid and maleic anhydride gave residual phosphorus levels of less than 50 mg/kg, and after refining, resulted in the best quality oil in terms of color, flavor and stability. The chemical degumming agents behaved similarly for expressed, solvent-extracted and blended oils of both varieties tested. One anomalous result was observed: Candle oil was not efficiently degummed by hydrocholoric acid, whereas the Tower oil gave excellent results. The experiments suggest that chemical degumming can significantly improve the quality of crude canola oil, and will lead to improved final products at lower cost to the refiner.

INTRODUCTION

The composition of Canadian rapeseed oil and meal has been dramatically altered during the past 20 years by a major plant breeding program. As a result, the erucic acid (22:1) content of the oil has been reduced to less than 1%, whereas the glucosinolate content of the meal has been reduced by a factor of 7-10. The new varieties of rapeseed are so radically different from traditional varieties that a new generic name — canola — is now used to denote the seed and its products.

The introduction of new seed varieties required a number of changes in processing conditions. Most Canadian rapeseed crushing plants produce only crude, water-degummed rapeseed oil, which is refined in a different location. In all currently operating refineries, the crude oil is first contacted with phosphoric acid prior to caustic refining. The "Candle" variety of rapeseed results in an oil that contains very high levels of phosphorus after aqueous degumming.

In 1978, the Rapeseed Association of Canada, now called the Canola Council of Canada, commissioned a study of chemical degumming techniques in an effort to improve the quality of crude, degummed canola oil. The following work summarizes the results of the project, supported by RUAP grant #79-1.

EXPERIMENTAL TECHNIQUES

Materials

Samples of Candle and Tower oil samples prepared at the P.O.S. Pilot Plant Corporation were obtained through the Rapeseed Association of Canada. For both varieties, samples of hexane-extracted and -expelled oils were obtained, whereas blended samples, which closely represent the commercial crude oil, were prepared by mixing expelled oil with extracted oil. In addition, a commercially prepared lot of combined Candle oil was used. Unfortunately, at the time of the tests, none of the Canadian crushing plants was receiving Tower seed exclusively and thus no commercial sample of pure Tower oil was available. The analysis of the starting oils is presented in Table I.

All degumming agents were reagent-grade. Pembina acid activated bleaching clay was used in the refining tests of selected degummed oils (Pembina Mountain Clay Co., Winnipeg).

Degumming Technique

Crude oil (300 g) was heated to 60 C with agitation at 200 rpm. An aqueous solution of the treatment chemical was added to the oil by drops using a small pipette to the desired concentration. After the oil was mixed for 10 min, a further aliquot of 2% water was added for hydration.

Chemicals with low solubility in water, such as oxalic and boric acids, were added together with the 2% water, as dilute aqueous solutions. Acid anhydrides, which hydrolyze on contact with water, were added directly to the oil as solids, and allowed to react for 10 min prior to water addition.

Agitation continued for a further 20 min; however, when diluted chemical solutions were added to the oil directly, as in the case of oxalic acid or sodium chloride, the total agitation period was reduced to 20 min. The degummed oil was analyzed for residual phosphorus level, free fatty acids (FFA) and color according to the AOCS Official Methods. The calcium and iron levels of low phosphorus oils were determined by atomic absorption spectrophotometry.

Refining Techniques

Based on the results of the screening tests, 2,000 g of the

TABLE I

Analysis of Crude Rapeseed Oils

Oil	Lovibond R	Color (1") Y		FFA (%)	PV (mg/kg)	IV	P (mg/kg)	Fe (mg/kg)	Ca (mg/kg)	S (mg/kg)
Candle expelled	3.4	40	0.4 N	0.83	0.99	120.4	320	3.94	182	0.5
Candle combined	4.4	60	0.2 N	1.20	0.93	120.3	755	3.73	239	3.5
Candle extracted	5.0	60	0.2 N	1.57	0.88	120.3	1,190	3.52	296	6.5
Tower expelled	4.6	70	0.9 B	0.70	1.83	111.9	286	1.85	149	0.5
Tower combined	5.5	70	0.9 B	0.96	1.87	111.8	622	2.62	168	3.0
Tower extracted	6.3	70	0.9 B	1.21	1.92	111.7	958	3.39	187	5.6
Candle commercial combined	4.1	40	1.0 N	0.62	1.31	120.0	508	2.04	118	3.3

extracted Candle oil, which was the most difficult oil to degum, was heated to 60 C with agitation in an open, 4-L vessel. Nitric and citric acids were added to the oil as 50% aqueous solutions and 85% phosphoric acid was used in its concentrated form; maleic anhydride was added directly as a fine powder. Chemical addition levels were the same as in the screening tests. After twenty min of agitation, 40 mL of water was added, and the agitation was continued for a further 40 min. After settling, the mixture was filtered and analyzed. In addition to the analyses performed in the screening tests, sulfur was also determined by the method described by Granatelli (1).

The degummed oils were alkali-refined in a batch system using 50% sodium hydroxide solution. The control oil was conventionally degummed with water, and then treated with 500 ppm phosphoric acid prior to neutralization; the phosphoric acid treatment was eliminated in the chemically degummed oils.

After washing, the oil was heated to 110 C, 2% bleaching clay was added, and the mixture was agitated and filtered.

The bleached oil thus prepared was split into 2 samples. Half of the oil was hydrogenated with 0.06% nickel catalyst Girdler G-49B. The hydrogenation conditions were 160 C at 200 kPa hydrogen pressure, to the final iodine value of ca. 90. The rate of hydrogenation was monitored by the measurement of refractive index.

Both the hydrogenated and the nonhydrogenated oil samples were deodorized using a CAMPRO laboratory deodorizer at 250 C. The resulting oils were analyzed for flavor, color, free fatty acids, peroxide value, AOM stability and phosphorus by the AOCS methods, and for sulfur by the Granatelli method.

DISCUSSION OF RESULTS

The scientific literature contains several reviews on gums and degumming techniques. Anjou (2), Lajara (3), Persmark (4), Solomon (5), Teasdale (6) and Wettström (7), gave excellent overviews of rapeseed gums and their removal. Recently, Hougen and Thompson (8) reviewed the literature related to all aspects of phosphorus removal from edible oils.

Despite the large body of literature on the subject, the behavior of the new varieties of canola during industrial processing is sufficiently different from the older strains of rapeseed, so that a complete review of chemical degumming of canola oils is warranted.

Hvolby (9) reported on a similar review of soybean oil degumming in 1971. He tested over 100 reagents, including a large number of calcium and magnesium binding reagents and a series of surfactants. Although he obtained phosphorus removal to residual levels well below 10 mg/kg, the chemical addition levels were in the range of 10,000 mg/kg, which would make commercial application of the process uneconomical.

In our work, we selected reagents from all chemical groups represented in the literature, including acids, anhydrides, salts, bases, carbohydrates, proteins, surfactants and chelating agents. Addition levels were generally kept in the 1,000-3,000 mg/kg range, consistent with the usual additional levels used by industry.

In order to establish differences in treatability, each of the starting oils was degummed using 4 well known degumming agent: phosphoric, hydrochloric and citric acids and water. The results summarized in Table III indicate that all

TABLE II

Comparison of Degummed Oils

Starting oil	Degumming agent	Addition level (mg/kg)	Degummed Oil[a] P (mg/kg)	Fe (mg/kg)	Ca (mg/kg)	FFA[a] (%)	Lovibond Color (1") R	Y	N
Candle expelled oil	Water		186	1.24	153	0.74	3.4	40	0.2
	Phosphoric acid	1,700	127	1.22	56	0.80	4.8	40	1.0
	Hydrochloric acid	2,000	22	0.76	15	0.84	4.8	40	1.0
	Citric acid	2,500	68	0.92	43	0.82	4.5	40	1.0
Candle combined oil (50:50 mixture)	Water		208	1.88	187	0.90	3.7	50	0.2
	Phosphoric acid	1,700	125	1.15	52	0.97	4.7	40	1.0
	Hydrochloric acid	2,000	150	1.00	44	0.99	4.9	40	1.0
	Citric acid	2,500	74	0.92	45	0.99	4.5	40	1.0
Candle extracted oil	Water		241	1.69	214	1.11	4.1	60	0.2
	Phosphoric acid	1.700	123	0.97	49	1.15	4.5	60	0.3
	Hydrochloric acid	2,000	218	2.41	98	1.25	4.9	60	0.3
	Citric acid	2,500	75	0.90	49	1.14	4.2	60	0.3
Tower expelled oil	Water		160	1.34	131	0.60	3.4	70	>0.9 B
	Phosphoric acid	2,000	170	1.37	30	0.68	5.2	70	>0.9 B
	Hydrochloric acid	2,000	32	1.04	21	0.75	5.0	70	>0.9 B
	Citric acid	2,500	55	1.39	30	0.70	4.5	80	>0.9 B
Tower combined oil (50:50 mixture)	Water		175	2.29	141	0.71	4.2	70	>0.9 B
	Phosphoric acid	1,700	162	1.25	31	0.75	5.5	110	0.9 B
	Hydrochloric acid	2,000	41	0.99	21	0.88	5.0	110	0.9 B
	Citric acid	2,500	51	1.77	26	0.79	4.9	110	0.9 B
Tower extracted oil	Water		180	2.79	152	0.82	4.6	70	>0.9 B
	Phosphoric acid	1,700	153	1.13	32	0.86	6.0	100	>0.9 B
	Hydrochloric acid	2,000	50	0.96	20	0.92	5.3	105	>0.9 B
	Citric acid	2,500	50	0.79	18	0.85	5.1	105	0.6 B
Candle commercial combined oil	Water		167	1.20	106	0.58	3.8	35	1.0
	Phosphoric acid	1,700	102	0.77	33	0.61	4.7	35	1.0
	Hydrochloric acid	2,000	23	0.47	5.2	0.59	4.4	35	1.0
	Citric acid	2,500	35	0.48	20	0.57	4.2	35	1.0

[a]FFA = free fatty acids.

of the oils follow the same trends in phosphorus reduction, with the exception of one anomalous result: hydrochloric acid did not effectively degum the extracted Candle oil. Hydrochloric acid degumming tests were repeated with several Candle oil samples, each of which confirmed that hydrochloric acid is not an effective degumming agent for the extracted Candle oil

The results shown in Table II indicate the extracted Candle oil is the most difficult oil to degum. In order to minimize the usage of the specially prepared oils, the commercial blended Candle oil was used for a preliminary screening test series consisting of a further 50 treatment chemicals. The results of the screening tests are presented in Table III.

Surprisingly, only acids and acid anhydrides reduced the phosphorus level below 100 mg/kg from the initial value of 508 mg/kg.

To ensure that the results were generally applicable, all promising treatments were repeated using blended Candle, extracted Candle and extracted Tower oils.

There were no major differences in the degumming behavior of the different starting oils. Treatments which were

TABLE III

Results of Screening Test for Degumming Commercial Candle Oil

	Addition Level (mg/kg)	P (mg/kg)	Fe (mg/kg)	Degummed Oil Ca (mg/kg)	Degummed Oil FFA (%)
Starting oil: commercial blended Candle oil	–	508	2.04	118	0.62
Degumming Agent					
Water	2%	167	1.20	106	0.56
Phosphoric acid	1,700	102	0.77	33	0.61
Hydrochloric acid	2,000	23	0.37	5.2	0.59
Nitric acid	2,000	70	0.85	28	0.48
Sulfuric acid	2,000	78	0.51	28	0.74
Ammonium hydroxide	2,000	129			0.44
Citric acid	2,500	35	0.48	20	0.57
Oxalic acid[a]	2,000	128	0.94	108	0.66
Tannic acid[a]	2,500	180			0.61
Acetic anhydride	2,500	172	1.10	72	0.72
Maleic anhydride[b]	2,500	65	1.28	19	0.63
Sodium chloride[a]	2,000	175	0.93	116	0.57
Sodium sulfate	2,000	162			0.56
Sodium nitrate[a]	2,000	170			0.59
Sodium citrate[a]	8,000	172			0.56
Potassium chloride[a]	2,000	177	0.88	114	0.57
Boric acid[a]	800	172			0.59
Acetic acid[a]	2,000	162			0.63
Trichloroacetic acid	1,700	172			0.75
Maleic acid	2,500	152			0.65
Sucrose[a]	2,000	181			0.57
Maltose[a]	2,000	174			0.56
Soluble starch[a]	200	159			0.57
Wheat flour[a]	600	185			0.58
Milk	20,000	171			0.56
HCl in milk	2,000	31	0.66	11	0.57
Na K tartrate	2,400	164			0.56
Tartaric acid	2,500	133			0.62
Succinic acid[a]	4,000	134			0.65
Sulfamic acid[a]	4,000	184			0.62
Sodium metaphosphate	2,500	174			0.56
Sodium oxalate[a]	700	154			0.58
Na tripolyphosphate[a]	2,000	151			0.55
Wheat flour + HCl[a]	2,500	158			0.64
Formic acid	2,500	58	1.38	51	0.75
Formaldehyde	1,850	160			0.56
Propionic acid	2,500	148			1.08
"Tween 80"	2,500	170			0.56
Urea	2,500	158			0.53
Na hexametaphosphate	2,500	170	1.32	149	0.54
Casein[a]	400	158			0.54
Ascorbic acid	2,500	142			0.57
Glutaric acid	2,400	164			0.72
Glucono-δ-lactone	2,400	178			0.60
Glycine	2,500	165			0.58
L-Aspartic acid[a]	100	168			0.56
L-Glutamic acid[a]	200	177			0.56
Hydrogen peroxide[a]	7,000	167			0.58
H_2O_2 + NH_4OH	7,000 + 2,000	115			0.52
Succinic anhydride[b]	2,500	131			0.65
L-Lysine HCl	2,400	159			0.60
L-Alanine	2,800	160			0.61
Na metasilicate	2,500	122			0.11
Na_4 pyrophosphate[a]	1,000	155			0.56

[a]No water added, solution or suspension supplied 2% water.

[b]Added as solid.

successful with the extracted Candle oil worked satisfactorily with all other oil samples, as well. The results showed that high molecular weight compounds such as tannic acid and starch were ineffective in removing phospholipids from the oil. Salts were equally unsatisfactory. Both organic and inorganic acids proved to be effective in terms of phosphorus and calcium removal. Accordingly, 3 acids, phosphoric, nitric and citric, plus maleic anhydride, were selected for more detailed evaluation.

Refining Tests

Degumming tests were repeated using 2,000-mL batches of oil. The chemically degummed oils were refined in an effort to determine the effect of the chemical degumming agent on the refining process and the final product quality.

There were significant differences in the final effect of these 4 chemical degumming techniques on the finished oils.

Phosphoric acid gave the highest residual phosphorus level in the degummed oils (117 mg/kg). However, the residual phosphorus did not influence the final oil quality. Nitric acid reduced the phosphorus level more effectively than phosphoric acid (80.4 mg/kg); however, the degummed, bleached and deodorized oils were somewhat dark in color, and the flavor stability was inferior to those obtained by the other degumming agents.

Excellent results were obtained by both maleic anhydride and citric acid. Phosphorus levels in the degummed oil were 28.6 and 29 mg/kg, respectively.

The calcium, iron and sulfur levels in the degummed oils followed similar trends to the residual phosphorus levels (Table IV). Because the residual sulfur levels were low, hydrogenation proceeded rapidly, with no sign of catalyst poisoning. There were no significant differences in the hydrogenation rates among the 5 degumming methods. The deodorized oils gave flavor score and color identical to those of the control, despite the elimination of the phosphoric acid pretreatment prior to the neutralization.

TABLE IV

Results of Processing Tests

	P (mg/kg)	Fe (mg/kg)	Ca (mg/kg)	S (mg/kg)
Crude Candle oil	1,190	3.52	296	6.5
Degummed oils:				
Water	222	1.32	169	1.2
Phosphoric acid	117.2	0.63	34.8	1.5
Nitric acid	80.4	0.69	29.8	0.85
Maleic anhydride	29.0	0.58	16.8	1.6
Citric acid	28.6	0.67	17.2	1.4

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