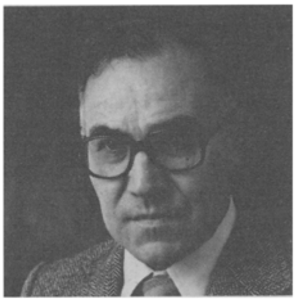
Canola Oil Processing in Canada



T.K. MAG, Research Centre, Canada Packers Inc., Toronto, Ontario, M6N 1K4, Canada

ABSTRACT

Canola is the registered trademark of the Canola Council of Canada for the seed, oil and meal derived from rapeseed cultivars low in erucic acid and low in glucosinolates. Conversion to canola cultivars on a commercial scale started in 1976; in 1981, ca. 87% of the brassica-based oil crop in Canada was of canola quality. Canola oil is the most important oil in Canada. Processing of the oil is, in its essentials, conventional. A few problems not usually encountered with other oils are its chlorophyll content which requires extra processing and analytical effort, and certain limitations in crystallization behavior when highly hydrogenated. Advantages are that stable oils can be produced at moderate degree of hydrogenation, and without hydrogenation in the case of salad oil. New developments in processing of the oil have led to the production of acid-degummed, crude oil on a commercial scale. This opens the possibility to apply physical refining to the oil.

INTRODUCTION

Canola, which is Canada's most important oilseed crop, supplied ca. 50% of the total vegetable oil consumed in August/September of 1981 (1). This was the first time that this level was reached. According to the latest statistics the trend to increased usage is continuing (2).

The name canola is a registered trademark in Canada. It refers to the seed, oil, and meal derived from rapeseed cultivars which are low in erucic acid and low in glucosinolates. The following specifications must be met (3):

This represents a significant quality improvement over previous cultivars. Conversion to seed of canola-quality on a commercial scale started in 1976; by 1981 this conversion was 87% complete (1).

COMPOSITION OF CANOLA OIL

The fatty acid composition is shown in Table II, together with high erucic acid rapeseed oil (*Brassica napus*) and soybean oil.

TABLE II

Fatty Acid Composition of Canola Oil Compared to Rapeseed and Soybean Oil (wt/wt%) (4)

		Canola	(Rapeseed)	Soybean
Palmitic	C16	4	(4)	11
Stearic	C18	2	(2)	4
Oleic	C18:1	60	(34)	21
Linoleic	C18:2	20	(17)	54
Linolenic	C18:3	10	(7)	9
Eicoscenoic	C20:1	2	(9)	trace
Erucic	C22:1	2	(25)	trace

The data in Table II show that the change from the long-chain, monounsaturated acids, mostly erucic, was primarily to oleic acid and to a small extent to the other C_{18}-acids. Linolenic acid is at about the same level as in soybean oil or marginally higher. Total unsaturation is lower than in soybean oil.

Distribution of the two fatty acids important to the stability of the oil, linolenic and linoleic, was found to be primarily in the 2-position of the triglycerides (5). In this respect, the oil has remained similar to high erucic acid rapeseed oil (6). This difference to the more usual random distribution for linolenic and linoleic acids, and the somewhat lower total unsaturation indicates better resistance to oxidation than with oils of otherwise similar linolenic acid content.

Free fatty acids, phospholipids in nondegummed and in water-degummed oil, and the content of unsaponifiables are similar to concentrations (Table III) found in other, common vegetable oils such as soybean or corn oil. Crude oils are available which are either water-degummed or acid-degummed. With the latter, phosphorus concentrations can be as low as 10 ppm. Canola oil differs from most other vegetable oils of similar fatty acid composition by its content of small, but significant, amounts of green-colored or "chlorophyll" compounds, and a small amount of sulfur compounds (ca. 50% of levels in oil from noncanola quality seed (7)).

Niewiadomski (11) showed that the green-colored compounds are chlorophyll A and B and their decomposition products, pheophytin A and B. The A- compounds are the only important ones quantitatively. They absorb energy in the range of 656-668 nm. In this paper, the term "chlorophyll" is used to refer to these two compounds and their spectrophotometric measurement as described by Yuen and Kelly (9). Removal of these compounds is of some importance in the processing of the oil.

TABLE I

"Canola"-Quality Seed Compared to Rapeseed Cultivars

	Canola	Rapeseed Cultivars
Erucic acid (oil)	<5% specified; <2% achieved	20-40%
Glucosinolates[a] (meal)	<26.5 μmol/g	70-120 μmol/g

[a] By TMS-gas liquid chromatography (TMS-GLC): includes 3-butenyl, 4-pentenyl and 2, hydroxy-3-butenyl glucosinolates.

TABLE III

Nontriglyceride Constituents of Crude Canola Oil (8)

Free fatty acids	0.4-1.0%
Phospholipids	up to 3.5%
Water-degummed (as P)	150-250 ppm
Acid-water degummed (as P)	10-50 ppm
Unsaponifiables	0.5-1.2%
Chlorophylls[a]	5-25 ppm
Sulfur[b]	3-15 ppm

[a] Method of Yuen and Kelly (9).

[b] Method of Daun and Hougen (10).

PROCESSING OF CANOLA OIL

The "refining" processes used with canola oil follow the practice for other oils very closely. The unit processes involved are degumming, alkali-refining, bleaching, hydrogenation, and deodorization. Alternatively, it may be possible at some time in the future to use acid-degumming, acid-contacting/bleaching with steam-refining/deodorizing in place of the present approach based on alkali-refining.

Degumming

This is usually done at the extraction plant. Conventional water-degumming was used exclusively until about mid-1981. Similar to the water-degumming of soybean oil, this involves the addition of ca. 2% water or steam to the crude oil at 70-90 C with more or less intensive mixing and allowing residence time of from less than 1 min to ca. 30 min. The water-hydrated, precipitated phosphatides are then separated in a disc-centrifuge. The degree of degumming usually achieved by this process is shown in Table III to be in the range of 150-250 ppm of P, depending on such factors as crop-year, storage time and conditions, and also on seed preparation techniques (12).

Most extraction plants in Canada are now capable of acid-degumming to achieve a better quality crude oil for refinery processing. The degree of degumming achieved is in the range of 10-50 ppm of phosphorus as shown in Table III. The principle of the acid-degumming process has been described by many workers, notably List (13) and Ringers (14). Most of the interest of these workers was in degumming of soybean oil. Diosady (15) in 1980 studied acid degumming techniques for canola oil (sponsored by the Rapeseed Association of Canada, now the Canola Council of Canada). Also various process equipment firms such as Alfa-Laval (16), De Smet (17), and HLS (18), describe the essentials of the process in papers and brochures.

The various process versions have the following in common: adjusting the temperature of the crude oil to ca. 60 C; reacting it with an acid and with water; cooling the reaction mixture either before or after contact with water to ca. 35 C; allowing some contact-time; centrifuging (possibly after raising the temperature to 60 C) to separate the precipitated phosphatides from the oil. In some instances, coagulants are added to the reaction mixture (16,18) to facilitate centrifugal separation of the phosphatide phase. The separation can present difficulties depending on such factors as the properties of the crude oil, the acid degumming agent used and the specifics of mixing, and residence time built into the process. Phosphorus concentrations as low as 10-20 ppm can be achieved. Most of the oil produced commercially at the present in Canada is in the range of 10-45 ppm of phosphorus. The main advantages of acid degumming are lower alkali-refining losses and the possibility of applying physical refining.

Another interesting approach to achieving better degumming (12) involves using higher seed-conditioning temperatures, 100 C instead of ca. 85 C, in the stack cooker to inactivate phospholipases. These are responsible for the formation of nonhydratable phosphatide breakdown products (19,20) in connection with the extraction of soybean oil. The oil extracted from seed conditioned at the higher temperature is higher in phosphatides, but water-degumming removes these to the very low levels achieved otherwise only in acid degumming. Disadvantages are that the concentration of sulfur compounds in the oil is raised, and that the residual oil content of the meal tends to be higher. These have deterred the adoption by the industry of this approach to better degumming.

Alkali-Refining

At the present, practically all commercially-processed oil is alkali-refined using the continuous process. The main steps are pretreating the crude oil with phosphoric acid at about 95 C, then, alkali-refining at that same temperature with very short contact time before centrifuging, followed by water-washing, centrifuging and drying of the oil. A 1.5-2.0% refining loss is representative of experience with water-degummed oil. With acid-degummed oil, the loss is ca. 0.5% (abs.) lower.

The pretreatment with phosphoric acid is worthy of some additional comment. Its main purpose is to help precipitate phosphatidic material. This tends to reduce oil-losses and improve soap removal in water-washing. Some effect on chlorophyll removal is also achieved. These effects were described by Ohlson and Svensson (21) in tests using different acids for the pretreatment of rapeseed oil. These authors showed that phosphoric acid was the best choice. Its use has become standard practice. Usual amounts are in the range of 0.05-0.5% with 0.1-0.3% most common. The most noteworthy effect on deodorized oil quality is a considerable improvement in color and flavor-stability. It is not clear to what extent the color improvement is due to the more efficient removal of phosphatidic material in refining and to what extent chlorophylls are affected in a way which leads to more efficient bleaching.

It is interesting to note that chlorophylls are not usually directly removed in alakali-refining except with batch refining, where there is much longer contact between the pretreated oil and the sodium hydroxide. This is shown in Table IV. However, even then the very low concentration of green-colored compounds which can be tolerated to avoid green oils is not achieved. This concentration is below 0.1 ppm. This low level can at present only be achieved in bleaching. However, bleaching is more efficient when phosphoric acid is used as a pretreatment in alkali-refining (20) even though no significant change in chlorophyll concentration takes place in the continuous process.

A typical analysis of an alkali-refined oil compared to the crude oil is shown in Table V.

Soapstock Acidulation

The acidulation of canola oil soapstock does not differ significantly from that of other soapstocks. The same problems are encountered, namely, difficulties with phase separation, which lead to high oil losses and aggravate the pollution problem represented by the acid-water stream of the process.

The pollution problem is being alleviated by reducing the amount of water used in refining. This is achieved by replacing standard heavy phase discharge centrifuges with self-desludging centrifuges, which require no bowl-flush water. Also, increasingly, continuous acidulation processes are used to save space and reduce maintenance and energy costs. Finally, the availability of acid-degummed oil tends

TABLE IV

Effect of Phosphoric Acid on Chlorophyll (666 nm) in Alkali-Refining of Canola Oil

Oil treatment	Chlorophyll[a]	
Crude oil (sample 1)	21	
(sample 2)		27
0.1% H_3PO_4 5 min at 90 C, alkali-refined	20	
0.3% H_3PO_4 30 min at 90 C, alkali-refined (sample 2)		25
0.1% H_3PO_4 30 min at 90 C, batch alkali-refined	6	
No acid, 90 C, batch alkali-refined	19	

[a] Method of Yuen and Kelly (9).

TABLE V

Analysis of Canola Oil

	Crude, water-degummed	Alkali-refined
Free fatty acids	0.1-1.0%	0.05%
Phosphorus	150-250 ppm	0-5 ppm
Sulfur	3-15 ppm	2-7 ppm
Chlorophyll	5-25 ppm	<1-25 ppm
Soap	–	0-50 ppm
Moisture	0.05%	0.05%
Fe	1-3 ppm	0.1 ppm
Cu	–	0.01 ppm

to reduce emulsion problems in soapstock processing (22).

Bleaching

Alkali-refined oil is bleached with acid-activated clays to remove oxidation products and colored material, notably the chlorophylls and related compounds. Bleaching conditions are essentially the same as those applied to other vegetable oils. The use of acid-activated clays is quite essential in removing chlorophylls (6) because acidic conditions destabilize the pigments. Carbon black is used to a limited extent to assist in the removal of green pigments.

Because green-colored compounds must be removed to very low levels, bleaching clay usage tends to be higher than with soybean oil or sunflower oil. From 0.5% to 2.0% is usually required, with ca. 1% being the most common. Chlorophyll levels at least as low as 0.1 ppm must be achieved as indicated earlier.

One of the main problems in bleaching canola oil lies in determining if adequate removal of chlorophylls has been achieved. At low concentrations, the green color of the chlorophyll is quite effectively masked by the red of carotenes also present. Until recently there was no reliable spectrophotometric method for in-plant use to give reproducible results rapidly. As already indicated, this is because of the fact that as many as four compounds contribute to green color. AOCS Method Cc 13d-55 measures chlorophylls at 670 nm which does not allow for the absorption peak occurring at a lower wavelength or for differences between instruments. Yuen and Kelly (9) have largely overcome these shortcomings by measuring the wavelength at which the main absorption peak occurs.

The new McCloskey colorimeter, which is capable of measuring yellow and red color in Lovibond units and chlorophyll down to the parts per billion range has potential as a good color measurement tool in canola oil processing.

In Table VI, some typical analyses from plant and lab processing are shown for alkali-refined, bleached, and deodorized oils. It can be seen from the plant tests that chlorophyll at an accuracy of ca. 1 ppm does not give a good prediction of adequate bleaching to avoid visually noticeable green color in the oil. Also, the amount of chlorophyll left after refining is not necessarily a good indicator of the amount of clay which may be required to achieve adequate removal. The use of phosphoric acid in alkali-refining is shown to be clearly beneficial to the removal of green color to the required very low levels, as shown in the lab tests. The difference in visual green after deodorizing due to a difference in chlorophyll of about 0.5 ppm is quite striking. This demonstrates the need for very accurate chlorophyll determination in the bleached oil.

It is worth noting that green-colored compounds in hydrogenated canola oil present additional difficulty. These compounds, formed during hydrogenation, are derivatives of the chlorophylls which were left in the oil after inadequate bleaching. They are of unknown composition and have absorbance peaks at 636 nm and 605 nm. They must be completely removed to avoid a greenish tinge in the oil. They are more difficult to adsorb on bleaching clay than the original compounds, which makes it advisable to ensure complete removal of the chlorophylls before hydrogenation. Table VII illustrates these points.

The data show that at 5 ppm of chlorophyll in nonhydrogenated oil, absorption peaks no longer occurred at 666 nm after hydrogenation, but at 636 nm, and to some extent at 605 nm. Continued hydrogenation would have reduced absorption at 636 nm and increased it at 605 nm, but at

TABLE VI

Bleaching of Alkali-Refined Canola Oils

Alkali-refined		Bleached			Deodorized	
Chlorophyll (ppm)	H_3PO_4 used (%)	Clay usage (%)	Chlorophyll[a] (ppm)	Lovibond red	Lovibond red	Visual green
Plant						
13	0.08	1.25	<1	4.0	0.5	V. Sl. Green
18	0.23	1.1	<1	4.6	0.8	Sl. Green
<5	0.5 (Batch)	1.5	<1	3.5	1.0	Sl. Green
Lab						
6	0.1 (Batch)	1.3	<1 (0.12)	6.0	1.0	Sl. Green
19	0 (Batch)	1.3	<1 (0.65)	5.0	1.2	Very Green

[a] Method of Yuen and Kelly (9).

lesser intensity (data not shown). Bleaching to remove green compounds was relatively difficult.

When the nonhydrogenated oil was bleached to 0.2 ppm of chlorophyll (absorption at 666 nm), a slight peak occurred after hydrogenation at 636 nm. Postbleaching removed this producing an oil without any visual green.

Hydrogenation

Hydrogenation process equipment, and conditions such as temperatures, pressures, catalysts, are essentially the same as used for soybean oil. The catalyst concentration used may be slightly higher than with soybean oil due to the presence of a few ppm of sulfur compounds even in canola-quality oil. A typical set of conditions (8) for making a margarine oil base stock would be temperature (H_2 gas on): 165 C; temperature (control): 200 C; pressure: 30-70 kpa (gauge); catalyst concentration in oil: 0.1-0.2% (25% Ni); and agitation (6-blade turbine, 2 sets): 80 rev/min.

For a shortening base oil stock, the temperature would be controlled at 165 C, for example, and the pressure at 200 kpa (8).

These two sets of conditions are often also referred to as "selective" and "nonselective," respectively. Typical iodine values, solid fat indices and fatty acid compositions for selectively and nonselectively hydrogenated canola oils are shown in Table VIII (23). The solid fat indices which can be produced are quite suitable for margarine and shortening base stocks and for frying fats. They are similar to the base stocks obtained with soybean oils and other oils in which C_{18}-acids predominate. It may be noted that the iodine values are ca. 5-10 units lower than for soybean oil of corresponding hardness.

In commenting on the fatty acid composition of the hydrogenated oil, it is noted that linoleic acid is reduced to low levels, such as with S2 at 3.5%, even at relatively moderate hardness. Even the nonselectively hydrogenated oil, NS2, at 7.7% is already quite low in this acid. This indicates relatively good stability at low solid fat levels. Hydrogenated canola oil has, in fact, an advantage in the formulation of liquid shortenings with good oxidative and heatstability. Hydrogenation is not needed for purposes of producing good, shelf-stable salad oil (8).

The fatty acid compositions in Table VIII also indicate a disadvantage of canola oil. With increasing degree of hydrogenation, as, e.g., S1 and S2, stearic acid and oleic acid make up an increasingly large proportion of the total fatty acid composition. In S2, these two acids constitute over 90% of the total. This degree of uniformity in fatty acid composition can result in crystallization problems when the oil is used in margarine and shortening formulations. A "grainy" texture develops. This is a well known phenomenon, which also arises with such oils as sunflower and, to a small extent, soybean and corn.

Steps which can be taken to minimize or prevent "grainy" textures from developing are: limiting the degree of hydrogenation; blending with other oils, notably those containing large amounts of non-C_{18} acids; interesterifying with other oils containing non-C_{18} acids; and addition of sorbitan tristearate. More detailed treatment of crystallization problems is given by Teasdale (8).

Deodorization

The final processing step, as with other oils, is deodorization. There are no special considerations which apply to this oil. As with any oil, it must be well refined and well bleached and low in oxidation products to achieve bland, stable oil products of acceptable color. In Table IX, the analysis of a typical deodorized canola oil is reviewed, together with the requirements on the bleached oil.

Physical Refining

The use of physical refining in place of alkali-refining has gained increasing prominence in discussions on edible oil processing in recent years. The need for elimination of the

TABLE VII

Bleaching of Hydrogenated Canola Oils

Bleached oil	Hydrogenated oil				Hydrogenated, bleached oil		
Chlorophyll (666 nm) (ppm)	Absorbance at nm			Visual green	Absorbance at nm		Visual green
	666	636	605		636	605	
5	0	0.27	0.05	Very green	0.03	0	Very green
0.2	0	0.006	0	None	0	0	None

TABLE VIII

Typical Analyses of Selectively and Nonselectively Hydrogenated "Tower" Canola Oil (22)

Sample	Iodine[a] value	Solid fat index (C)					*trans* Fatty acids (% by GLC)					*trans* Fatty acids[b]
		10.0	21.1	26.7	33.3	40.0 C	C_{16}	C_{18}	C_{18}^1	C_{18}^2	C_{18}^3	
Nonhydrogenated	118.5	–	–	–	–	–	4.9	1.9	57.0	74.0	10.4	–
S1	86.2	10.8	1.4	0.1	–	–	4.8	4.3	78.1	10.6	tr.	34.0
NS1	86.0	6.2	1.8	1.2	0.4	–	4.9	10.0	67.5	14.4	0.4	24.6
S2	72.8	41.3	22.5	15.9	5.3	–	4.8	12.9	76.7	3.5	–	51.9
NS2	71.6	24.5	13.4	8.2	4.5	–	4.8	18.3	67.0	7.7	–	31.7

[a] Calculated from GLC analyses.

[b] Percent of double-bonds having *trans*-configuration.

TABLE IX

Quality of Deodorized Canola Oil

	Bleached oil	Deodorized oil
Color	2-6 R	0.5-1.5 R
Chlorophyll	<0.1 ppm	No visual green
FFA	0.05-0.25%	<0.05%
P	<5 ppm	<5 ppm
Ni	<0.3 ppm	<0.3 ppm
Fe	<0.1 ppm	<0.1 ppm
Cu	<0.01 ppm	<0.01 ppm
Flavor	–	Bland

water pollution problems associated with the acidulation of soapstock in particular, is adding to the interest in physical refining. Water standards are becoming more stringent and energy costs are increasing.

Work on physical refining of oils high in phosphatides has so far centered mostly around soybean oil. Few papers discussing plant experience have been published, but those by Tandy (24), Grothues (25) and Kock (20) should be mentioned. Also, List et al. (26) have published data on physical refining of soybean oil based on laboratory processing.

In principle, the requirements in preparing canola oil for successful physical refining are the same as those for soybean and other oils. They are very thorough degumming to less than 5 ppm of phosphorus, thorough bleaching, and removal of traces of iron and copper.

There have been what might be called two approaches to pretreating oils such as soybean oil (and by implication, canola oil):

- Starting with water-degummed oil at about 100 ppm of P and using high amounts of acid and clay and high temperatures (170 C) (24,25,27).
- Starting with acid-degummed oil at about 30 ppm of P and using relatively low amounts of acid and clay at standard bleaching temperature (105 C) (20,26).

The attempts at pretreating water-degummed oil at well above 30 ppm of P oil for physical refining are now largely abandoned. It was found to be too costly, and oil of good quality could not be produced reliably (25). Instead, the approach via the production of low-gum oil either by acid degumming or special pretreatment of beans (seed) is being emphasized (20).

The advent of acid-degumming on a plant-scale in Canadian canola extraction plants (in preference to high-temperature seed pretreatment) to produce oils below 50 ppm of phosphorus allows Canadian refiners to consider physical refining on a plant scale for test purposes. Table X compares the quality of plant acid-degummed, alkali-refined, bleached and deodorized oil with that of acid-degummed pretreated, physically refined/deodorized oil from a pilot plant process. The tabulation shows that "refining" by the two different process routes produced oil of essentially equally good quality. A problem appears to be that it was more difficult in the pretreatment for physical refining to remove green-colored compounds, since there was a more noticeable green tinge to the physically refined oil and a somewhat higher Lovibond red color. These deficiencies will have to be overcome before this type of processing can be reliably applied on a plant scale.

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TABLE X

Comparison of Alkali-Refined and Physically Refined Canola Oils

	P	Chlorophyll (ppm)	FFA (%)	Color (R)	Flavor (10→1)
Crude oil, acid-degummed	15	20	0.6	–	–
1. Alkali-refined, bleached	2	<1	0.1	4.6	–
2. Acid-clay pretreated	1	<1	0.7	7	–
1. Deodorized	–	–	0.03	0.5	8
2. Steam-refined, deodorized	–	Sl. vis. green	0.03	0.9	8