Recent Advances in Canola Oil Hydrogenations

S.S. Köseoğlu and **E.W. Lusas**
Food Protein Research and Development Center, Texas Engineering Experiment Station, Texas A&M University, College Station, TX 77843

Rapeseed oil has been the source of edible oils in many parts of the world. In the last decade, Canadian plant breeders have developed new rapeseed cultivars which yield oil low in erucic acid and meal low in glucosinolates. These cultivars were named "canola" by the Canadian rapeseed industry. Literature on the hydrogenation characteristics of canola oil is limited; however, in recent years, several aspects of canola oil hydrogenations with commercial nickel catalysts have been reported including the formation of *trans*-isomers, trisaturated glycerides and physical properties. In addition, as the methods for determination of sulfur compounds in canola oil developed, the effect of some isothiocyanates on the hydrogenation rate was further investigated to determine the relative catalyst poisoning ability of several of these sulfur compounds. However, during the last few years, most of the efforts were directed towards development of novel, selective and active catalysts for canola oil hydrogenations. These studies cover a wide range of homogeneous and heterogeneous catalysts including sulfur poisoned nickel, gold supported on silica, arene-$Cr(CO)_3$, $RuCl_2(CO)_2(PPh_3)_2$, palladium on carbon, palladium black and nickel and arene-$Cr(CO)_3$ mixtures. Effects of temperature, pressure, catalyst concentration and catalyst preparation procedure on the hydrogenation rate, selectivity, catalyst life and quality of the oil were examined and compared with that of commercial nickel catalysts. A brief discussion about continuous hydrogenations of canola oil with commercial fixed bed catalysts is also included.

TABLE 1

Comparison of Canola and Other Rapeseed Cultivars (1)

	Canola	Traditional rapeseed
Oil composition		
Erucic acid (%)	<1	45
Linolenic acid (%)	13	9
Linoleic acid (%)	20	14
Oleic acid (%)	60	15
Phospholipids (%)	3.6	3.3
Sulfur ppm	<17	25-40
Meal glucosinolates	<26.5 μmol/g	70-120 μmol/g

TABLE 2

Effect of Pretreatment and Bleaching on Various Contaminants of Canola Oil (5)

Contaminants	Acid degummed oil	Acid pretreated/ bleached oil
Phosphorous (ppm)	10-45	<5
Chlorophyll (ppm)	5-35	<0.1
Lovibond red (5 1/4″ cell)	>10	5-18
Fe (ppm)	0.5-1.5	<0.1
FFA (%)	0.4-1.0	0.5-1.1
PV[a] me/Kg	0.5-3.0	0
S (ppm)	<5	<1

[a]Milliequivalent of oxygen per 1000 grams of fat.

In the last decade, Canadian plant breeders have developed new rapeseed cultivars which yield oil low in erucic acid and meal low in glucosinolates. These cultivars were named "canola" by the Canadian rapeseed industry. The important properties of both canola and high erucic acid rapeseed cultivars are shown in Table 1 (1). Plant breeding efforts resulted in reduction of glucosinolate content that has a drastic effect on residual sulfur content of the oil. Devinat *et al.* (2) have classified sulfur compounds into volatile, thermolabile and nonvolatile groups. They suggested that volatile sulfur compounds are suspected of catalyst poisoning. Most of the sulfur compounds are believed to originate from decomposition of glucosinolates (3). They are mainly isothiocyanates, thiocyanates and sulfates which also can further decompose to give oxazolidine-2-thione, hydrogen sulfide and several other sulfur compounds as secondary decomposition products. A recent study by Wijesundra and Ackman (4) has identified nonvolatile sulfur-containing fatty acids (9,2, 8,11 and 7,10 epithio stearic acids) which contribute sulfur to the oil in the stable form of triglycerides that resist refining procedures. Canola oil with sulfur increases the required catalyst usage if the oil has not been properly degummed, refined and bleached. As can be seen in Table 2, even these processes cannot completely reduce the residual phosphorous, sulfur and coloring pigments of the oil (5). The remaining sulfur increases catalyst and hydrogen usage and changes the product selectivity by forming nickel-sulfur compounds on the surface of the catalyst that will have different selectivities and activities than the active nickel.

Reductions of erucic acid content have been reflected in increases of oleic and linoleic contents, which have been increased from 15 and 14% to 60 and 20%, respectively. The majority of longer chain fatty acids has been replaced mainly by oleic acid and, to some extent, by linoleic acid, thus raising the level of C18 fatty acids to about 95%. This change has affected the melting characteristics and polymorphic behavior of the hydrogenated canola oil, which mainly exists in the β form crystal structure having 5-25 μm crystal size and undesirable grainy texture (6).

The canola oil has fairly large amounts of oleic and linolenic acids as compared to other oils. The linolenic acid content possesses a stability problem due to the high oxidation rate of linolenic, which is 15 times greater than for oleic acid (7).

The composition of canola oil is similar to that of peanut and olive oil, with large amounts of oleic acid, which is desirable in frying oils. Another distinct advantage of canola oil is a low saturated fatty acid content (8).

The composition of canola oil is compared with other oils of commercial significance in Table 3. Due to their high phospholipid and free fatty acid contents, both soybean and canola oil require degumming and refining in

---

*To whom correspondence should be addressed.

TABLE 3

Comparison of Composition of Crude Soybean, Canola, Palm and Peanut Oils

	Soybean^a	Canola^b	Palm^a	Peanut^a
Fatty acids	0.3-0.7	0.4-1.0	4.6	0.5-1.0
Phosphatides (gum) (%)	1.5-2.5	3.6	0.05-0.1	0.3-0.4^e
Sterols/triterpene alcohol (%)	0.33	0.53	0.1-0.5	0.2
Tocopherols (%)	0.15-0.21	0.06	0.003-0.1	0.02-0.06
Carotenoids (mg/kg)	40-50	25-50	500-1600	>1
Chlorophyll/ pheophytins (ppm)	1-2	5-25		
Sulfur (ppm)		12-17		
Iodine value	123-139	112-131	44-60	84-100

[a] Ref. 8.

[b] Ref. 1.

contrast to palm and peanut oils which can be directly physically refined. Canola oil can easily be degummed either by water and/or steam treatment or a combination of both water and acid (citric, phosphoric and/or malic acid) treatment. The residual phosphorous contents of the oils are important factors in hydrogenation and are approximately 200 and 50 ppm from water degumming and acid degumming, respectively (5).

The content of tocopherol, a natural antioxidant in canola, is comparable to those of peanut and palm oil but is less than that of soybean oil. This is an important factor for oils with high linolenic acid contents as natural antioxidants can reduce the shelf life of the product and prevent its oxidation during storage and processing.

Canola oil is rich in chlorophyll and pheophytins which must be removed by bleaching in order to obtain good quality oil. The green color of chlorophyll is usually converted to russet-colored pheophytins during extraction by partial loss of magnesium. Either of these pigments can reduce the hydrogenation rate (9). Oils with chlorophyll content of up to 20 ppm can be adequately bleached, but additional steps are needed to bring the color to acceptable levels when chlorophyll exceeds 20 ppm (10).

CANOLA OIL HYDROGENATIONS

Batch hydrogenations. Information on canola oil hydrogenation and properties of the hydrogenated products was scarce in the early 1980's. During the last five years, however, literature on canola oil has mushroomed, providing data on every aspect of hydrogenation, process design, theory, development of catalysts and physical properties, chemistry and crystal structure of the hydrogenated products. These developments are discussed in the following sections.

Hydrogenation of canola oil with commercial nickel catalysts. Reports have been published by deMan and El-Shattory (11), El-Shattory *et al.* (12-15) and Bansal and deMan (16,17), who examined the hydrogenation behavior of these oils with commercial heterogeneous nickel catalyst.

El-Shattory *et al.* (12,13) examined effects of temperature and hydrogen pressure on hydrogenation of canola oil from the cultivar Zephyr. Pressure and temperature increased the rate of hydrogenation, whereas the selectivity rations were influenced more by pressure than by temperature. In a later study (14), the influence of catalyst concentration on the hydrogenation of canola oil, Tower variety, was examined. It was determined that nickel catalyst concentration of more than 0.2% did not result in any appreciable improvement in the rate of hydrogenation. Tower canola oil was hydrogenated under selective (200°C and 48 KPa H_2 pressure) and non-selective conditions (176°C and 303 kPa) using different commercial and AOCS nickel catalysts (13). *Trans*-isomer content, iodine values, fatty acid composition and physical properties such as the dropping point and solid fat content were compared.

The chemical composition and physical properties of canola oil extracted from mixed seeds of the cultivars Regent, Tower and Candle, and from the cultivar Regent alone were subject to another study by Bansal and deMan (16,17). Table 4 illustrates the effect of reaction conditions on activity, percentage of *trans*-isomer formation, SII and linoleic selectivity. Comparison of the samples taken at 40 min (Table 4) shows high activity, as well as the *trans*-isomer formation for the reactions performed at the selective conditions. SII values also indicate the formation of high *trans*-isomers, which is thermodynamically more favorable compared to *cis*-isomers. *Trans*-isomer content as a function of iodine value in selective and nonselective hydrogenated canola oil using commercial nickel catalysts is shown in Figure 1. Their study (16) also indicates that loss of *cis-cis*-methylene interrupted dienes occurred in the early stages of the hydrogenation process. Catalysts had a great influence on the physical properties of the obtained products.

The deviation between dilatometry and NMR was greater at higher values than at lower values. The solid fat content of the samples obtained at 40 min with wet reduced nickel catalyst H were nearly twice as high as those obtained from dry reduced nickel catalyst F (Fig. 2). However, hydrogenation of the same oil for 80 min under nonselective conditions using the same catalysts showed behavior which was opposite to that obtained from selective conditions (Fig. 3). On the other hand, samples obtained from the hydrogenation of Regent canola oil in the

TABLE 4

Hydrogenation of Canola Oil with Nickel Catalyst (16)

Time (min)	Reaction conditions	Activity AIV/min	IV	*Trans* (%)	SII	Linoleic selectivity
20	Selective^a	0.79	102.7	29.5	187.9	46.7
40	Selective	0.74	88.8	46.5	157.1	9.8
60	Selective	0.61	81.6	55.6	151.1	8.5
40	Non-selective^b	0.34	104.8	19.7	144.9	—^{c}
80	Non-selective	0.42	84.9	35.3	105.4	—^{c}
120	Non-selective	0.39	71.7	42.0	89.9	—^{c}

[a] 200°C, 48 kPa and 0.2% nickel catalyst.

[b] 160°C, 303 kPa and 0.2% nickel catalysts.

[c] Not available.

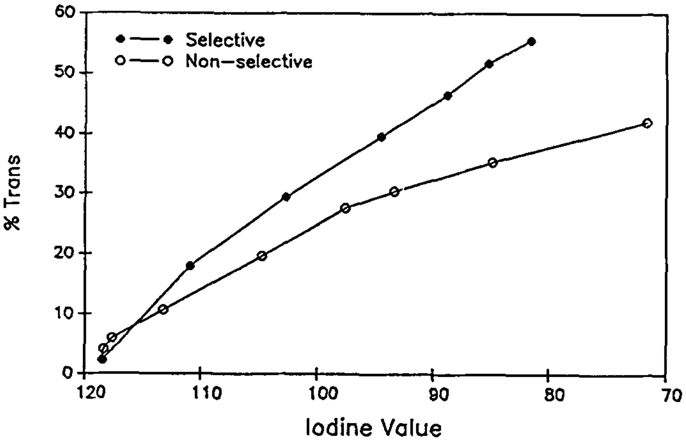

FIG. 1. *Trans*-isomer content as a function of iodine value in selective and non-selective hydrogenated canola oil using commercial nickel catalyst (16).

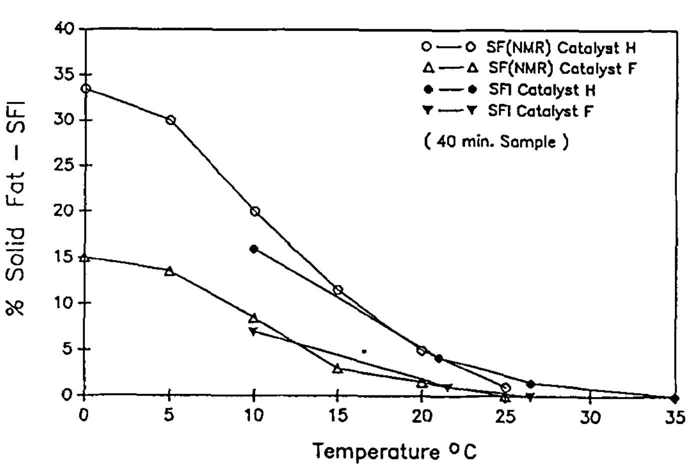

FIG. 2. Solid fat index and solid fat content (NMR) profiles for selective hydrogenation of canola oil using nickel catalysts (16).

presence of a nickel catalyst initially had lower solid fat contents, but upon continuation of the reaction this catalyst produced higher solid fat contents. Differences in activities and selectivities of the oils were related to trace amounts of sulfur compounds (17). deMan *et al.* (18) and Teasdale (19) have illustrated that different catalysts and processing conditions would cover a wide range of iodine values and solid fat index (Fig. 4 and Table 5). The detailed evaluation of a commercial catalyst, Pricat 9906, has shown that the required selectivity and activity can be obtained by careful temperature and pressure control. This also affects the contents of trisaturates, which can

TABLE 5

Analysis of Selectively and Non-selectively Hydrogenated "Tower" Canola Oil (19)

	Temperature °C				
IV	10.0	21.1	26.7	33.3	40.0
Selective conditions[a]					
118.5	—	—	—	—	—
86.2	10.8	1.4	0.1	—	—
83.6	19.4	5.1	1.5	—	—
79.5	27.0	7.8	0.1	—	—
72.8	41.3	22.5	15.9	5.3	—
68.8	50.2	31.8	25.0	11.8	1.5
64.3	58.8	43.4	38.3	23.1	7.3
61.3	62.3	49.9	45.3	30.1	11.8
Non-selective conditions[b]					
86.0	6.2	1.8	1.2	0.4	—
83.8	9.5	3.1	1.9	0.4	—
79.3	14.0	5.0	3.2	0.7	—
76.6	16.5	6.4	4.3	1.4	—
71.6	24.5	13.4	8.2	4.5	0.2
70.4	27.3	14.0	9.8	6.1	1.3
64.3	36.3	21.1	16.3	11.3	4.1
60.5	43.2	27.9	22.7	17.2	7.9

[a] T = 205°C, P = 42 kPa, nickel concentration = 0.05%.
[b] T = 135°C, P = 415 kPa, nickel concentration = 0.05%.

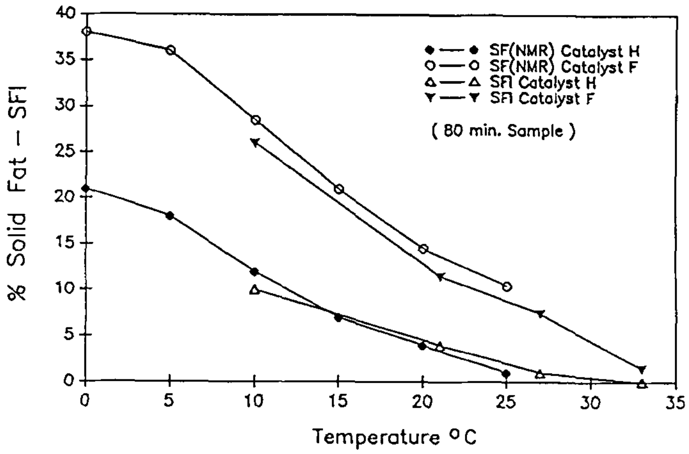

FIG. 3. Solid fat index and solid fat content (NMR) profiles for non-selective hydrogenation of canola oil using nickel catalysts (16).

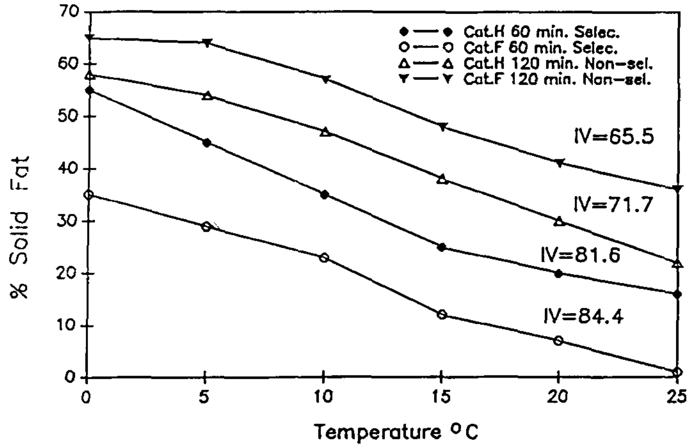

FIG. 4. Solid fat (NMR) after 60 min selective and 120 min non-selective hydrogenation of canola oil using nickel catalysts (17).

increase the stability of the product by promoting formation of β-crystals (18).

Catalyst recycling, a common practice in the edible oil industry, has resulted in marked increases in iodine value and steeper solid fat index curves under both selective and nonselective conditions. Additions of fresh catalysts helped to flatten solid fat index curves (20).

In another study (21) the effects of selected processing conditions on the overall reaction rate and *trans*-isomer formation during hydrogenation of low erucic acid rapeseed oil were studied. *Trans*-isomer formation was strongly influenced by temperature. Pressure and catalyst concentration had minimal effect on *cis/trans*-isomerization. In addition, it is suggested that the extent of *trans*-isomer formation was also controlled by the nature and amount of the unsaturation in the oil and overall reaction rate. The effect of solvents on the rate of reaction and *trans*-isomer formation was determined. Selectivity was increased when n-hexane was used instead of 2-propanol.

Effects of the presence of sulfur during hydrogenation of canola oil were studied by deMan *et al.* (22) by introducing 1, 3 and 5 ppm of allyl isothiocyanate into refined and bleached oil. Their results indicate that added sulfur has an important effect on canola oil hydrogenation and that this effect is greatly influenced by the selective and nonselective reaction conditions (Fig. 5). The poisoning effect of the sulfur compound was greater under selective conditions than under non-selective conditions. Relatively more sulfur compounds and/or its decomposition products were attached to the active surface of the catalyst at lower temperature and higher pressure. Addition of 3 ppm or more sulfur complexes into the reaction mixture resulted in considerable increases in *trans*-isomer formation, mainly because of the change in composition of the active nickel catalyst. Ni-S complexes are well known as promoters of the side reaction of isomerization (23).

Reactivity of fatty acids in the different positions of the triglyceride structure during hydrogenation of canola oil were the same (24). This is in contrast to results obtained for soybean, cottonseed, sesame, sunflower (25), linseed and cod liver oils (26).

Most of the fats can exist in α-, β- and β'-forms, and the fatty acids are packed in hexagonal, orthorombic and triclinic crystals, respectively (27). In margarine production, the β'-form is preferred because of its smaller crystal size. However, during storage β' is converted to β, which has larger crystals and gives margarine a sandy texture. The oils of new cultivars of rapeseed (especially canola oil) contain less than 1% erucic acid, and the contents of C18 acid have increased to about 95%. This affects the melting characteristics and polymeric behavior of hydrogenated canola oil. Semi-quantitative measure of β' to β transformation during storage can be followed by a densitometer (28). A selectively-hydrogenated canola oil sample with an IV of 70 was found to be more stable compared to other samples obtained under nonselective conditions. The degree of stability correlates wth the amount of *trans*-isomers formed. Therefore, it is suggested that *trans*-isomers may perturbate the crystal lattice, thus preventing rearrangement to the β modification (28). Scanning electron microscopy studies of the crystal structure (29) of hydrogenated canola oil showed that selective conditions promote the transformation of β' crystal to β form.

Refined bleached canola oil was hydrogenated in the presence of various levels of chlorophyll ranging from 1–10 ppm (9). The hydrogenation rate is greatly slowed by chlorophyll under both selective and non-selective conditions (Fig. 6). Chlorophyll not only affected the rate of reaction and selectivity, but also caused variations in the physical properties of the hydrogenated products. Dropping points were slightly different for both samples under different conditions. However, 1 ppm or more chlorophyll increased solid fat and *trans*-isomer content of the samples more under selective conditions than under nonselective conditions. Chlorophyll also accelerated the reduction of linolenic acid and production of stearic acid. Catalyst poisoning by chlorophyll seems to be more physically than chemically oriented. Chlorophyll may collect at the entrance of the pores and prevent triglyceride molecules from exiting the pore, and only triglyceride molecules on the surface of the catalyst can be completely hydrogenated.

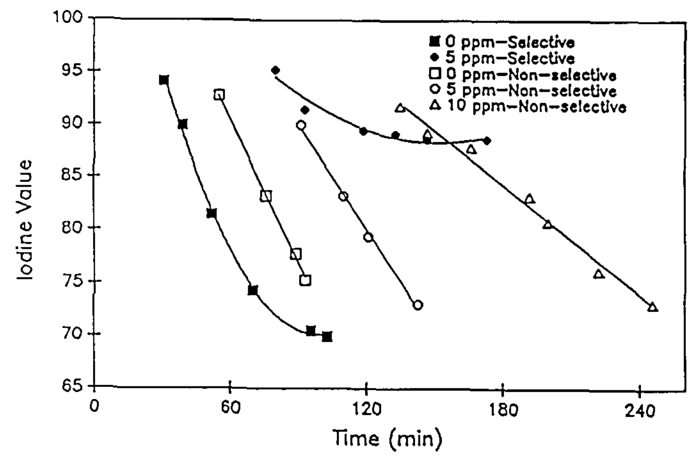

FIG. 5. Hydrogenation of canola oil with nickel catalyst in the presence of sulfur compounds, ally isothiocyanates, under selective and non-selective conditions (22).

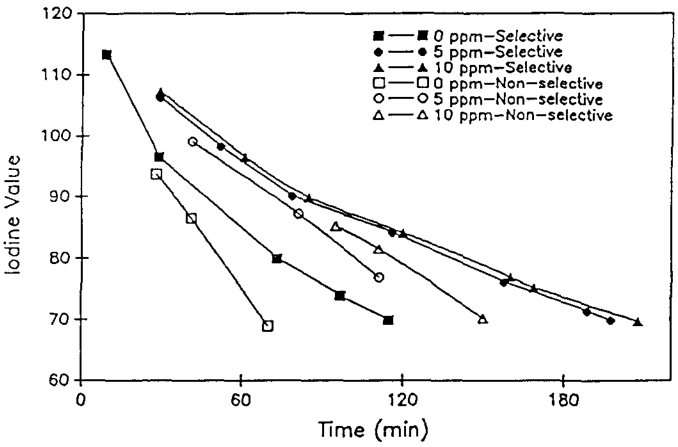

FIG. 6. Hydrogenation of canola oil with nickel catalyst in the presence of chlorophyll compounds under selective and non-selective conditions (9).

Development of novel catalyst with high activity and selectivity. The "perfect" hydrogenation catalyst would have high activity, selectivity, be highly resistant to poison, easy filtration characteristics, stability at high temperatures and long life expectancy. The "perfect" catalyst would reduce linolenic acid content to acceptable levels, while at the same time retaining nutritionally-important linoleic acid, minimize geometrical and positional isomerization, and produce any range of Solid Fat Index values that the consumer requires. The source of the edible oil and/or type of impurity would be of minor concern and low energy requirements could lower the processing costs. Of course, no "perfect" catalyst is available now. However, developments in this area have brought us one more step closer to those goals.

Hydrogenation of canola oil in the presnce of Arene-Cr(CO)$_3$ complexes. Hydrogenation of canola oil using methyl benzoate Cr-(CO)$_3$ was examined (30,31) in the temperature range of 145–175°C, pressures of 2.5–5.4 MPa, catalyst concentrations of 2 and 4 g metal/l and at an agitation rate of 565 rpm (Table 6). The triene content of canola oil was reduced to 0% to 4.3%, and total *trans*-isomer content ranges of 2% to 6.5%. The monoene content was increased from 60% in the original oil to 86.1% in hydrogenated products. No change in stearate content of the product was observed. Dienes ranged from 16.1% to 5.7%. The activity was highest at 175°C, and decreased as the temperature was reduced to 145°C. Figures 7 and 8 illustrate the changes in iodine values and *trans* content during hydrogenation at different temperatures. *Trans* contents of products obtained at 175°C was higher than those at 145 and 165°C. No direct correlation between pressure and *trans*-isomer formation was found. The results indicate that trienes and dienes are hydrogenated to produce a product of mostly monoenes. No increase in saturates was observed during hydrogenation.

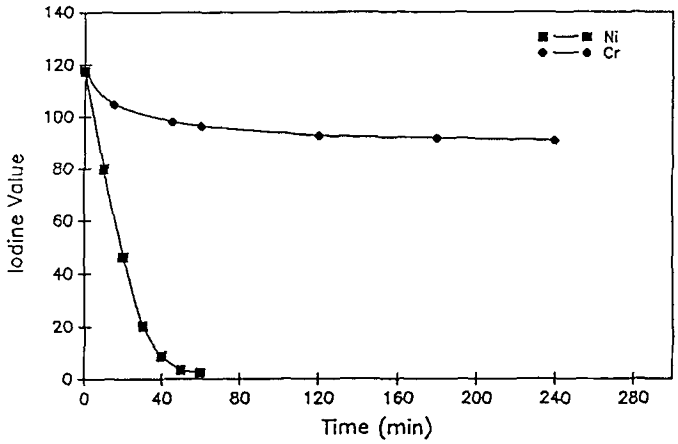

FIG. 7. Iodine value vs time for canola oil hydrogenation using nickel and MB-Cr(CO)$_3$ catalysts at equal metal concentrations (30,31).

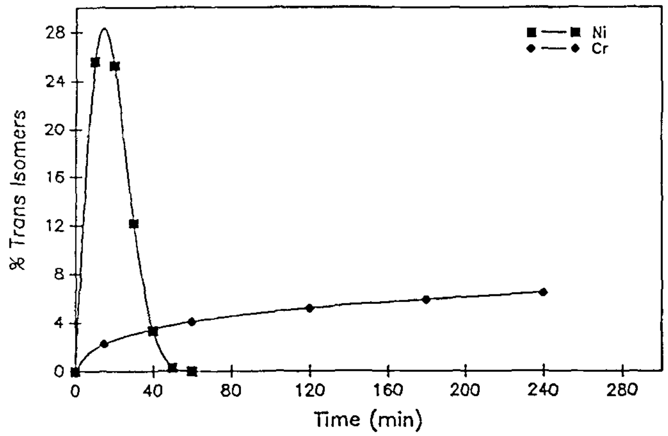

FIG. 8. *Trans* fatty acid vs time for canola oil hydrogenation using nickel and MB-Cr(CO)$_3$ catalysts (30,31).

Hydrogenation of canola oil using benzene-Cr(CO)$_3$ and toluene-Cr(CO)$_3$ was examined at the same range of conditions. The relative activities of the catalysts and *trans*-isomer formation decreased in the order of coordinated arenes: $C_6H_5COOCH_3 > C_6H_6 > C_6H_5CH_3$. It is suggested that this order results from an increase in stability of the arene-Cr bond caused by electron donating groups.

TABLE 6

Hydrogenation of Canola Oil by Arene-Cr(CO)$_3$ Complexes[a]

Conditions		MB[b]	B[c]	T[d]
Catalysts (arene)		MB[b]	B[c]	T[d]
(metal g/l) Cr		2.0	2.0	2.0
Analysis				
Palmitate	4.1	4.3	4.5	4.5
Stearate	1.4	1.6	1.5	1.6
Monoenes	60.0	75.0	72.1	71.7
Dienes	22.7	14.4	15.8	15.8
Trienes	10.5	2.0	2.5	4.7
Iodine values	117.6	100.0	101.4	104.8
Trans-isomer	0.0	2.5	2.4	1.9
Linolenate selectivity	—	1.85	1.90	1.22
Specific isomerization index	—	13.98	15.06	14.69
Activity	—	0.073	0.068	0.053

[a] Temperature, 165°C; agitation, 565 rpm; pressure, 3.4 MPa; time, 4 hr (30,31).
[b] Methyl benzoate.
[c] Benzene.
[d] Toluene.

Figure 9 is a typical graph showing levels of trienes, dienes, monoenes and stearate and iodine values during hydrogenation of canola oil using methyl benzoate, benzene and toluene-Cr(CO)$_3$ complexes. Selectivity towards *cis*-isomer formation, rapid hydrogenation of *cis,cis*-methylene interrupted dienes, no formation of saturates and production of high levels of monoenes have been well explained on the basis of the proposed cisoid mechanism (30,31), Methyl benzoate-Cr(CO)$_3$ catalyzed hydrogenation of canola oil resulted in a Specific Isomerization Index of 25.30 at an iodine value of 90.6. The Specific Isomerization Index for nickel catalyzed hydrogenation was 67.9 at an iodine value of 79.9. The activity of nickel was five times higher than that of methyl benzoate-Cr(CO)$_3$, based on the amount of metal per liter of oil under identical conditions. Köseoḡlu's results (30) show that the methyl benzoate-Cr(CO)$_3$ complex is very selective in hydrogenation of canola oil. The

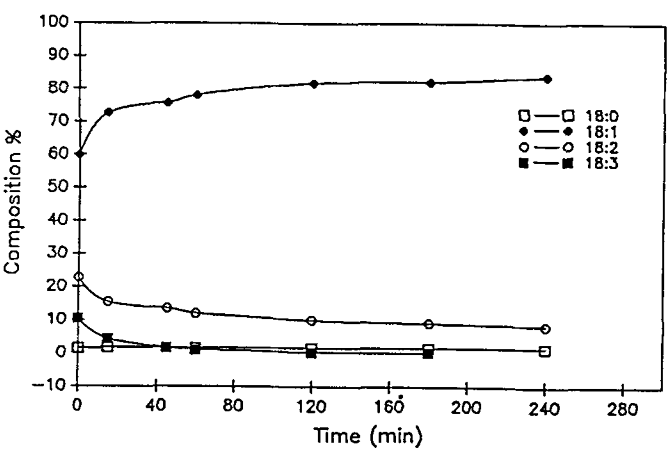

FIG. 9. The change in composition of canola oil during the methyl benzoate-Cr(CO)$_3$ catalyzed hydrogenation (175°C, 3.4 MPa, 2 g Cr/liter, 565 rpm) (30,31).

TABLE 7

Hydrogenation of Canola Oil by Methyl Benzoate-Cr(CO)$_3$ and Nickel

Conditions						
Catalysts		A	B	C	D	E
(metal g/l) Ni		2.0	2.0	2.0	2.0	2.0
(metal g/l) Cr		0.0	2.0	0.48	0.22	0.0
(molar ratio) Ni/Cr			0.89	3.73	7.19	
Analysis						
Palmitate	4.1	3.4	3.4	3.3	3.5	4.4
Stearate	1.4	75.4	2.1	3.4	5.9	1.5
Monoenes	60.0	19.3	71.1	66.6	72.6	76.7
Dienes	22.7	0.0	17.9	20.0	14.4	14.0
Trienes	10.5	0.0	3.6	4.7	1.8	2.5
Iodine values	117.6	20.4	104.1	105.4	95.1	100.4
Trans-isomer	0.0	10.7	2.6	6.5	12.8	3.1
Linolenate selectivity			1.89	2.05	1.89	1.5
Linoleate selectivity			62.56	13.11	13.56	—
Specific isomerization index		11.0	19.31	53.32	56.89	51.07
Activity		3.24	0.45	0.41	0.75	0.57

Temperature 175°C, agitation 565 rpm, pressure 3.4 MPa, time 30 min (30,31). A, B, C, D, and E are the mixed catalysts and their composition given as g/metal/liter oil.

TABLE 8

Hydrogenation of Canola Oil with RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ (33)

Catalyst type	Max. *trans*-isomers %	IV	SII
Nysel HK-4	26.2	95.4	91.6
AOCS catalyst	26.1	92.6	83.1
RuCl$_2$(CO)$_2$(PPh$_3$)$_2$	27.4	58.6	41.9

T = 140°C, P = 750 psig, Ru = 179.9 10^{-4}%, IV° = 124.

products of hydrogenation contained 3-7% *trans*-isomers and less than 0.1% linolenate at an iodine value of 90. Positional isomer analysis of the products also clearly support the proposed mechanism.

In contrast to superior selectivity towards *cis*-isomer production, high linolenate and linoleate selectivities and stability towards catalyst poisons, methyl benzoate Cr-(CO)$_3$ catalysts are less active and more expensive than nickel, and are difficult to separate from the products.

Hydrogenation of canola oil in the presence of mixed catalyst system of commercial nickel and methyl benzoate-Cr(CO)$_3$ complexes. The unique selectivity of methyl benzoate-Cr(CO)$_3$ toward production of *cis*-monoenes without formation of saturates, as well as the reasonable linolenic content combined with superior activity and low cost of the commercial nickel catalyst has stimulated researchers to find ways to combine them to produce a catalyst that has the advantages of both catalysts. The first study was done by Köseoḡlu (30,32), who examined the hydrogenation characteristics of a mixed catalyst system composed of heterogenous nickel and homogeneous methyl benzoate chromium carbonyl complex.

When equal amounts of both catalysts were used during hydrogenation, the changes in IV, *trans*-isomer content and product composition were almost identical to those produced by the methyl benzoate Cr-(CO)$_3$ complex alone (Table 7). It was suspected that the methyl benzoate chromium tricarbonyl blanked off all the active sites of the nickel catalyst. Only when the chromium tricarbonyl complex was reduced to about a tenth of the original concentration, while keeping the nickel concentration constant, did the characteristic behavior of the nickel begin to emerge. The molar ratio Ni:Cr = 7.19 was found to be the transition point below which point the catalyst behaves like pure nickel, while above this ratio, its action resembles that of methyl benzoate chromium tricarbonyl. Without Ni, the Cr catalyst at this concentration would be completely inactive. The *trans*-content of the oil was higher than that obtained with chromium alone, but it was only half of that resulting from Ni under the same conditions. At this ratio and an iodine value of 95.1 the final product contained low stearate, less than 3% linolenic acid and high levels of linoleate and oleate, but had a *trans*-isomer content of 12.8%. It was suggested that the advantages of both heterogenous nickel and homogeneous methyl benzoate chromium tricarbonyl complex could be combined by optimization of pressure and temperature at the transition point. Activity of the mixed catalyst is 50 times more than the chromium carbonyl complex alone. Linoleate and linolenate selectivities also are at desirable levels resulting in products similar in composition to olive oil (Table 7). Research on the interaction between nickel and methyl benzoate chromium carbonyl can produce valuable theoretical information on the nature and number of active catalyst sites available for the hydrogenation.

Mixed catalyst systems seemed to offer a method of producing an immobilized homogeneous catalyst that can be removed by filtration after completion of hydrogenation. One can also combine homogeneous and heterogeneous catalysts to produce custom-designed catalyst systems for the edible oil processors while retaining the advantages of both.

Hydrogenation of canola oil in the presence of RuCl$_2$-(CO)$_2$(PPh$_3$)$_2$. Dichlorodicarbonylbis (triphenylphosphine) ruthenium (II) catalyzed hydrogenation of canola oil was studied for effects of temperature, pressure, catalyst concentration on activity, selectivity and product

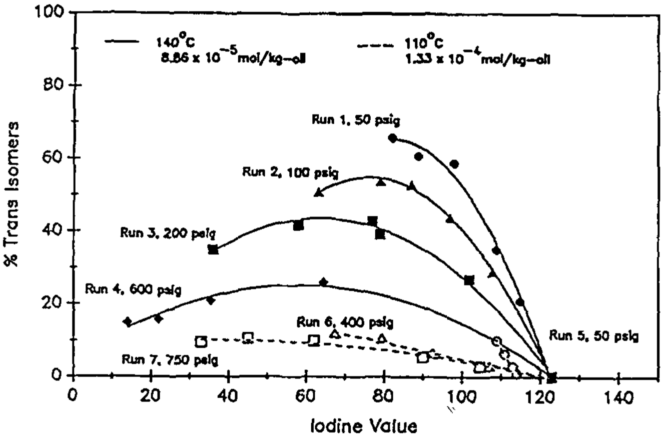

FIG. 10, Effect of pressure on *trans*-isomer formation for hydrogenation of canola oil in the presence of $RuCl_2(CO)_2(PPh_3)_2$ catalyst (33).

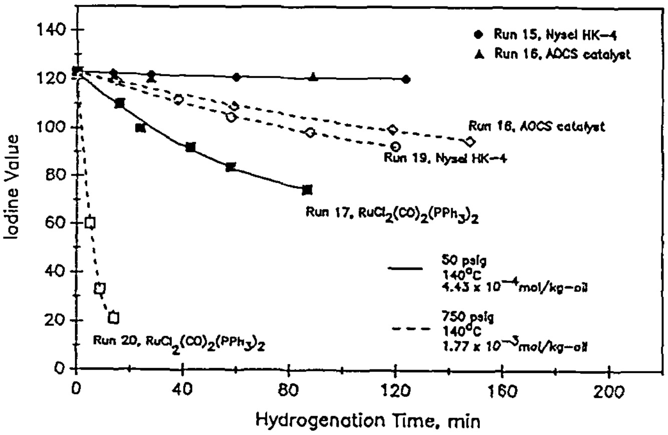

FIG. 11. Comparison of the activities of $RuCl_2(CO)_2(PPh_3)_2$ and commercial nickel catalysts (33).

distribution and then compared with that of the AOCS and a commercial catalyst (33). An increase in pressure from 50 to 600 psi increased the average activity during the first 15 min from 0.55–4.0 as expressed ΔIV/min. Low pressures had a significant effect on *trans*-isomer formation (Fig. 10) and SII, which increased from 22.1 to 157.1 with the decrease of pressure from 750 psi to 50 psi. The reaction below 100°C was very slow in contrast to temperature ranges of 180–100°C. Below 180°C the ruthenium complex had a high initial activity but leveled off after reaching an iodine value of about 80. The distribution of products obtained from gas chromatographic analyses indicated that this levelling off resulted from decomposition of the ruthenium complex. The relationship between the catalyst concentration and iodine values was not linear, and no significant change was observed in *trans*-isomer formation. Linoleanate selectivity ranged from 1.8–2.5, which is comparable to that of nickel, but linoleate selectivity was less than one tenth of the nickel catalyzed reactions.

Table 8 compares products obtained from the hydrogenation of canola oil in the presence of the AOCS catalyst, Nysel HK-4 (20) and $RuCl_2(CO)_2(PPh_3)_2$ complex. Figure 11 clearly illustrates high activity of ruthenium catalyst compared to that of the AOCS and commercial nickel catalyst. Lowest *trans*-isomer production was obtained with the ruthenium catalyst, which took only 15 min to complete the hydrogenation.

Homogeneous ruthenium catalysts showed extremely high activity and fairly good selectivity towards the minimal formation of *trans*-isomers. The major drawbacks of these catalysts are their low linoleate selectivity and filterability (33). However, they may be excellent continuous hydrogenation catalysts if immobilized on a support.

Hydrogenation of canola oil with gold catalyst. The catalytic activity and selectivity of gold supported on silica or γ-alumina, its reuse and effect of catalyst supporting methods and conditions in the hydrogenation of canola oil have been examined by Caceres *et al.* (34). The hydrogenations were performed at 150–250°C and 3.55–5.62 MPa with catalysts loadings of 1–5% Au w/w on silica and γ-alumina. Alumina supported catalysts were found to be more stable than the silica supported gold catalysts. Activities of gold catalysts differed depending on supporting method, reduction time, conditions and procedure. However, low pressure reduction stabilized the catalysts and gave reproducible results. At the same concentrations, the activity levels of gold catalysts were about 30 times lower than that of the AOCS catalyst. The alumina supported gold catalysts were reused up to 20 times. A gradual increase in the activity of the catalyst was observed with continuing reuse, up to three times of that of the fresh catalyst. This may be due to a combined effect of further reduction and decrease in the particle size of the support. Major fatty acids, *trans*-isomer content and IV of the products obtained from gold catalyzed hydrogenation of canola are given in Table 9. The product with IV of 103.4 resembles brush hydrogenated oils. It contains only 2.7% linolenic, 1.8% stearate, 8.8% *trans*-isomer and also retains most of linoleic acid. If the hydrogenation is continued further, it produces mostly monoenes in a *trans*-form and saturates. The gold catalyst produces nearly colorless oil free of traces of gold probably due to the rapid hydrogenation of the pigments during the initial part of the reaction. The catalyst's high stability, easy separation from the oil, multiple use and the initial selective reduction of linolenic makes it a good candidate for the continuous hydrogenation.

Hydrogenation of canola oil in the presence of palladium catalysts. The use of palladium black and palladium supported on carbon, Al_2O_3 and $BaSO_4$ as a replacement for commercial nickel catalyst was investigated by Hsu *et al.* (35,36).

TABLE 9

Major Fatty Acids of Hydrogenated Canola Oil Using Gold Supported on Alumina (34)

IV	% *trans*	C18:0	C18:1	C18:2	C18:3
117.0	0.0	1.7	60.1	22.7	10.5
103.4	8.8	1.9	71.8	19.3	2.7
92.4	24.2	2.4	86.0	7.1	—
81.2	51.1	7.1	88.3	—	—
70.1	57.6	17.6	77.8	—	—

T = 200°C, P = 500 psig, C = 2.3 g Au/l oil.

In their earlier study (35) they have reported formation of a black precipitate at the end of a very slow hydrogenation of canola oil with a mixture of dichlorobis triphenylphosphine palladium (II) and stannous (II) chloride dilhydrate at 500 psig and 110°C. When the "palladium black" precipitate is used as the catalyst, hydrogenation can be performed at 70°C and 750 psi pressure. The following experiments were done using commercially available palladium black. Activity of the catalysts, measured as the overall rate constant, increased with a fivefold increase in pressure that was more drastic at 70°C than at 50°C.

Pressure had an inverse effect on *trans*-isomer formation, and increasing the pressure from 250 to 750 psig resulted in the SII value dropping from 82 to 34.6. Pressure did not effect linolenate selectivity, but the linoleate selectivity increased as pressure decreased. Canola oil hydrogenations using 560 ppm palladium at 30° and 50°C produced rate constants of 0.13×10^{-2} min^{-1} and 4.03×10^{-2} min^{-1}, a 30-fold increase over the 20°C temperature increment. However, a temperature increase from 50–70°C did not increase the rate at the same magnitude as before, probably due to mass transfer limitations. Linolenate selectivities ranged from 1.2 to 4.4, depending on the temperature of the reaction. Palladium black can catalyze the reaction at a level of only 6% of commercial nickel catalyst, and produces 20% less *trans*-isomers than the nickel catalyst does. Palladium black has higher activity at low temperature, produces less *trans*-isomers, and can be used at 50–150 times lower concentration than nickel, but is 150–250 times more expensive. It is more difficult to completely remove from the mixture than nickel is, and its recovery is key for commercial utilization. In a later study, Hsu *et al.* (36) reported on the hydrogenation characteristics of supported palladium catalysts. Activity, selectivity and *trans*-isomer formation characteristics of palladium on three supports: carbon, alumina and barium sulfate at the temperature, pressure and catalyst concentration range of 50–110°C, 50–750 psig and 5–100 ppm, respectively, are shown in Table 10.

Activities of 5% Pd on alumina and 5% Pd on $BaSO_4$ were almost identical, especially at the earlier part of the reaction (Fig. 12). On the other hand, in contrast to Riesz and Weber's findings (37), $BaSO_4$ promoted more *trans*-isomer formation than the other supports (Fig. 13). The advantages of alumina and barium sulfate supported catalysts, including high activity and selectivity towards *cis*-isomer production, is shown in Table 10. The least active catalyst was palladium black.

TABLE 10

Hydrogenation of Canola Oil using Palladium (35,36)

Catalyst	IV	% *trans*	SII	S_{Ln}	S_{Lo}	k × 1000 (min^{-1})
Pd black^a	67.6	15.0	32.0	1.2	2.5	0.18
Pd on C	78.5	13.0	36.1	1.1	3.9	3.43
Pd on Al_2O_3	73.9	9.4	23.2	1.0	2.7	8.90
Pd on $BaSO_4$	76.6	14.4	38.0	1.3	4.5	8.73
Pd on Al_2O_3 Pellets	77.9	12.9	35.2	1.5	4.2	6.10

T = 70°C, P = 750 psig, C = 50 ppm.

^{a}C = 64 ppm.

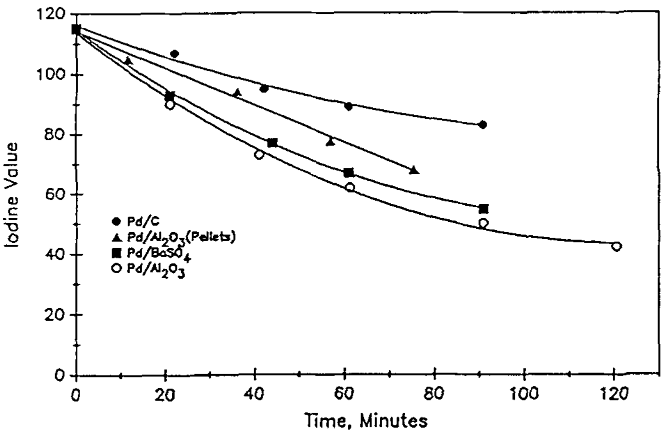

FIG. 12. Effect of catalyst support on activity during the canola oil hydrogenations at 5.1 MPa, 70°C and 50 ppm Pd (36).

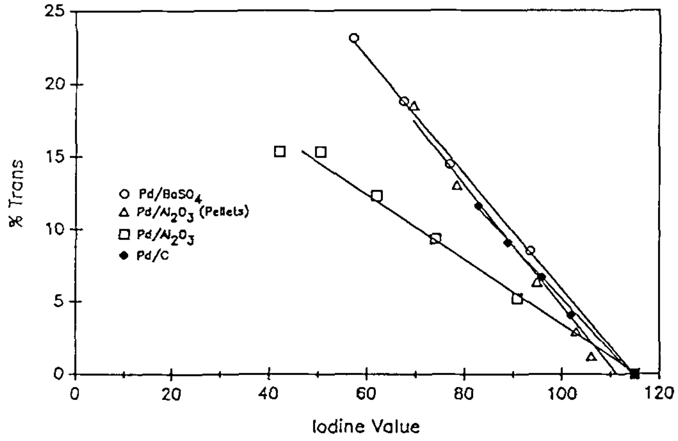

FIG. 13. Effect of catalyst support on *trans*-isomer formation during canola oil hydrogenation at 5.1 KPa, 70°C and 50 ppm Pd (36).

An increase in pressure, temperature and catalyst concentration increased the rate of reaction. The *trans*-isomer content was mostly affected by pressure and was reduced from 37 to 9% for the pressures of 50 and 750 psig, respectively. No change was observed when the catalyst concentration increased from 5 ppm to 100 ppm. Temperature had a minor effect, and the only change was from 10.5 to 17.3 for 60°C and 90°C. A comparative study of canola oil and soybean oil hydrogenations with different catalyst concentration showed that the starting oil type also affects reactivity.

The pressure showed the largest effect on linoleic selectivity and ranged from 17.8 to 2.4. A change in catalyst concentration slightly increased linoleate selectivity. Linolenate selectivities were found to be constant with catalyst concentration and were reduced by change in pressure. Higher hydrogen pressures suppressed positional isomerization (36). No difference in positional isomer formation was observed between the unsupported and supported palladium complexes.

In conclusion, palladium-supported catalysts seem to offer an alternative to commercial nickel catalyst. However, work on catalyst reuse and evaluation of the physical properties of hydrogenated products—including solid fat index, crystallization and melting point characteristics—needs to be determined.

Continuous hydrogenation of canola oil. Continuous hydrogenations of canola oil with commercial fixed bed catalysts have been reported in the literature (38). Discussions in this paper include the effect of process parameters, such as hydrogen flow rate, oil flow rate, temperature on iodine value drop, selectivity and *trans*-isomer formation. However, no information is presently available about the life expectancy of the catalyst, selectivity and activity after continuous catalyst reuse, equipment design, sensitivity towards different types of feedstock and commercial feasibility of the process.

REFERENCES

1. Ackman, R.G., in *High and Low Erucic Acid Rapeseed Oils*, edited by J.K.G. Kramer, Academic Press, New York (1983).
2. Devinat, G., S. Biasini, and M. Naudet, *Rev. Fr. Corps Gras 27*:229 (1980).
3. Rutkowski, A., S. Gwiazda, and S. Krygier, *J. Am. Oil Chem. Soc. 59*:7 (1982).
4. Wijesundera, R.C. and R.G. Ackman, *Ibid. 65*:959 (1988).
5. Mag, T.K., *Ibid. 64*:632 (1987).
6. Weinberg, B., *Can. Inst. Food Sci. Technol. J. 5*:A57 (1972).
7. Haroldson, G., *Proceedings of Symposium on Hydrogenation Oils*, Rimini September 29-30, 1980.
8. Swern, D., *Bailey's Industrial Oil and Fat Products*, Vol. 1, J. Wiley & Sons, New York (1979).
9. Abraham, V. and J.M. deMan, *J. Am. Oil Chem. Soc. 63*:1185 (1986).
10. Dahlen, J.A., *Ibid. 50*:312A (1973).
11. deMan, J.M. and Y. El-Shattorty, *Food Chem. Microbiol. Technol. 7*:83 (1981).
12. El-Shattory, Y., L. deMan, and J.M. deMan, *J. Food Technol. 18*:519 (1981).
13. El-Shattory, Y., L. deMan, and J.M. deMan, *Ibid. 18*:527 (1981).
14. El-Shattory, Y., L. deMan, and J.M. deMan, *Can. Inst. Food Sci. Technol. J. 14*:53 (1981).
15. El-Shattory, Y., L. deMan, and J.M. deMan, *Chemie. Microbiologie Technologie der Lebensmittel 7*:117 (1982).
16. Bansal, J.D. and J.M. deMan, *J. Food Sci. 47*:1338 (1982).
17. Bansal, J.D. and J.M. deMan, *Ibid. 47*:2004 (1982).
18. L. deMan, J.M. deMan, R.G. Ackman, and W.M.N. Ratnayake, *J. Am. Oil Chem. Soc. 62*:703 (1985).
19. Teasdale, B.F., in *Oilseed and Pulse Crops in Western Canada*, Western Co-operative Fertilizers Ltd., Calgary, Alberta (1975).
20. Beke, B., D. Shewfelt, and B.E. MacDonald, in *Research on Canola Seed, Oil, Meal and Meal Fractions*, Canola Council of Canada, Winnipeg, Canada, 1987.
21. Puri, P.S. and J.M. deMan, *Fette Seifen Anstrichmittel 85*:99 (1983).
22. deMan, J.M., E. Pogorzelska, and L. deMan, *J. Am. Oil Chem. Soc. 60*:558 (1983).
23. Beckmann, H.J., "Practical Hydrogenation" presented at the AOCS World Conference on Oilseed and Edible Oil Processing, the Hague, the Netherlands, October 3, 1982, Harshaw Technical Bulletin, The Harshaw Chemical Company, Beachwood, OH.
24. Fan, T., L. deMan, and J.M. deMan, *J. Am. Oil Chem. Soc. 63*:899 (1986).
25. Kaimal, T.N.B., and G. Lakshminarayana, *Ibid. 57*:578 (1979).
26. Drozdowski, B., *J. Am. Oil Chem. Soc. 54*:600 (1977).
27. Opfer, W.B., *Chemistry and Industry*, September, p. 681 (1978).
28. Naguip-Mostafa, A. and J.M. deMan, *J. Am. Oil Chem. Soc. 62*:756 (1985).
29. Naguip-Mostafa, A., A.K. Smith, and J.M. deMan, *Ibid. 62*:760 (1985).
30. Köseoğlu, S.S., Ph.D. Thesis, University of Toronto, Toronto, Canada (1984).
31. Diosady, L.L., W.F. Graydon, S.S. Koseoglu, and L.J. Rubin, *Can. Inst. Food Sci. Technol. 17*:218 (1984).
32. Rubin, L.J., S.S. Koseoglu, L.L. Diosady, and W.F. Graydon, *J. Am. Oil Chem. Soc. 63*:1551 (1986).
33. Bello, C., L.L. Diosady, W.F. Graydon, and L.J. Rubin, *Ibid. 62*:1588 (1985).
34. Caceres, L., L.L. Diosady, W.F. Graydon, and L.J. Rubin, *Ibid. 62*:906 (1985).
35. Hsu, N., L.L. Diosady, W.F. Graydon, and L.J. Rubin, *Ibid. 63*:1036 (1986).
36. Hsu, N., L.L. Diosady, and L.J. Rubin, *Ibid. 66*:232 (1989).
37. Riesz, C.H. and H.S. Weber, *Ibid. 41*:400 (1964).
38. Lee-Poy, F.V., P.V. Sleggs, R.I. Matanic, and S.S. Koseoglu, *Ibid. 64*:632 (1987).

[Received May 16, 1989; accepted August 23, 1989]
[J5722]