Industrial Hydrogenation of Rapeseed Oil with Nickel Catalyst

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ABSTRACT

Refined and deodorized rapeseed oil was hydrogenated using Girdler nickel catalyst at a starting temperature of 140 C and at 25 and 30 psig hydrogen gas pressures. The studies revealed that the hydrogenation was more effective, as determined by rate of decrease in iodine value (Wi js) and increase in the melting point, at 25 psig than at 30 psig. The rate of effectiveness was, however, not significant. The rate of hydrogenation was compared to cottonseed oil subjected to hydrogenation under identical conditions. Cottonseed oil showed a better, though insignificant, rate of increase in melting point per unit increase in time.

INTRODUCTION

Hydrogenation is one of the most valuable processes of the edible oil industry because using it, liquid oils can be made into plastic fats for shortening and hardened oils for margarine manufacture. Rapeseed oil, unlike other vegetable oils, is hydrogenated with difficulty because of the presence of sulfur compounds (originating from break-down of glucosinolates by rapeseed enzyme–myrosinase) that poison the catalyst. Even carefully refined oil is likely to contain traces of such sulfur-containing compounds. Daun and Hougen (1) have identified 7 types of sulfur compounds in industrially extracted rapeseed oil. Others have also reported the presence of organically bound sulfur in rapeseed oil (2-5).

Since the catalytic action of nickel is restricted to a limited number of "active spots," only traces of such compounds greatly affect the rate of hydrogenation. Babuchowski and Rutkowski (6) have reported that the inactivation of the catalyst occurred in proportion to the amount of the sulfur present in the oil. An amount of 5 ppm sulfur reduced the catalytic activity by ca. 50%. They also found that an addition of 0.65 mg percent phosphorus as rapeseed lecithin resulted in total retardation of hydrogenation process. Tremazi et al. (7) reported that rapeseed oil hydrogenated at ca. one-half the rate observed for cottonseed oil. Reynolds and Youngs (8) have described a technique for rapeseed that gives an oil requiring ca. 0.03-0.08% nickel for hydrogenation. Cecchi and Hirschauer (9) hydrogenated rapeseed oil (sulfur content: 11.4 ppm) with 70 ppm nickel at 120 C and 15 bars hydrogen pressure. These conditions produced oil high in monoenoic fatty acids with elimination of 75% of the linoleic acid content and fluidity at 25 C.

Nickel catalyst is widely used for hydrogenation of vegetable oils. Because of its susceptibility of undergoing poisoning by sulfur compounds, the possibility of using other catalysts also have been studied. Govorov and Budnikov (10) prepared a catalyst for the hydrogenation of sulfur-containing organic compounds from a mixture of aluminium, cobalt, molybdenum or their oxides, hydroxides, salts of ores. A ground coking coal also was added to the mixture to improve the properties of the catalyst. Kaganowicz (11) studied the effect of different industrial catalysts on the rate of hydrogenation and transisomerization. Presence of fresh nickel and Ni-Cu catalysts accelerated the rate of hydrogenation. Paulose et al. (12) have reported a comparison of the performance of copper-chromium catalyst under different conditions of hydrogenation. Schmidt (13) observed a better triene selectivity by Cu-Cr and nickel catalysts in continuous hydrogenation of soybean oil. Kurucz-Lusztig et al. (14) have reported that during industrial hydrogenation of traditional and low-erucic-acid rapeseed oils, the bond saturation and isomerization occurred in a similar way. They also observed that the use of fresh catalyst favored saturation reactions whereas used catalyst favored geometric isomerization. Jakubowski and Pezinski (15) have reported improvement in stability by hydrogenating normal and low-erucic-acid rapeseed oil with Cu-Cr catalysts.

MATERIALS AND METHODS

The well refined and deodorized batches of rapeseed oil with no sulfur content were hydrogenated as follows. A batch of rapeseed oil (ca. 2 tons) containing nickel catalyst (Girdler-G53: 24% Ni) was charged into a dead-end type reaction vessel made of mild steel–prevacuated and filled with hydrogen gas (99.9% pure, produced by electrolytic process), and heated to a starting temperature of 140 C with constant stirring by means of submerged propeller-type stirrers running at 100 rpm. The doses (of catalyst) used were 0.11 and 0.098% Ni. The samples were drawn at a 20-min time interval and were analyzed for iodine (Wijs) value and melting point to follow the course of hydrogenation.

A batch of cottonseed oil was hydrogenated at a starting temperature of 140 C at 25 psig gas pressure using 0.098% Ni as catalyst and compared with rapeseed oil hydrogenated under identical conditions.

RESULTS AND DISCUSSION

Hydrogenation, chemically speaking, means reducing the degree of unsaturation of oil by adding hydrogen at the double bond in the fatty acid radical, thereby raising the melting point and lowering the iodine value. Elimination of double bond improves the shelf life of oil or foods containing such oil by increasing its resistance to atmospheric oxidation.

In these studies, the commercial samples of rapeseed oil, refined and deodorized, and containing no sulfur compounds (16) were hydrogenated for ca. 3 hr under industrial conditions as already mentioned. The changes in iodine value are given in Table I. The difference in change of iodine value as influenced by hydrogen gas pressure and catalyst concentration is nonsignificant. Similar nonsignificant differences were found with respect to melting point in all these variables. Although the differences observed in all these cases were nonsignificant, the rate of hydrogenation was relatively slower at 30 psig as compared to 25 psig. This is contrary to what is normally expected during hydrogenation.

The rate of hydrogenation of rapeseed oil was compared to cottonseed oil hydrogenated under identical conditions. The rate of increase in melting point was noted in both the cases and is reported in Table II. In both the cases, i.e., rapeseed oil and cottonseed oil, the correlation coefficient (r) was 0.993 and 0.984, the regression coefficient (b) = 0.09 and 0.101 and the interaction point of ordinate (a) = 16.5 and 19.512, respectively. This indicates that a unit increase in time (min) caused an increase of 0.09 C and 0.101 C in melting point of rapeseed oil and cottonseed oil, respectively, thereby revealing that rapeseed oil can be effectively hydrogenated under these conditions. Although the difference is nonsignificant, the rate of hydrogenation of rapeseed oil is slower compared to cottonseed oil. Unlike other vegetable oils, rapeseed oil is required to be steam-deodorized prior to hydrogenation in order to eliminate steam volatile sulfur-containing compounds for enhanced rate of bond saturation.

TABLE I

Changes in Iodine Value of Rapeseed Oil during Hydrogenation under Varying Conditions

	Hydrogen pressure			
	25 psig		30 psig	
Time (min)	Catalyst concentration (% Ni)		Catalyst concentration (% Ni)	
	0.11%	0.098%	0.11%	0.098%
20	102	102	102	102
40	101	101	99	98
60	96	97	96	97
80	92	93	95	95
100	88	89	94	92
120	87	88	92	90
140	87	87	89	88
160	84	84	88	88
180	82	82	86	85
200	80	80	84	85

TABLE II

Changes in Melting Point of Rapeseed Oil and Cottonseed Oil during Hydrogenation

	Melting point (C)	
Time (min) X	Rapeseed oil Y_{rso}	Cottonseed oil Y_{cso}
60	–	24.5
80	–	28.5
100	25.0	30.5
120	27.5	32.0
140	28.5	33.5
160	30.5	36.0
180	33.0	–
200	34.0	–

Regression equations:

$Y_{rso} = 16.5 + 0.09X$

$Y_{cso} = 19.512 + 0.101X$

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