An Evaluation of Commercial Nickel Catalysts During Hydrogenation of Soybean Oil

Yan-Hwa Chu* and **Li-Hui Lin**
Food Industry Research and Development Institute, Hsinchu, 30099, Taiwan, Republic of China

The activities of several commercial nickel catalysts were determined by measuring their activation energies. Among these catalysts, G95E, Resan 22, Nysosel 222 and 325, all with low activation energy, were more active than DM3 and G95H, which had higher activation energy. However, the less active catalysts increased the linoleate selectivity of soybean oil during hydrogenation. The yields of both *trans* isomers and winterized oil were higher for the more selectively hydrogenated oil catalyzed by the less active catalysts. In the sensory evaluation, the fractionated solid fat that contained more *trans* isomers was lower in flavor scores than the fractionated liquid oil after hydrogenation and winterization of soybean oil.

KEY WORDS: Activation energy, fractionation, hydrogenation, linoleate selectivity, nickel catalyst, winterization.

Hydrogenation of vegetable oils is an important practice in the modification of fats and oils. The hydrogenation course and the composition and properties of the final product depend on various operating factors, including catalyst type and concentration, agitation, hydrogen pressure and temperature. Among these factors, the most important one is the type of catalyst (1). Currently, the most widely used commercial catalyst for edible oil hydrogenation is active nickel supported on an inert substance (2,3). The other less commonly used metal catalysts are Cu-Cr (4,5), and precious metals such as Pt and Pd (6,7).

During oil hydrogenation, parameters of the reaction affected by the operating factors include reaction rate, linoleate selectivity, *trans* isomer formation and melting point. Reaction rate relative to catalyst activity greatly affects the cost of the whole reaction. Selectivity determines the course of the reaction. A selective hydrogenation results in a soft product at a low iodine value or a product with minimum melting point at a given iodine value (8). The *trans* isomer content in a hydrogenated product has a significant effect on its physical properties. In this study, catalyst performance in such areas as reaction rate, linoleate selectivity and isomerization activity was determined for several commercial nickel catalysts. The aim of this study was to provide the industry with information about the properties of several commercial nickel catalysts used in oil hydrogenation. From the given information the industry is able to choose the correct type of catalyst for oil hydrogenation based on the desired properties of the final product.

MATERIALS AND METHODS

Materials. RBD (refined, bleached and deodorized) soybean oil was purchased from a local market. The commercial nickel-based catalysts used in this experiment were Nysel DM3 (24.8% Ni), Resan 22 (22% Ni), Nysosel 222 (22% Ni) and 325 (22% Ni) (Harshaw Chemical Co., Cleveland, OH); G95H (22% Ni) and G95E (22% Ni) (Nissan Girdler Catalyst Co., Tokyo, Japan); and UP 9900 (22% Ni) (Unichema Chemie GmbH, Emmerich, Germany).

Hydrogenation. The hydrogenation process was carried out in a two-liter parr pressure reactor. After introduction of 1 Kg of RBD soybean oil, the reactor was sealed and evacuated during the heat-up cycle. The catalyst slurry was charged into the reactor as the process conditions became stable. When the oil/catalyst slurry reached the desired temperature, hydrogen was introduced into the system. This moment of hydrogen introduction was considered as the initial point of the reaction. The hydrogenation progress was monitored by sampling 10–20 mL of hydrogenated oil at different intervals and measuring the reduction of refractive index. After hydrogenation, the oil was bleached with 0.1–0.2% of activated clay, filtered and deodorized according to the commercial process (240°C, 1 hr, at 1 torr).

Winterization. Partially hydrogenated/deodorized soybean oils, which were previously heated to 60°C, were winterized at 15°C for 90 min and then filtered (9). In the sensory evaluation, a 20-member taste panel, trained to identify oil flavors, evaluated oils by using a flavor intensity scale ranging from 0 (strong) to 10 (bland) (10,11). Significance of flavor scores was statistically computed by analysis of variance.

Analysis. The following analyses were done according to standard AOCS methods: Iodine value Cd 1-25; refractive index Cd 7-25; total isolated *trans* isomers Cd 14-61 (12). The composition of methyl esters of fatty acids was measured on a gas liquid chromatograph equipped with a 30 m × 0.25 mm (ID) SP2330 fused silica capillary column and with flame ionization detector. Methyl esters were prepared by refluxing the oil with 0.2% sodium methoxide and excess methanol for 1 hr. Linoleate selectivity was determined by the program proposed by Allen (13).

RESULTS AND DISCUSSION

Activation energy of nickel-based catalysts. The overall rate of hydrogenation for a batch run in a dead-end reactor followed the first order reaction (14,15). The rate constant (k) at each temperature (shown in Table 1) for each catalyst used in the hydrogenation of soybean oil to 80-IV was derived from $\ln[(IV)initial/(IV)t]=kt$, where t is time elapsed during reaction. According to the Arrhenius equation, $\mathrm{Log}\ k = (E_a/2.303R)\times(1/T) + \mathrm{Log}\ A$, where k is the reaction constant; A, constant; R, gas constant; E_a, activation energy and T (°K), absolute temperature. The rate constant in the logarithmic form at each temperature is well correlated with each inverse absolute temperature for each catalyst as shown in Table 2. From the linear equation between Log k and 1/°K, the values of Log A and $E_a/2.303R$ were obtained. Furthermore, the activation energy of each catalyst can be calculated from the value

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*To whom correspondence should be addressed at Food Industry Research & Development Institute, P.O. Box 246, Hsinchu, 30099, Taiwan, R.O.C.

TABLE 1

Rate Constants at Different Temperatures for a Variety of Catalysts[a]

T	Rate constant (k)						
(°C)	DM3	Resan 22	Nysosel 222	Nysosel 325	Unichema UP 9900	G95E	G95H
150	1.2519	2.2630	2.1030	2.2583	2.0930	2.1576	1.1464
165	1.6859	2.6276	2.5948	2.8014	2.6441	2.4205	1.8094
180	2.4288	3.1603	3.0659	3.4425	3.1716	2.6857	2.7383
195	2.8603	3.4249	4.1051	4.2728	3.6779	3.4661	3.5307

[a] Hydrogenation conditions: 180°C, 0.03% catalyst based on Ni content, 2.5 Kg/cm^2 H_2 pressure.

of $E_a/2.303R$. For instance, for the catalyst DM3, the equation y = 3.9466 − 1629.9294x (Table 2) is derived from each rate constant and each temperature at 150, 165, 180 and 195°C, as shown in Table 1. The values of 3.9466 and 1629.9294 represent Log A and $E_a/2.303R$, respectively. As R is 8.3134 KJ/°K mole, the value of 31.21 KJ/mole is thus obtained for E_a. Among these catalysts, Resan 22, G95E, UP 9900, Nysosel 222 and 325, which had low activation energies, were more active than DM3 and G95H. Therefore, in accordance with the relationship between the rate constant and the activation energy, the activity of each catalyst during reaction can be evaluated.

Comparison of linoleate selectivity. Soybean oil hydrogenation was performed at 180°C, 2.5 Kg/cm^2 hydrogen pressure and different commercial nickel catalysts at 0.03% nickel-based content. As shown in Table 3, the more active catalysts, *i.e.*, Resan 22, G95E, UP 9900, Nysosel 222 and 325, had lower linoleate selectivity than the less active catalysts, *i.e.*, DM3 and G95H. The fatty acid compositions showed that soybean oil hydrogenated with DM3 and G95H catalysts to 80-IV had lower stearic but higher oleic acid content. High selectivity has been defined as stepwise conversion of linoleic acid to monounsaturated acids prior to substantial stearic acid formation (16–18), which implies that the hydrogenated product contains a low proportion of stearate. In order to obtain high yield of liquid oil during partial hydrogenation of soybean oil, the choice of more selective catalysts, such as DM3 or G95H, would be considered primarily for the preferable conversion of linolenic acid to oleic acid through linoleic acid.

TABLE 2

Activation Energies of Different Catalysts

Catalyst	Equation[a]	r	E_a(KJ/mole)
DM 3	y = 3.9466 − 1629.9294x	−0.9910	31.210
R 22	y = 2.2962 − 820.3777x	−0.9923	15.708
N222	y = 2.6487 − 981.2682x	−0.9989	18.789
N325	y = 2.5938 − 941.8877x	−0.9898	18.035
UP 9900	y = 2.8716 − 1076.1937x	−0.9973	20.607
G95E	y = 1.9859 − 701.0400x	−0.9968	13.423
G95H	y = 5.2213 − 2177.9435x	-0.9955	41.703

[a] y = a − bx Where y = logk; a = logA (A is constant); b = $E_a/2.303R$ (E_a = activation energy, R = gas constant = 8.3134KJ/°K mole); x = 1/°K, °K = °C + 273.

Effect of catalysts on yields, trans *isomers and melting points of winterized and hydrogenated soybean oil.* G95H and DM3, when used in the hydrogenation of soybean oil, produced higher yields, *trans* isomers and melting points of hydrogenated winterized soybean oil (HWSBO) at 90-, 100- and 110-IV when compared to the other catalysts (Table 4). Higher amounts of *trans* isomers were found in the hydrogenation of soybean oil by more selective catalysts, such as G95H and DM3, than by the less selective catalysts. In addition, a higher yield of HWSBO was obtained by more selective hydrogenation. To obtain more selective oil hydrogenation, the conditions that were employed for the process include: i) choice of more selective catalysts; ii) higher temperature; and iii) lower hydrogen pressures (19). In this study, we found that UP 9900,

TABLE 3

Fatty Acid Compositions (%) and Linoleate Selectivity Ratio (SL) of 80-IV Hydrogenated Soybean Oils Prepared by Using Different Catalysts[a]

Catalyst	C16:0	C18:0	C18:1	C18:2	C18:3	SL
DM3	11.0 ± 0.3	4.7 ± 0.5	72.2 ± 0.2	9.5 ± 0.1	0	24 ± 2
R22	11.0 ± 0.3	6.3 ± 0.7	68.7 ± 1.0	10.7 ± 0.6	0	14 ± 1
N222	10.9 ± 0.2	5.9 ± 0.5	69.9 ± 0.9	10.5 ± 0.4	0	16 ± 1
N325	10.7 ± 0.4	5.3 ± 0.3	71.0 ± 0.7	10.2 ± 0.9	0	17 ± 1
UP 9900	10.8 ± 0.4	4.7 ± 0.5	71.7 ± 0.3	9.9 ± 0.2	0	17 ± 2
G95E	10.6 ± 0.8	6.4 ± 0.5	66.2 ± 0.7	10.9 ± 1.6	0	11 ± 3
G95H	10.7 ± 0.2	4.6 ± 0.3	73.4 ± 0.2	9.4 ± 0.6	0	29 ± 3

[a] Fatty acid composition of unhydrogenated soybean oil is: C16:0 = 10.2, C18:0 = 4.0, C18:1 = 23.0, C18:2 = 54.6, C18:3 = 6.8. Hydrogenation conditions: 180°C, 0.03% catalyst based on Ni content, 2.5 Kg/cm^2 H_2 pressure. Values are given as means ± S.D. (n=4).

TABLE 4

Yields, *trans* Isomer Contents and Melting Points of Winterized Oils in Relation to Iodine Values of Various Hydrogenated Soybean Oils Prepared with Different Catalysts[a]

Catalysts	IV = 90	IV = 100	IV = 110
DM3			
Yield (%)	55.4 ± 0.7	73.3 ± 0.7	86.3 ± 0.9
trans (%)	28.9 ± 0.4	23.3 ± 0.8	19.1 ± 0.7
M.P.	16.3 ± 0.6	15.0 ± 0.3	13.2 ± 0.1
R22			
Yield (%)	52.2 ± 0.7	68.2 ± 0.8	83.8 ± 0.5
trans (%)	27.4 ± 0.4	18.8 ± 0.4	12.9 ± 0.2
M.P.	15.3 ± 0.4	14.3 ± 0.3	12.1 ± 0.4
N222			
Yield (%)	53.1 ± 0.9	70.2 ± 0.8	85.4 ± 0.9
trans (%)	27.6 ± 0.3	19.3 ± 0.7	13.7 ± 0.5
M.P.	15.5 ± 0.6	14.5 ± 0.5	12.0 ± 0.6
N325			
Yield (%)	53.2 ± 0.9	71.2 ± 0.9	86.1 ± 0.7
trans (%)	28.0 ± 0.4	20.4 ± 1.1	14.4 ± 1.0
M.P.	16.3 ± 1.2	15.0 ± 0.3	12.2 ± 0.6
UP 9900			
Yield (%)	53.4 ± 0.9	72.5 ± 0.9	86.1 ± 1.0
trans (%)	28.5 ± 0.6	21.8 ± 0.5	16.2 ± 0.3
M.P.	16.2 ± 0.3	14.8 ± 0.5	12.6 ± 0.1
G95E			
Yield (%)	52.3 ± 0.8	68.1 ± 0.8	83.7 ± 1.4
trans (%)	25.3 ± 1.0	19.4 ± 0.4	13.0 ± 0.1
M.P.	15.2 ± 0.3	14.2 ± 0.2	12.0 ± 0.1
G95H			
Yield (%)	57.3 ± 1.1	75.2 ± 1.0	87.3 ± 0.9
trans (%)	29.3 ± 0.3	26.1 ± 0.6	20.9 ± 0.5
M.P.	16.6 ± 0.3	15.3 ± 0.2	13.4 ± 1.1

[a] Hydrogenation conditions: 180°C, 0.03% catalyst based on Ni content, 2.5 Kg/cm^2 H_2 pressure. Values are given as means ± S.D. (n=3).

TABLE 5

***trans* Isomer Content in Solid Fat and Liquid Oil at 90-IV from Hydrogenations at 180°C, 2.5Kg/cm^2 H_2 Pressure, with Different Catalysts at 0.03% Nickel-Based Content**

Kind of catalysts	Solid fat *trans* (%)	Liquid oil *trans* (%)
DM3	33.7	28.9
R22	29.5	27.4
N222	31.0	27.6
N325	31.0	28.0
UP 9900	31.1	28.5
G95E	29.0	25.3
G95H	33.9	29.3

TABLE 6

Sensory Evaluation of 90-IV Hydrogenated Soybean Oil (HSBO)[a]**, Fractionated Solid Fat and Liquid Oil for 90-IV HSBO After Winterization**

Oil	Flavor scores[b]
HSBO	4.60
Solid fat	4.25
Liquid oil	5.85

[a] Prepared with catalyzed R22.

[b] LSD = 0.30; size of taste panel was 20.

N325 and 222, aside from DM3 and G95H, were also adequately used in the catalysis of soybean oil hydrogenation, if salad-cooking oil at iodine value of 110–115 is required. However, the selectivity of the catalyst becomes important for good yields of HWSBO at lower iodine values during further hydrogenation. For instance, under similar conditions of hydrogenation, G95H and DM3 yielded 6–10% more HWSBO than R22 when hydrogenation was stopped at 90-IV.

trans Isomers and sensory evaluation of solid fat and liquid oil after winterization. Hydrogenated and deodorized soybean oil (90-IV) prepared from different catalysts was fractionated into solid fat and liquid oil. The difference in the *trans* isomer content between the solid fat and liquid oil fractions is shown in Table 5. The *trans* isomer contents in the fractionated solid fats were higher than in the fractionated liquid oil (Table 5). For sensory evaluation, a 20-member taste panel was trained to evaluate hydrogenated oil flavor in fractionated solid fat and liquid oil. The solid fat and liquid oil were prepared by mixing equal portions of each solid fat or liquid oil from the R22 catalyst. It was found that the scores were lower in HSBO as compared with fractionated liquid oil (HWSBO), and the scores were even lower in fractionated solid fat than in HSBO (Table 6). In a previous study, 6-*trans*-nonenal, 2-*trans-trans* octadienal, and higher alcohols and lactones had been reported to play an important role in contributing to the hydrogenation flavor (16). As a consequence, the higher *trans* isomer content in the fractionated solid fat could have been responsible for the more objectionable oil flavor.

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