A Comparison of Commercial Nickel Catalysts Effects on Hydrogenation of Soybean Oil

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Abstract: Due to the importance of catalysts in hydrogenation of edible oils and health hazards of trans fatty acids, the aim of this study was the comparison of practical characteristics of five typical commercial nickel catalysts used in Iranian oil industry, in order to provide helpful information about of these catalysts to edible oil and fat manufacturers. Refined and bleached soybean oil was hydrogenated in a 2 liter laboratory scale converter at 150°C and 3 bars hydrogen pressure. Five commercial nickel catalysts namely Pricat 9910, Pricat 9920, G-53 plus, Harcat and DM-3 Plus were used in this study. The hydrogenation process was terminated at IV 80. All hydrogenated samples were analyzed for FFa composition, selectivity ratio and slip melting point. The activity of catalysts was determined by Arhnius equation. Data were analyzed by ANOVA and Tukey test using SPSS software (ver. 13). Catalysts showed significant differences (p<0.01) considering selectivity ratio, effect on fatty acid composition and trans isomer formation, slip melting points and the ratio of polyunsaturated to sum of saturated and trans fatty acids [P/(S+T)]. Pricat 9910 was the most active and Pricat 9920 had the lowest activity among the catalysts. G-53 and Pricat 9910 had low selectivity and Pricat 9920 showed the highest selectivity. G-53 produced low amount of TFA and DM-3 Plus and Harcat produced high TFA. The ratio of P/(S+T) was higher with Pricat 9910 and G-53, but lower with Pricat 9920. Slip melting points of samples hydrogenated by G-53 and Pricat 9910 were higher than those hydrogenated by Pricat 9920. It was concluded that when medium selectivity, high activity and low TFA content is required, Pricat 9910 at nonselective conditions will be the best choice followed by G-53. If the latter catalyst is used, it will be a greater challenge to find optimum reaction conditions considering trans formation and selectivity. Pricat 9920 although highly selective, produced less trans isomers as compared to other selective catalysts. Selection of a catalyst should be considered along with application of other methods, such as blending, to minimize the formation of TFA content.

Key words: Hydrogenation · soybean oil · nickel catalyst · trans fatty acid · selectivity

INTRODUCTION

Hydrogenation is a means of converting liquid oils to semisolid plastic fats suitable for margarine, shortening, frying fats and other specialty products. Nickel catalyst is the most common catalyst currently used in the hydrogenation of fats and oils. During hydrogenation, some of double bounds that are normally in the cis-configuration change into the trans-configuration [1, 2]. The consumption of foods high in TFA has been shown to raise LDL-C and decrease HDL-C level which increases the risk of developing coronary heart disease (CHD) [3-10]. Due to increased concern about TFA on health, legislation in the United States approved in June 2003, requires the nutrition facts panel on all food labels to indicate TFA content by January 1, 2006 [3].

A few researches have been conducted to comparison of commercial nickel catalysts properties. In 1991, Chu and Lin comprised the seven commercial nickel catalysts during soybean oil hydrogenation and determined the activity energies and selectivity ratios of them. Among these catalysts, G95E, Resan 22, Nysosel 222 and 325, were more active than DM3 and G95H. However, the less active catalysts increased the linoleate selectivity. The yields of both trans isomers and winterized oil were higher for the more selectively hydrogenated oil catalyzed by the less active catalysts [4]. In 2005, Musavi and coworkers monitored trans

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isomer formation, reaction rates, selectivity ratios during the hydrogenation of soybean oil using two different commercial catalysts (Nysosel 222 and SP-10) [5].

In Iran, more than 70% of vegetable oils use hydrogenated with about 38% TFA content. Due to the importance of nickel catalysts effect on TFA formation during hydrogenation of edible oils and necessity to minimize TFA content [14-25], the aim of this study was to compare the practical characteristics of five typical commercial nickel catalysts used in Iranian oil industry. In this study the effect of nickel catalysts on fatty acid composition and slip melting point of hydrogenated soybean oil was determined. Different catalysts were also compared for their activities and selectivity ratios.

MATERIALS AND METHODS

Materials: Refined and bleached soybean oil was purchased from Safola Vegetable Oil factory. Fatty acid composition and physico-chemical properties of initial soybean oil are showed in Table 1 and 2, respectively. The commercial nickel catalyst obtained from different processors: Pricat 9910 and Pricat 9920 (Synetix, 22% and 23% nickel content respectively) from Safola Vegetable Oil factory, G-53 (United Catalysts, with 23% Ni) from Shokoofeh Vegetable Oil factory, Harcat (Harshaw, with 20% Ni) from Kesht va Sanat Shomal Vegetable Oil Factory and DM-3 Plus (Engelhard Co., with 23% Ni) from Pars Vegetable Oil Factory. Methyl ester standards of fatty acids were GC grade and purchased from Sigma-Aldrich (Fluka).

Hydrogenation method: Hydrogenation processes were done in 2 liter converter at 150°C and 3 bar hydrogen pressure (for determining of activation energy, hydrogenation was carried out also at 120 and 180°C). First, the exact amount of catalyst (0.06% based on Ni content) was weighed by analytical scale and heated with some oil. Slurry of oil/catalyst was poured into the converter, then sealed and deairated by vacuum pump. The converter content was heated to near 150°C. The moment of introduction of hydrogen gas into the converter was considered as the beginning of reaction.

Temperature of reaction was monitored by thermal sensor Pt-100 and controlled by cooling coils. Progress of hydrogenation was controlled by regular sampling and checking the refractive index of samples. Iodine value was calculated from corrected refractive index at 25°C by Zeleny & Neustadt formula: $n_D^{25} = 1.45765 + 0.0001164 IV$ [26]. Then iodine value plotted against the time (min) to predict when IV of hydrogenated oil will reach 80 (Fig. 1). After the process stopped, hydrogenated oil was bleached by 0.1-0.2% active clay, then filtrated.

Analyses: The following analyses on initial and final hydrogenated soybean oil wre done by AOCS official methods: Iodine value Cd 1-25 (Wijs method), moisture Ca 2e-48 (karl Fischer method), slip melting point Cc 1-25, phosphorous content Ca 12-55, p-anisidine value Cd 18-90, peroxide value Cd 8-53, refractive index Cc 7-25 [27]. Methyl esters of fatty acids were prepared according to ISO 5508 method [28] and the fatty acid composition of samples were analyzed according to ISO 5509 method [29] by Gas Chromatograph apparatus (HP-Agilent GC model 6890+) equipped with FID and capillary column (BPX-70: 120 m, 0.25 mm ID, 0.25 μm df). Injector and detector temperature were 250°C, oven constant temperature was 198°C and constant carrier (nitrogen) flow was 0.5 ml min⁻¹.
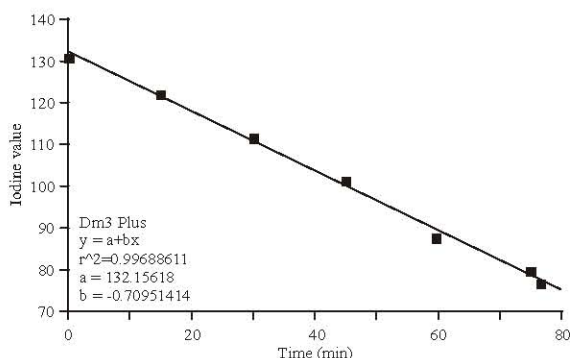

Fig. 1: Diagram of iodine value-time (min) for hydrogenation process by catalyst DM-3 Plus (temperature 150 °C, H₂ Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)

Table 1: Fatty acid composition of the initial refined and bleached soybean oil and other

Fatty acid	C16:0 (%)	C18:0 (%)	C18:1 (%) trans	C18:1 (%) cis	C18:2 (%) trans	C18:2 (%) Cis	C18:3 (%)	>C20 (%)	P/(S+T)
value	10.69	3.75	0.0	25.01	0.0	52.66	7.14	0.75	4.141

Table 2: Physico-chemical properties of the initial refined and bleached soybean

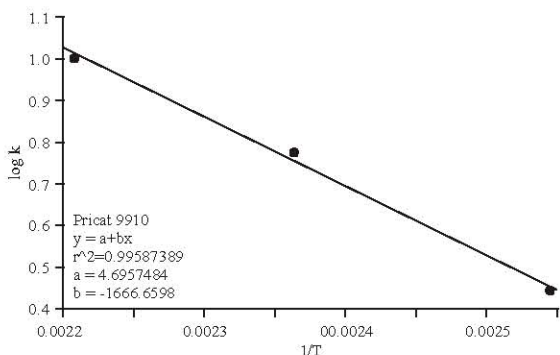| Factor	FFA g/100	Peroxide value (meq kg⁻¹)	Iodine value	H₂O %	Refractive index (25°C)	Anisidin value	Phosphorous (ppm)
value	0.02	0.05	131	0.01	1.4730	2	1

Fig. 2: The line relating log k and 1/T obtained by catalyst Pricat 9910 at 120, 150 and 180°C (constant condition: H_2 Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)

Determination of catalysts activities: Since overall rate of batch hydrogenation in the dead-end reactor follows first order reaction, thus the constant rate of reaction can be calculated as $k = \ln (IV_0/IV_t)$, in which IV_0 is the iodine value of initial soybean oil and IV_t is the iodine value of hydrogenated soybean oil at time t. Activation energies were determined by Arhnis equation: $\log k = (Ea/2.303R) \times (1/T) + \log A$, where k is constant reaction rate, A is constant, R is gas constant = 8.3134KJ/°Kmole, Ea is activation energy and T is the absolute temperature in Kelvin degree [12]. If log k values were plotted against 1/T, a straight line is obtained as y = a-bx similar to Arhnis equation so that b = (Ea/2.303R). Figure 2 showed an example that is obtained by catalyst Pricat 9910 at 120, 150 and 180°C.

Selectivity Ratio calculation: Selectivity ratio was calculated by following formula [25]:

$$SR = \frac{100}{S - S_0} \frac{1}{\exp[b(L)/L_0]c \exp[-d(L)/L_0]}$$

Where S and S_0 are the amount of stearic acid percent, L and L_0 are the amount of linoleic acid percent in soybean oil and hydrogenated soybean oil, respectively. For soybean oil hydrogenation, the constants are: a = 1.260, b = 2.065, c = 0.771 and d = 2.299.

RESULTS

Rate constants (k) of hydrogenation for soybean oil at 3 different temperatures (120, 150 and 180°C) using 4 commercial nickel catalysts and

Table 3: The values of log k for hydrogenation processes at 120, 150 and 180 by tested catalysts *

	Log k		
Catalyst	120 (°C)	150 (°C)	180 (°C)
DM-3 Plus	0.375461	0.781793	1.023509
Harcat	0.265855	0.776529	1.014366
Pricat 9910	0.445187	0.776529	1.005411
Pricat 9920	0.239241	0.727124	1.042395

*(constant condition: H_2 Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)

Table 4: The equation of line, regression coefficient and activation energy calculated for tested catalyst*

Catalyst	Equation y = a-bx	R^2	Ea(KJmole^{-1})
DM-3 Plus	y = 5.3077-1931.1645x	0.9891	37.558
Harcat	y = 5.9902-2236.3314x	0.9725	42.814
Pricat 9910	y = 4.6957-1666.6598x	0.9959	31.908
Pricat 9920	y = 6.3415-2391.1739x	0.9932	45.779

*Equation is: y = a-bx, where y = log k, a = log A that A is constant value, b = Ea/2.303R, R = Gas universal constant that is 8.313 KJ/mole and x = 1/°K that °K = °C+273
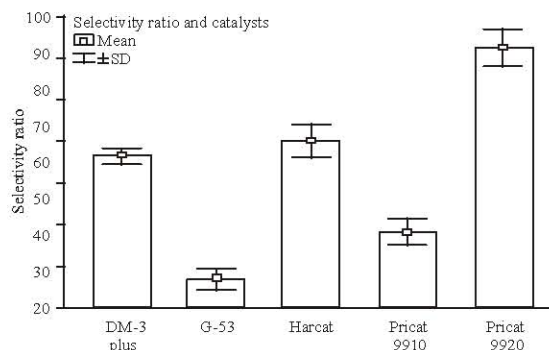

Fig. 3: Selectivity ratios calculated for commercial nickel catalysts (temperature 150 °C, H_2 Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)

activation energy of these catalysts are showed in Table 3 and 4, respectively. Since G-53 did not showed any reaction at 120°C (during 120 minute of hydrogenation, no reduction of iodin value were observed). Pricat 9910 and Pricat 9920 had the lowest and highest activation energy, respectively.

Catalysts were significantly different (p<0.01) considering their selectivity ratios (Table 5 and Fig. 3). By Tukey test, in terms of selectivity the catalysts were divided into 3 groups: low selective catalysts (G-53 and Pricat 9910), medium selective catalysts (DM-3 Plus and Harcat) and finally high selective catalyst (Pricat 9920). As

Table 5: Fatty acid composition, SR, P/(S+T) and slip melting point of hydrogenated soybean oil (p<0.01)*

Catalyst	C18:0 (%)	C18:1t (%)	C18:1c (%)	C18:2t (%)	C18:2c (%)	C18:3 (%)	TFA (%)	SR	P/(S+T)	Slip M.P.
DM-3 Plus	5.5±0.2	27.3±0.5	46.1±0.4	3.5±0.1	6.2±0.1	0	31.2±0.5	61±2	0.131±0.001	29.3±0.6
G-53	7.7±0.3	25.1±0.5	42.7±0.3	4.4±0.1	8.5±0.5	0.27±0.06	29.4±0.2	28±3	0.185±0.014	34.5±0.7
Harcat	5.4±0.1	29.2±0.2	43.6±0.9	3.3±0.2	6.8±0.4	0	32.4±0.3	66±4	0.137±0.013	31.3±0.6
Pricat 9910	6.4±0.2	28.2±0.6	43.6±0.1	2.4±0.1	7.8±0.2	0.24±0.04	30.5±0.3	41±4	0.168±0.003	33.7±0.6
Pricat 9920	4.8±0.2	27.1±0.2	48.0±0.4	3.6±0.2	5.2±0.2	0	30.7±0.2	91±5	0.112±0.005	31.5±0.7

*(temperature 150 °C, H$_2$ Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)
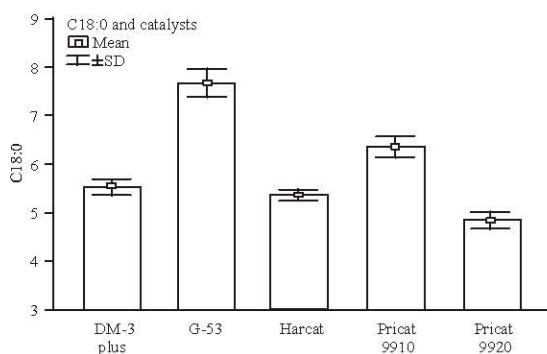

Fig. 4: Effect of commercial nickel catalysts on C18:0 formation during hydrogenation of soybean oil (temperature 150 °C, H$_2$ Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)
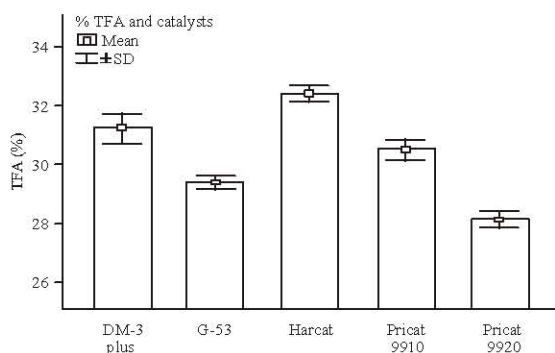

Fig. 5: Effect of commercial nickel catalysts on TFA formation during hydrogenation of soybean oil (temperature 150 °C, H$_2$ Pressure 3 bars, agitation 200 rpm, catalyst concentration 0.06% based on nickel content)

shown in Table 5, the lower the selectivity, the more stearic and linoleic acid content.

The average TFA formation by different catalysts are showed in Table 5. The hydrogenated samples were significantly different from each other (p<0.01). By Tukey test, considering TFA formation the catalysts are categorized into 3 groups: low TFA content was formed by catalyst G-53, medium TFA content was formed by catalysts Pricat 9910 and Pricat 9920 and high amounts of TFA were formed by catalysts DM-3 Plus and Harcat. The amounts of P/(S+T) ratios for tested catalysts were significantly different at p<0.01 as showed in Table 5. Pricat 9920 had the lowest P/(S+T) ratio and Pricat 9910 and G-53 had the highest P/(S+T) ratio. As shown in Table 5, G-53 and Pricat 9910 produced hydrogenated soybean oil with the highest slip melting point whereas Harcat and DM-3 Plus produced the lowest melting point product.

DISCUSSION

During the past years, the activity of edible oil hydrogenation catalysts increased significantly by improving nickel surface area and decreasing the particle size. In general, higher activity is incorporated into nickel catalysts by maximizing nickel metal surface area, optimizing structure and particle size and balancing acceptable filterability and selectivity [30, 31].

As shown in Table 4 and 5, the more active catalysts such as Pricat 9910, the lower selectivity ratio compared to the less active catalysts such as Pricat 9920 (Fig. 3). This result is accorded with Chu and Lin result [12]. The composition of fatty acids showed that there is low stearic but high linoleic acid content in hydrogenated soybean oil by more selective catalyst (Fig. 4). Any factors resulted in insufficient hydrogen on the catalyst surface (such as low pressure of hydrogen gas, mild stirring, high temperature and concentration of catalyst) increases both selectivity and isomerisation [1, 2]. So that, to produce the lowest solid fat and the highest liquid oil, selective catalysts (such as Pricat 9920) must be chosen and while manufacturer intend to lower TFA content in hydrogenated product the low selective catalyst (such as G-53 and Pricat 9910) must be used in non-selective condition. However, relative high amounts of stearic acid are formed in this process. This result accorded with other researches [19, 21, 23, 25].

By comparison of Table 4 and 5, the five commercial nickel catalysts can be grouped in 3 categories: medium selective and active catalyst (i.e. G-53 and Pricat 9910), high selective and relative active catalysts (i.e. Harcat and DM-3 Plus) and very high selective catalyst (i.e. Pricat 9920).

Active nickel catalysts are usually used for hydrogenation when saturation of double bounds is more desirable than selectivity of the process. However, many of products such as confectionary coating products, filling creams and spreads need fats that are produced under highly selective conditions in order to be semisolid at room temperature but melt easily at near body temperature.

According to the Table 5, the more selective catalyst, the lower melting point of hydrogenated products and the lower selective catalyst, the higher melting point of products due to high amount of saturated fatty acids formation.

CONCLUSION

When medium selectivity, high activity and low TFA content is required, Pricat 9910 at nonselective conditions will be the best choice followed by G-53. When G-53 is used for hydrogenation, its very difficult to obtain optimum condition of reaction variables, selectivity and TFA content. However, by using DM-3 Plus and Harcat catalysts, the reaction was selectively developed with high TFA content. Pricat 9920 although highly selective, produced less trans isomers as compared to other selective catalysts. Choice of a catalyst should be considered along with application of other methods, such as blending, to minimize the formation of TFA.

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