

# Monitoring of Hydrogenation with Various Catalyst Ratios

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**ABSTRACT:** Soybean oil was hydrogenated using two different nickel-based commercial catalysts (Nysosel 222 and SP-10) at various ratios in 4-L reactors under constant conditions (165°C, 2 bar hydrogen pressure, and 500 rpm stirring rate). *Trans* isomer formation, reaction rates, selectivity (*S*) ratios, and melting behaviors of the samples were monitored during the reactions. When Nysosel 222 was used at 0.02, 0.03, and 0.04%, iodine values (IV) were reduced from 130.1 to 70.6, 50.9, and 44.7 and total *trans* isomers increased from 0 to 34.2, 43.3, and 40.5%, respectively, after 100 min of hydrogenation. However, SP-10 reduced IV from 130.1 to 77.2, 75.7, and 71.3 after 100 min when used at 0.1, 0.15, and 0.2%, respectively, whereas total *trans* isomers were 58.6, 70.4, and 70.7%. Reaction rates increased with catalyst ratio and time but were higher for Nysosel 222 than for SP-10 although 5–10 times less Nysosel 222 was used than SP-10. Linoleate selectivity ( $S_{32}$ ) was almost constant for Nysosel 222, whereas it was higher but fell with time for SP-10. Increasing the catalyst ratio decreased the time needed to reach the highest oleate selectivity ( $S_{21}$ ) ratios, and the IV values where the highest  $S_{21}$  were attained were different for the catalysts. Increases in m.p. of SP-10 samples were slower after IV values of 80 were attained, where  $S_{21}$  ratios reached to higher values. Solid fat contents (SFC) of these samples fell markedly above 21.1°C, and steeper SFC curves were obtained.

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**KEY WORDS:** Catalyst ratio, hydrogenation, melting behaviors, reaction rate, selectivity, soybean oil, *trans* isomers.

Hydrogenation reduces the relative unsaturation of oils and promotes geometric and positional isomerization (1). Formation of *trans* isomers affects the physical and chemical properties of the final products, as they have higher m.p. and greater stability than *cis* isomers (2). Since the late 1980s, hydrogenation has become less accepted in the formulation of food products because of the *trans* FA that form during the reaction. The main concern has been with *trans*-18:1 isomers. It has been shown that *trans* FA intake raises LDL cholesterol and lipoprotein (a) levels in blood, causing higher levels of coronary heart diseases and greater risks for atherosclerosis risks (3,4). Despite this, hydrogenation is still one of the most applied techniques in the fats and oils industry for producing a wide range of hardened fats with different melting properties.

Hydrogenation, a catalytic reaction, involves the saturation of  $\pi$ -bonds of FA with hydrogen on a catalyst surface. Owing to the mechanism of the reaction, the rate of isomerization re-

actions is variable (5). The type of catalyst and its concentration in oil, the type of oil and its properties, the reaction temperature, hydrogen pressure, and stirring rate affect the concentration of hydrogen on the catalyst surface and thus change the course of the reaction. The choice of reactor type also can affect the reaction as a result of agitator design characteristics (6). Among these parameters, the type of catalyst and the concentrations applied are the most important ones in choosing hydrogenation conditions. Nickel catalysts supported on silica or alumina are the ones most used in industry because of their low cost vs. activity and easy filterability (7,8). The course of hydrogenation can be monitored by determining parameters such as reaction rate, isomer formation rate, selectivity, solid fat content (SFC), and m.p.

## MATERIALS AND METHODS

Soybean oil having a FA composition of 10.20% palmitic, 3.77% stearic, 30.70% oleic, 46.44% linoleic, and 8.46% linolenic acid was used in hydrogenation reactions. These were carried out in a 4-L Snap-Tite reactor (Autoclave Engineers, Union City, PA) under  $2 \pm 0.03$  bar  $H_2$  pressure, at  $500 \pm 3$  rpm stirring rate and  $165 \pm 0.5^\circ C$ . Two different commercial nickel-based catalysts (Nysosel 222 and SP-10) were kindly donated by Engelhard (Iselin, NJ).

A mix of 37 FAME ( $C_4$ – $C_{24}$ ) as well as methyl esters of *cis*-11-vaccenic acid and a *cis-trans* isomer mix of linoleic acid was purchased from Supelco (Bellefonte, PA). Methyl esters of *trans*-11-vaccenic acid, *cis*-12-oleic acid, CLA, and *cis-trans* isomers of linolenic acid methyl esters were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were reagent grade.

Soybean oil was introduced into the reactor and sparged with nitrogen under agitation. A partial vacuum was applied to the reactor after heating to 175°C under nitrogen. The oil/catalyst slurry was charged into the reactor, and the mixture was cooled to 165°C by cooling water. Hydrogen was introduced into the medium when the conditions were stable. Samples were withdrawn at 10-min intervals during the 100-min reaction time, filtered to remove the catalyst, and subjected to analysis.

The methyl esters of the FA and the isomers were prepared according to the IUPAC (9) and analyzed using a Trace 2000 gas chromatograph (Milan, Italy) equipped with an SP 2560 column (100 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu m$  film thickness) (Supelco). Injector, column, and detector temperatures were 230, 175, and 240°C, respectively. The split ratio was 1:100. The carrier gas was helium at a flow of 0.7 mL/min.

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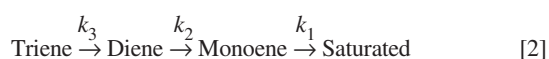
Iodine values (IV) were calculated from the FA composition using AOCS Official Method Cd 1c-85 (10).

The SFC of the sample was measured by low-resolution pulsed NMR using Maran SFC (Resonance Instrument Ltd., Witney, United Kingdom) according to AOCS Official Method Cd 16b-93 (11). The slip melting point (SMP) was determined in triplicate according to the AOCS Official Method Cc 3-25 (12).

Reaction rate constants were calculated using a first-order reaction equation:

$$k = \ln (IV_0/IV_t)/t \quad [1]$$

and selectivity ratios  $S$  were calculated according to the step-by-step saturation scheme:



and saturation of each component was accepted to be a first-order reaction, where

$$S_{32} = k_3/k_2 \quad \text{and} \quad S_{21} = k_2/k_1 \quad [3]$$

## RESULTS AND DISCUSSION

Soybean oil was hydrogenated using various ratios of two different nickel-based commercial catalysts (Nysosel 222 and SP-10) under constant conditions for 100 min. The ratios for Nysosel 222 were 0.02, 0.03, and 0.04%, and for SP-10 were 0.1, 0.15, and 0.2%. During the reactions, *trans* isomer formation, reaction rates, selectivity ratios, and melting behaviors of the samples were monitored.

As seen in Table 1, the IV was reduced from 130.1 to 70.6, 50.9, and 44.7 after 100 min of the reaction when Nysosel 222 was used at the percentages of 0.02, 0.03, and 0.04%, respectively. However, SP-10 reduced IV from 130.1 to 77.2, 75.7, and 71.3 after 100 min even though it was used at ratios 5–10 times higher than Nysosel 222. Increases in catalyst ratio of Nysosel 222 were effective with reaction time in reducing IV, particularly when it was increased from 0.02 to 0.03%. However, the effect of raising the ratio to 0.04% was only slightly different from the effect at 0.03% with respect to reducing IV. The effect of the catalyst ratios of SP-10 on IV reduction were not as remarkable as those of Nysosel 222.

Similar results were obtained for reaction rate constants of both catalysts because they were calculated according to the reduction of IV with time by using a first-order kinetic equation.

**TABLE 1**  
Iodine Values (IV) and Slip Melting Points (SMP) of Hydrogenated Samples and Reaction Rates Constants<sup>a</sup>

Catalyst ratio	Nysosel 222								
	0.02%			0.03%			0.04%		
Sample	IV	SMP	$k^b$ (×1000)	IV	SMP	$k^b$ (×1000)	IV	SMP	$k^b$ (×1000)
10	129.4	<15	5.2	127.2	<15	22.7	124.8	<15	41.4
20	125.3	<15	37.8	118.9	<15	90.0	111.5	<15	154.6
30	120.3	<15	78.0	112.1	<15	148.9	97.7	19.8	286.0
40	114.4	<15	128.3	102.5	19.5	238.4	85.6	24.3	418.5
50	107.8	17.9	187.9	92.5	22.7	340.6	78.2	28.1	509.5
60	99.6	21.6	267.4	81.2	28.8	471.6	72.4	32.5	586.1
70	90.6	24.3	361.6	71.4	33.4	596.5	64.2	38.4	706.6
80	83.4	27.6	445.0	64.4	40.4	703.5	58.2	42.9	803.9
90	75.6	32.1	542.4	57.4	44.3	818.6	51.2	45.6	932.4
100	70.6	37.6	610.7	50.9	48.3	939.1	44.7	49.8	1068.9
Catalyst ratio	SP-10								
	0.1%			0.15%			0.2%		
Sample	IV	SMP	$k$ (×1000)	IV	SMP	$k$ (×1000)	IV	SMP	$k$ (×1000)
10	126.0	<15	31.7	124.4	<15	44.5	123.1	<15	55.1
20	119.7	<15	83.3	117.7	<15	99.8	115.2	<15	121.4
30	113.1	<15	140.0	109.3	<15	174.1	106.3	15.2	201.6
40	106.8	<15	197.0	104.3	<15	221.1	96.4	22.2	299.6
50	102.7	17.7	236.7	97.0	21.2	293.1	87.5	23.1	396.2
60	95.4	21.0	309.9	89.4	23.2	375.6	80.3	29.5	482.3
70	90.5	23.6	363.0	82.2	28.9	459.5	77.6	29.8	516.6
80	84.8	28.3	428.0	80.4	29.3	481.1	75.9	33.0	539.3
90	80.6	28.6	479.2	77.2	29.5	522.0	73.5	33.6	571.3
100	77.2	28.8	522.0	75.7	30.8	540.8	71.3	34.0	601.0

<sup>a</sup>Nysosel 222 and SP-10 supplied by Engelhard (Iselin, NJ).

<sup>b</sup>A first-order reaction is assumed.

**TABLE 2**  
**Selectivity Ratios<sup>a</sup> with the Various Catalyst Concentrations During Hydrogenation**

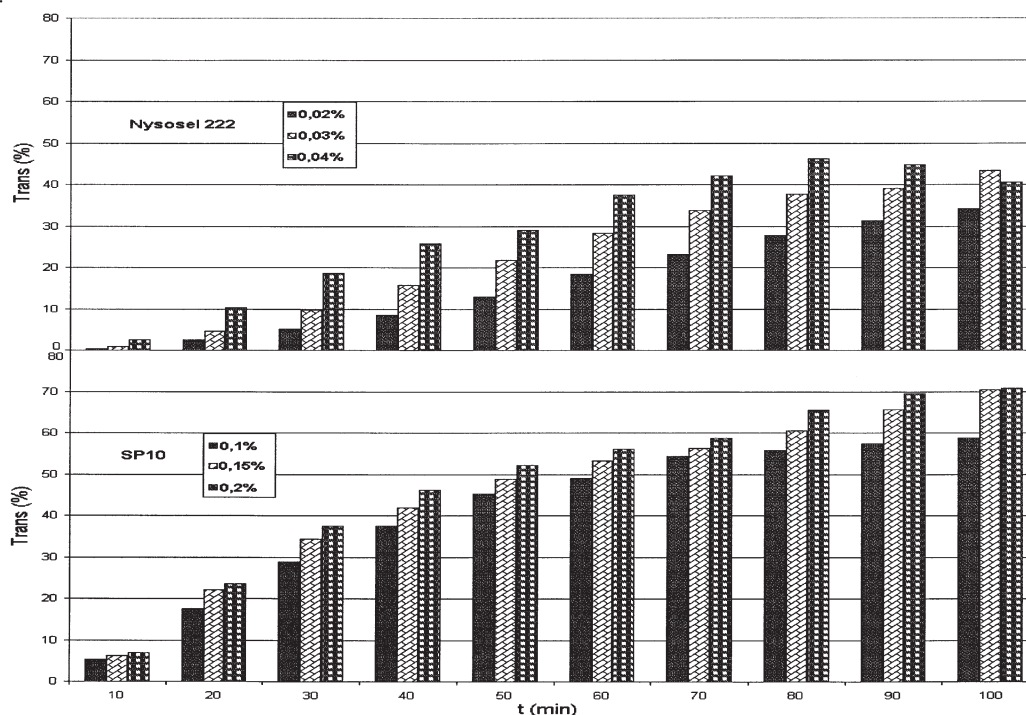
Sample #	Nysosel 222						SP-10					
	0.02%		0.03%		0.04%		0.1%		0.15%		0.2%	
	$S_{32}$	$S_{21}$	$S_{32}$	$S_{21}$	$S_{32}$	$S_{21}$	$S_{32}$	$S_{21}$	$S_{32}$	$S_{21}$	$S_{32}$	$S_{21}$
1	0.43	10.48	1.93	3.1	1.84	3.83	5.2	0.8	4.86	0.97	4.1	1.25
2	1.46	4.01	6	3.63	1.63	4.31	4.05	1.47	3.64	1.74	3.29	2.05
3	1.71	3.38	1.69	4.12	1.77	6.55	3.59	2.03	3.29	2.57	3.17	3.02
4	1.57	4.47	1.67	5.58	1.48	14.54	2.88	2.78	3.07	3.17	2.64	5.15
5	1.45	5.56	1.48	9.03	0.78	45.96	2.93	3.68	5.09	4.82	1.91	8.99
6	1.43	7.4	1.1	24.22	1.42	108.31	2.25	5.54	2.08	7.80	0.91	27.70
7	1.37	13.33	2.83	502.96	2.07	10.52	2.19	7.31	1.36	16.48	1.43	20.81
8	1.12	26.15	2	10.21	2.64	4.0	1.86	11.41	1.19	23.19	2.15	21.42
9	0.42	38.7	2.85	3.59	—	1.9	1.04	22.87	—	18.99	—	22.39
10	1.33	7.07	—	1.80	—	0.94	—	19.20	—	19.71	—	37.31

<sup>a</sup> $S_{32}$ , linoleate selectivity;  $S_{21}$ , oleate selectivity. Nysosel 222 and SP-10 supplied by Engelhard (Iselin, NJ).

Reaction rates increased with catalyst ratio and time and were higher for Nysosel 222 than for SP-10. Because SP-10, a sulfided nickel catalyst, inhibits hydrogen access to the metal surface, it reduces the dissociation of hydrogen and lowers the reaction rate. When its concentration was increased from 0.1 to 0.15% (1.5 times), reaction rates increased between 1.04 and 1.4 times; and from 0.15 to 0.2% (1.33 times), they increased between 1.09 and 1.36 times. However, when Nysosel 222 was increased with same ratios, reaction rates increased between 1.51 and 4.4, and 1.14 and 1.92 times, respectively. These results indicate that increasing the Nysosel 222 concentration from 0.02 to 0.03% is more effective on reaction rates as well.

Chu and Lin (13) measured reaction rate constants for Nysosel 222 during soybean oil hydrogenation at four different temperatures (150–195°C) and 2.5 kg/cm<sup>2</sup> H<sub>2</sub> pressure. The  $k$  values for this catalyst varied from 2.1 to 4.1 depending on reaction temperature. Their findings are considerably higher than our findings, which might be attributable to different agitator design, different agitator rate, and/or slightly higher hydrogen pressure.

Selectivities of the reactions were also calculated using first-order kinetic equations and are presented in Table 2.  $S_{32}$  selectivity was almost constant for Nysosel 222 whereas it was higher, but decreasing with time, for SP-10 owing to saturation.



**FIG. 1.** *Trans* isomer formation with various catalyst ratios during hydrogenation.

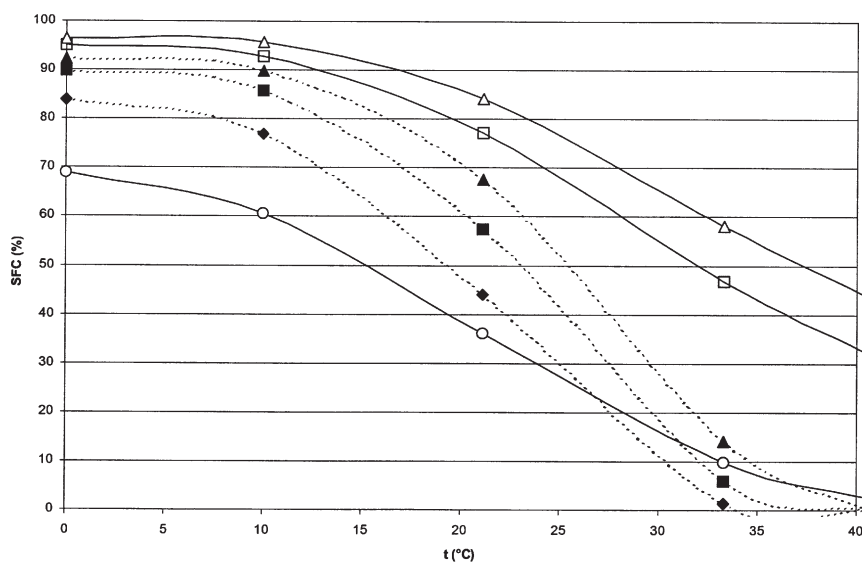


FIG. 2. Solid fat content (SFC) of samples hydrogenated for 100 min. (SP-10: (◆), 0.1%; (■), 0.15%; (▲), 0.2%. Nysosel 222: (○), 0.02%; (□), 0.03%; (△), 0.04%.

Increasing catalyst ratio shortened the time to reach the highest  $S_{21}$  ratio, which was dependent on certain IV for both catalysts and their concentrations. That is, maximal  $S_{21}$  values of Nysosel 222 were obtained at lower IV (about 73) than those of SP-10 (about 80) because conversion to stearate is more favored by Nysosel 222 than *trans* formation. However, once reaching the highest  $S_{21}$ , the values of Nysosel 222 were reduced considerably to lower values than those of SP-10 which were almost constant below an IV of 80 because double bonds were converted to *trans* isomers rather than being saturated. These findings suggest that catalyst type is the most important factor for selectivity ratio even though the concentrations of catalysts used shortened the time to get higher selectivities owing to increasing the reaction rates

Figure 1 shows total *trans* isomers of the samples at 10-min intervals during the reactions. No big differences were observed in the *trans* isomer formation between the various catalyst ratios of SP-10. The highest percentages were reached after 100 min of the reaction but isomerization was slowing at that time. In contrast to SP-10, almost 40–45% less *trans* isomerization occurred when Nysosel 222 was used, and isomer concentrations were reduced after reaching to the highest ratio at an IV of 58 for 0.04% catalyst ratio. Isomerization kept increasing even after 100 min when other concentrations (0.02 and 0.03%) of Nysosel 222 were used because of slower reaction rates. It can be concluded from these findings that *trans* isomer formation does not depend on catalyst concentration, but rather on IV and catalyst type.

Values for SMP for the samples and SFC of the end products are given in Table 1 and Figure 2, respectively. Increasing Nysosel 222 from 0.02 to 0.03% was effective in raising SMP and SFC of the samples as well as reducing IV. Other concentrations of both catalysts slightly influenced melting behaviors

of hydrogenated samples. But increases in the m.p. of SP-10 samples were slower after an IV of 80, where  $S_{21}$  ratios reached higher values. SFC values of these samples drastically fell after 21.1°C, and steeper SFC curves were obtained owing to the *trans*-isomer-forming characteristic of this catalyst.

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