Fixed-Bed Continuous Hydrogenation of Soybean Oil With Palladium-Polymer Supported Catalysts

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To compare a continuous hydrogenation system with batch hydrogenation, soybean oil was treated with Pd and Ni catalysts in a fixed-bed system under conditions that gave trickle flow. The influence of processing variables such as space velocity, pressure, temperature and hydrogen flow on the selectivity, specific isomerization and the activity was investigated. Both the Pd and Ni catalysts gave significantly lower specific isomerization (*trans* isomer per drop in Iodine Value) when compared to reported values for batch hydrogenation with similar type catalysts. The linolenate and linoleate selectivities were also significantly lower. Heterogenized homogeneous Pd-on-polystyrene catalyst gave lower specific isomerization formation and higher selectivity than carbon-supported Pd catalyst at same conditions. This work indicates that Pd-on-styrene, Pd-on-carbon and extruded Ni catalysts, in fixed-bed continuous hydrogenation can produce soybean oil of desirable composition after further optimization.

Continuous reactor systems for hydrogenating vegetable oils have been reported to offer several advantages over a batch system, including improved heat economy, equipment and labor utilization, and product uniformity (1-3). Use of continuous catalyst/oil slurry systems for the hydrogenation of soybean oil has shown little advantage over that of batch systems in selectivity or specific isomerization (4-6). However, fixed-bed hydrogenation of vegetable oils has been claimed to lower formation of *trans* isomers in partially hydrogenated oils (7). In one study, fixed-bed hydrogenation gave low selectivity values (2), but in other studies the selectivity of continuous fixed-bed hydrogenation was found to be equal to that of batch hydrogenation with copper catalyst, at a lower reaction temperature (8), or with a supported cobalt catalyst (9).

Heterogenized homogeneous catalysts have been reported by numerous authors (10-13) for the hydrogenation of olefins. We have found that crosslinked polystyrene-Cr(CO)$_3$ was effective for the selective hydrogenation of fatty esters and could be recycled from 2 to 10 times (14). We also observed during batch hydrogenation with Pd-polystyrene as catalyst that a possible fragmentation of the catalyst particles might reduce activity when the catalyst is recycled (15). A continuous fixed-bed system was therefore investigated to determine if it would prevent bead disintegration and maintain the initial activity. This paper reports a study aimed at comparing the effect of Pd and Ni catalysts on the hydrogenation of soybean oil in a continuous fixed-bed catalyst system.

EXPERIMENTAL PROCEDURE

The commercially refined and bleached soybean oil used in this work had the following fatty acid composition: C16:0, 11.4%; C18:0, 3.7%; C18:1, 23.7%; C18:2, 53.0%, and C18:3, 8.0%. The calculated iodine value (IV) was 133. The soybean oil was passed through alumina prior to hydrogenation to remove impurities that might act as catalyst poisons and interfere with catalyst evaluation.

The continuous hydrogenation system consisted of an oil charging vessel, pump, hydrogen supply, heated tube reactor and receiver. The stainless steel reactor (7 mm i.d. × 33 cm long) was packed loosely with 5 or 10 cc catalyst (2 or 4 g) and inserted in an electrically heated, thermostatically controlled aluminum block. A layer of glass wool on top of the catalyst bed provided a zone for preheating the incoming oil and gas to reaction temperature. Temperature of the catalyst bed was measured with a thermocouple inserted axially at the center of the reactor from the bottom. Refined and bleached soybean oil was pumped (Milton Roy Mini Pump, Milton Roy Co., Philadelphia, Pennsylvania) from the charging vessel at 35-100 cc per hr through the glass wool plug and then onto the catalyst bed; H_2 was admitted immediately above the catalyst bed and flowed concurrently with the oil. The inlet gas line was used to purge the reactor (with N_2 or H_2) and to introduce the reactant gas into the reactor. Check valves in the gas lines prevented back flow of gas or oil into the lines. A back pressure valve in the receiver vent line regulated the system pressure. A flow meter in the vent line measured the volume of exiting surplus H_2. Oil samples were withdrawn periodically from the reactor exit line for GLC analysis.

Methyl esters of the oil samples were analyzed by GLC (Varian 1800, Varian Associates, Inc., Sunnyvale, California) in a column packed with 15% EGSS-X and heated isothermally at 190°C. Linoleate (Lo) and linolenate (Ln) selectivities (S_{Lo}, S_{Ln}) were calculated according to AOCS Method TZ lb-79 (16) using the computer calculating procedure. Catalytic activity was calculated as decrease in IV per unit time through the catalyst bed (IV/hr). The percentage of isolated *trans* double bonds was determined as methyl elaidate either by IR analysis according to AOCS Method Cd 14-161, or by glass capillary GLC analysis (Perkin Elmer Model 3920) with a Silar 10 C column heated isothermally at 170°C (17). Specific isomerization was expressed as the amount of *trans* per drop in IV (% *trans*/IV). Pd-on-styrene catalysts were prepared by Holy (18) by complexing $PdCl_2$ with anthranilic acid on polystyrene macropore SM4 (20-50 mesh) beads (Bio-Rad Laboratories, Richmond, California) to final concentrations of 3% Pd (Catalyst I) and 4% Pd (Catalyst II). These catalysts were compared with commercial 1% Pd-on-carbon catalyst (0.18-0.42 mm) (Catalyst III) and with extruded nickel catalysts: Catalyst IV and IVB (0.03 mm - 50% Ni) and Catalyst V (0.06 mm -39% Ni).

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RESULTS

Hydrogenation experiments were performed at varying temperatures (100-260°C), pressures (20-50 psig), liquid hourly space velocities, LHSV (7-14 cc hr^{-1} and hydrogen flow (210-4000 STP L/h). At these conditions of trickle oil flow the gas phase is considered continuous. Variations in LHSV and hydrogen flow had little impact on catalyst activity values (Fig. 1 and Tables 1, 2 and 3).

Palladium catalysts. Both Pd-on-polystyrene catalysts (I and II) formed less *trans* isomers than the supported Pd-on-carbon catalyst (III) when the differences in iodine value drop are taken into account as shown by the specific isomeration (Si) values (Table 1). With increasing temperature there was no significant change in the specific isomerization with either of these types of catalysts. Compared to similar hydrogenation with the same type of catalyst under approximately the same conditions in the batch process (19), the continuous process yields a significantly lower specific isomerization value.

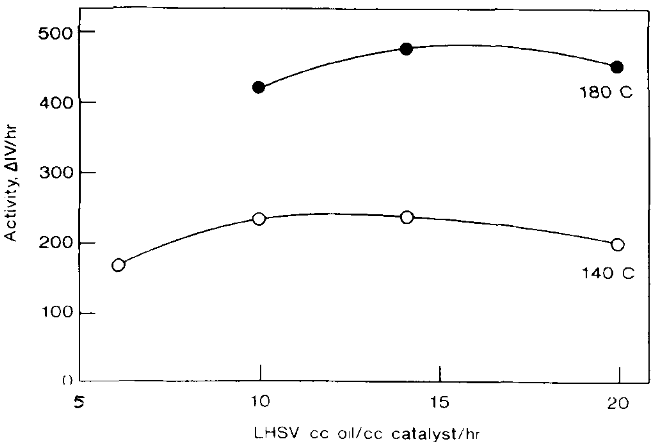

FIG. 1. Relationship of catalyst activity to Liquid Hourly Space Velocity (LHSV) for continuous fixed-bed hydrogenation of soybean oil with Ni catalyst (IVB) at 140 and 180°C, 50 psig.

The selectivity values (S_{Ln} and S_{Lo}) were low compared to similar batch hydrogenation (15). The Pd-on-polystyrene catalysts showed higher values for S_{Ln} than Pd-on-carbon, but there was no significant difference in the S_{Lo} values among the three catalysts.

The activity for the three catalysts, compared at identical temperature and pressure, increased in the following order:

Pd-on-carbon (III) < Pd-on-polystyrene (I) < Pd-on-polystyrene (II). Pd-on-polystyrene (II) was approximately 10 times more active than Pd-on-carbon at 100°C and 50 psig. The activity increased as expected with increasing temperature. With Pd-on-polystyrene (I) this effect of temperature leveled off at about 140°C. At this temperature a significant pressure drop over the catalyst bed was observed, which was probably due to softening of the polystyrene beads, thus lessening the catalyst activity. This effect establishes an upper temperature limit for these heterogenized homogeneous catalysts in a fixed-bed system.

The product obtained with the most active Pd-on-polystyrene catalyst (II) at 100°C had a linolenate content and a *trans* content sufficiently low to be commercially acceptable for cooking and frying.

Nickel catalysts. In a series of experiments soybean oil was hydrogenated with an extruded Ni catalyst before and after activation. The purpose of activation prior to the hydrogenation was to remove adsorbed carbon dioxide. CO_2 was used in the catalyst's manufacture to stabilize the reduced Ni on the catalyst surface against oxidation. To avoid possible hot spots, which might give a sintering of the catalyst, a procedure recommended by the manufacturer was used during the activation. The catalyst bed was first purged with N_2 at ambient conditions. The temperature in the bed was raised to 150°C to desorb moisture and CO_2.

TABLE 1

Continuous Fixed-Bed Hydrogenation of Soybean Oil with Supported Palladium Catalysts

Conditions and analyses[a]	Pd-on-polystyrene (I)			Pd-on-polystyrene (II)		Pd-on-carbon (III)	
Temperature, °C	100	140	170	80	100	100	170
Pressure, psig	50	50	50	50	50	50	50
LHSV, hr^{-1}	5	5	5	6	6	14	14
Hydrogen flow, L/hr[b]	210	210	210	2000	2000	210	210
Fatty acid composition							
C16:0	11.0	11.1	11.3	11.5	11.5	11.2	11.5
C18:0	5.7	8.2	7.9	7.3	18.7	4.0	10.2
C18:1	27.3	28.8	28.8	27.4	40.1	25.2	33.2
C18:2	49.8	45.8	46.1	48.7	27.4	52.7	39.5
C18:3	6.2	6.1	5.9	5.1	2.3	6.9	5.6
IV(calculated)	126	120	120	121	88	131	112
Conjugated dienes	—	—	—	—	—	—	—
trans, %	2	4	3	3	12	3	17
S_{Ln}	1.1	1.0	1.2	2.0	1.4	0.6	0.8
S_{Lo}	1.3	1.1	1.0	2.4	1.8	1.4	1.4
S_i, % *trans*/IV	0.3	0.3	0.2	0.2	0.3	1.5	0.8
Activity, IV/t, hr	47	78	78	84	282	28	101

[a] LHSV, Liquid hourly space velocity; S_{Ln}, linolenate selectivity; S_{Lo}, linoleate selectivity; S_i, specific isomerization.

[b] Measured at receiver vent.

TABLE 2

Continuous Fixed-Bed Hydrogenation of Soybean Oil with Supported Nickel Catalysts

Conditions and analyses[a]	Ni-(nonactivated) IVA			Ni-(activated) IVB		
Temperature, °C	150	150	180	180	140	180
Pressure, psig	50	50	50	50	50	50
LHSV, hr^{-1}	10	10	10	10	10	10
Hydrogen flow, L/hr[b]	210	4000	210	4000	4000	4000
Fatty acid composition						
C 16:0	11.6	11.6	11.4	11.3	11.3	11.3
C 18:0	10.6	11.2	15.4	16.1	11.1	15.3
C 18:1	33.2	34.0	37.5	37.7	33.5	42.4
C 18:2	39.3	38.4	31.7	31.3	38.9	27.9
C 18:3	5.0	4.7	3.7	3.7	5.0	2.9
IV(Calculated)	110	108	97	96	109	93
Conjugated dienes	—	—	—	—	—	—
trans, %	10	10	15	15	—	—
S_{Ln}	1.3	1.3	1.3	1.2	1.3	1.3
S_{Lo}	1.5	1.5	1.7	1.7	1.5	2.4
S_i, % *trans*/IV	0.4	0.4	0.4	0.4	—	—
Activity, IV/t, hr	246	265	375	385	240	410

[a]LHSV, Liquid hourly space velocity; S_{Ln}, linolenate selectivity; S_{Lo}, linoleate selectivity; S_i, specific isomerization.

[b]Measured at receiver vent.

TABLE 3

Continuous Fixed-Bed Hydrogenation of Soybean Oil with Supported Nickel Catalyst

	Ni-(V)					
Temperature, °C	140	180	180	220	220	260
Pressure, psig	50	50	20	20	20	20
LHSV, hr^{-1}[a]	10	10	14	14	14	14
Hydrogen flow, L/hr[b]	210	210	210	210	4000	4000
Fatty acid composition						
C 16:0	11.8	11.5	11.4	11.5	11.6	11.9
C 18:0	8.6	12.0	7.4	6.9	7.1	6.7
C 18:1	29.5	34.1	28.6	32.1	33.1	35.1
C 18:2	44.2	37.8	46.1	43.4	42.3	40.6
C 18:3	5.9	4.6	6.5	6.1	5.9	5.7
IV (Calculated)	117	107	121	119	117	116
Conjugated dienes	—	—	0.5	0.7	0.8	2.0
trans, %	3	7	4	7	8	12
S_{Ln}	1.0	1.1	0.7	0.8	0.8	0.8
S_{Lo}	1.1	1.4	1.1	1.8	1.9	2.4
S_i, % *trans*/ IV	0.2	0.3	0.3	0.5	0.5	0.6
Activity, IV/t, hr	160	265	168	196	224	238

[a]LHSV, Liquid hourly space velocity; S_{Ln}, linolenate selectivity; S_{Lo}, linoleate selectivity; S_i, specific isomerization.

[b]Measured at receiver vent.

To prevent the temperature exotherm in the catalyst bed from exceeding 300°C, H_2 was blended gradually into the N_2 stream until the H_2 concentration in the reactor reached 100%. Catalyst IVB activated according to this procedure was found to be slightly more active than Catalyst IVA without this activation (Table 2). The activation had no significant effect on the selectivity of the catalysts. The reason for this small difference in activity was probably that Catalyst IVA was activated in situ during the hydrogenation and that the high oil flow through the catalyst bed prevented hot spots and sintering of the catalyst.

Figure 1 shows activity as function of the space velocity (LHSV) for catalyst IVB (activated) at two different temperatures (140 and 180°C). Maximum activity was reached at LHSV of 12 and 15 hr^{-1} at 140°C and 180°C, respectively.

Increasing the hydrogen flow through the catalyst bed from 210 to 4000 L/h had only a slight effect on the activity of catalysts IVA and V (Tables 2 and 3). Catalyst V was used at varying temperatures (140 to 260°C), space velocities (7-14 hr^{-1}), pressures (20 and 50 psig) and hydrogen flows (210 and 4000 L/h).

Increasing temperature had a positive effect on the activity, although this effect leveled off at higher temperature. The specific isomerization and the formation of conjugated double bonds increased with increasing temperature. The temperature had no significant effect on the S_{Ln}, whereas S_{Lo} increased slightly with the temperature.

Although continuous fixed-bed hydrogenation produced low *trans* isomers, the linolenate and linoleate selectivities were low for both the Ni and Pd catalysts compared to batch hydrogenation with similar types of catalysts. According to Bailey (20), low *trans* isomers and low selectivity during hydrogenation result when a large interfacial area exists between the oil and hydrogen, such as in our fixed-bed reactor. Lush (21) concluded that the continuous hydrogenation process keeps the catalyst working at its maximum efficiency in supplying hydrogen and thus results in a minimum amount of *trans* produced at any given temperature. Coenen (2) suggested that the low selectivity may be the result of triglyceride diffusion becoming rate-limiting in the hydrogenation process. Although the extruded nickel catalysts, used in this study, contained no binders and were reportedly not compressed during their preparation, the pore size of these catalysts may not have been large enough to permit the triglyceride to enter and leave the catalyst pores without excessive "over hydrogenation" of the oil.

This work, shows that, under the proper operating conditions, Pd-on-polystyrene, Pd-on-carbon and extruded Ni catalysts can be used in fixed-bed continuous hydrogenation of soybean oil without excessive formation of isomeric products. Operating conditions should be optimized, however, before choosing the catalyst and determining the economic advantages of continuous fixed-bed hydrogenation of soybean oil.

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