Continuous Slurry Hydrogenation of Soybean Oil with Nickel Catalysts

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ABSTRACT

Soybean oil was hydrogenated continuously in the presence of nickel catalysts. The iodine value of the products was varied by changing the oil flow rate and temperature of the reaction. Sulfur-promoted nickel catalyst increased the selectivity for linolenate hydrogenation, but formed much higher proportions of *trans* isomers. Linoleate selectivity improved with temperature with both nickel and sulfur-promoted nickel catalysts, but *trans* isomerization also increased. The feasibility of this continuous reactor system was demonstrated as a practical means to prepare hydrogenated stocks of desired composition and physical characteristics at high throughput.

INTRODUCTION

Commercial processing of vegetable oils, particularly soybean oil, is carried out continuously except for hydrogenation, which often is carried out as a batch operation. Several continuous flow hydrogenation processes are proposed in the patent literature (1-3), and a few laboratory and pilot-plant studies have been described (4-8). These processes fall primarily into two categories. In one type, the oil-catalyst slurry along with hydrogen gas is passed continuously through a reactor, consisting of either a pipe or a column in which stirring is provided by means of baffles or trays. Details of operation of this type at one commercial plant are discussed in a recent report (9). In the second type, the catalyst is packed in a stationary column while the oil and gas are passed over the catalyst. The stationary catalyst system generally has the disadvantage of low selectivity, because the oil is contacted with a large excess of catalyst. In the continuous slurry system, insufficient mixing of the constituents results in slow reaction, and back mixing could result in lowered selectivity.

We previously have described a continuous slurry reactor (10) for use with copper catalyst. This paper reports the use of this equipment to study the continuous hydrogenation of soybean oil in the presence of nickel and sulfur-promoted nickel catalysts.

EXPERIMENTAL

The same equipment was used as previously described (10), except the receiver (1 gal) was replaced by a Jerguson gage (Jerguson Gage and Valve Co., Burlington, Massachusetts) to allow continuous sample collection. The same analytical methods as described previously (10) also were used. Harshaw/Filtrol Partnership, Beachwood, Ohio, provided the sulfur-promoted nickel (NYSEL SP-7) and NYSEL nickel catalysts. Central Soya Co., Inc., Fort Wayne, Indiana, provided the refined and bleached soybean oil.

RESULTS AND DISCUSSION

In our previous study (10) with copper catalysts, samples were withdrawn from different sections of the reactor to obtain hydrogenated oils of varying degrees of unsaturation. In the present study with nickel catalysts, the oil-catalyst slurry was allowed to react through the entire length (120 ft) of the reactor. The extent of hydrogenation was changed by varying the flow rate of the oil and the temperature of reaction, while catalyst concentration was kept constant (0.025 wt % nickel for Nysel and 0.075 wt % Ni for sulfur-promoted nickel). Pressure was maintained at the inlet of the reactor at 100 psig for nickel catalyst and at 100 and 350 psig for sulfur-promoted catalyst. We studied the effect of changing the oil flow rate, temperature of the reaction and hydrogen pressure on the extent of hydrogenation, selectivity of the reaction and formation of *trans*-isomers.

Effect of oil flow. As expected, the extent of hydrogenation decreased with the increase in oil flow rate at each temperature (Table I). Increasing the oil flow rate decreased the residence time, causing a decrease in the extent of hydrogenation. The exact residence time could not be calculated because the relative volumes of oil and gas in the reactor were not known. The volume of hydrogen gas was continuously changing as it was consumed in the reaction and as the pressure dropped across the reactor. The oil flow rate had no effect on isomerization as measured by % *trans* per unit IV drop. Selectivity of the reaction also was unaffected by a change in oil flow.

Effect of temperature. The extent of hydrogenation increased with temperature at any given oil flow rate with a few exceptions (Table I). At 1 l/hr oil flow, the extent of hydrogenation increased over the entire temperature range. At 2-3 l/hr oil flow, iodine value (IV) decreased with temperature up to 180 C. Above this temperature, very little or no further reduction in IV occurred. At 4 l/hr oil flow, the IV of the product was constant in the 180-225 C range. No explanation could be offered for this anomalous behavior except that the residence time was very small at high flow rates.

Isomerization increased with temperature, as evidenced by the increase in % *trans*/ΔIV from 0.37 at 140 C to 0.67 at 225 C. Linolenate selectivity (K_{Le}/K_{Lo}) was unaffected by temperature, with average values ranging between 1.5-1.6. Linoleate selectivity (K_{Lo}/K_{Ol}) improved with temperature from an average value of 3 at 140 C to 15 at 225 C.

Sulfur-promoted nickel. Sulfur-promoted nickel was much less active than unpromoted nickel (Table I). Even at the highest temperature of 225 C and a low oil flow of 0.25 l/hr, the IV of the product was 92. Hydrogenation rate increased when pressure was increased from 100 to 350 psig. Isomerization was much greater with sulfur-promoted nickel than with Nysel nickel catalyst. Linolenate selectivity was higher with the former catalyst (K_{Le}/K_{Lo} = 2.6-3.5), whereas linoleate selectivity was about the same as commercial nickel catalyst.

Solid fat index. From the results in Table I, it is apparent that the fatty acid composition of the products depends upon the flow rate of oil and the temperature of the reaction. By judicious choice of conditions, a variety of hydrogenated products could be produced that might find use as base stocks for shortenings and cooking oils. The solid fat index (SFI) curves for some of these products are shown in Figure 1. Except for one sample with an IV of 59, all were completely liquid at 38 C. Some of these samples have potential as base stocks for shortenings and margarines (11). Samples 1-4 represent products obtained under identical conditions except for a change in flow rate (reaction time). The desired IV of the product and SFI could be obtained by changing the flow rate. Samples 5 and 6 were hydrogenated with sulfur-promoted nickel catalyst, and their steep SFI curves suggest their utility as margarine base stocks (11). Samples 3, 5 and 6 have the same IV, yet

TABLE I

Continuous Hydrogenation of Soybean Oil with Nickel Catalysts (H_2 Flow 1 liter/min at 100 psig)

Temp., C	Oil flow l/hr	Fatty acid composition St^a	M	D	T	Calc. IV	*trans* %	% *trans*/ΔIV	Selectivity K_{Le}/K_{Lo}	K_{Lo}/K_{Ol}
0.025% Ni										
–	–	4.2	22.8	54.1	8.8	136.3	–	–	–	–
140	0.5	7.4	39.5	38.7	4.2	112.0	8.6	0.35	1.7	4.2
140	1.0	6.0	31.8	45.7	6.3	123.0	5.1	0.38	1.5	3.2
140	2.0	5.3	27.9	49.4	7.2	128.4	2.9	0.37	1.7	2.6
140	2.5	5.3	26.6	50.1	7.8	130.1	–	–	1.3	2.0
140	3.0	5.0	26.0	50.9	7.8	131.1	–	–	1.5	2.1
160	0.5	13.4	60.7	15.0	0.7	80.0	22.4	0.40	1.7	7.7
160	1.0	9.2	52.4	26.1	2.1	95.8	16.6	0.41	1.6	7.0
160	1.5	8.3	48.5	30.2	2.7	101.1	13.9	0.39	1.6	6.3
160	2.0	6.9	41.1	37.6	4.2	111.5	9.7	0.39	1.6	5.4
160	2.5	6.2	37.9	41.1	4.8	116.3	8.2	0.41	1.7	5.8
160	3.0	6.1	35.8	42.7	5.3	118.6	6.9	0.39	1.6	4.8
180	0.5	25.6	59.5	4.9	0.0	59.7	–	–	–	–
180	1.0	16.4	63.7	9.5	0.4	72.3	–	–	1.5	8.5
180	2.0	8.1	56.0	24.0	1.6	94.0	–	–	1.7	10.5
180	3.0	6.2	46.1	34.3	3.3	107.7	–	–	1.7	10.4
180	4.0	5.7	39.6	39.8	4.6	115.1	–	–	1.6	7.8
200	0.8	25.6	60.1	4.3	0.0	59.1	–	–	–	–
200	1.6	11.7	68.3	9.3	0.5	76.2	30.0	0.50	1.4	14.3
200	2.0	8.2	57.4	22.3	1.8	92.7	21.0	0.48	1.5	11.0
200	3.0	6.2	49.0	31.1	3.3	104.6	16.0	0.50	1.4	11.1
200	4.0	5.5	40.7	38.7	4.8	114.6	10.5	0.48	1.5	9.2
225	1.0	33.0	56.7	0.0	0.0	48.9	35.3	–	–	–
225	2.0	7.1	58.6	22.5	1.7	93.8	28.0	0.66	1.5	16.0
225	3.0	5.8	50.9	30.2	3.0	103.9	22.4	0.69	1.5	17.4
225	4.0	5.2	42.6	37.5	4.5	113.4	15.3	0.67	1.5	14.1
225	5.0	4.9	37.9	41.6	5.4	118.8	11.2	0.64	1.5	12.9
0.075% Ni-S										
225	0.25	6.9	60.0	22.8	0.3	91.8	66.9	1.50	3.2	17.6
225	0.50	5.6	43.2	38.3	2.6	110.3	45.5	1.75	2.6	10.1
200^b	0.5	8.7	51.4	28.8	1.0	96.7	51.1	1.29	2.7	7.0
225^b	0.5	9.0	55.6	25.2	0.3	92.0	62.8	1.42	3.5	8.3

^{a}St = Stearate; M = monoene; D = diene; T = triene.
^{b}350 psig H_2.

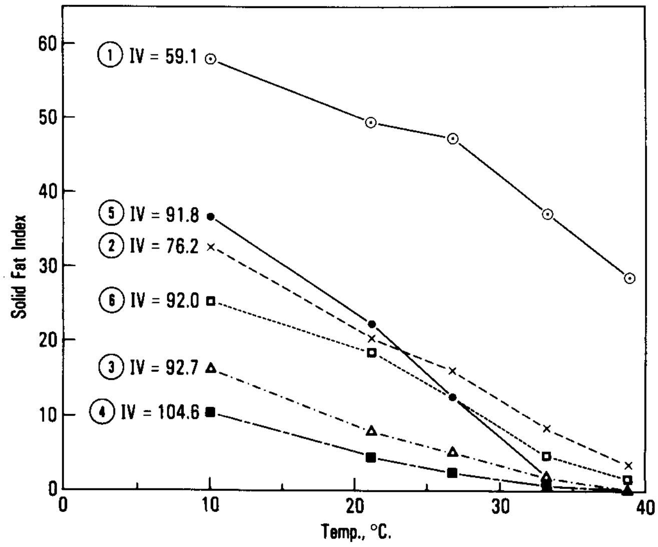

FIG. 1. Solid fat index curves for various hydrogenated oils. Curves 1 to 4 hydrogenated at 200 C, 100 psig, 0.025% Ni, with oil flow rates of 0.8, 1.6, 2.0, and 3.0 l/hr, respectively; curve 5, 225 C, 100 psig, 0.075% Ni-S, and 0.25 l/hr oil flow, and curve 6, 225 C, 350 psig, 0.075% Ni-S, and 0.5 l/hr oil flow.

the SFI curves are quite different, which suggests that conditions of reaction could be changed to obtain products with different physical characteristics.

The stability of hydrogenated oils prepared by continuous process remains to be established. The continuous system described has been used for the large scale preparation of hydrogenated soybean oils. The evaluation of these oils will be reported in a future communication.

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