Reuse of Copper Catalyst in Continuous Hydrogenation

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ABSTRACT

Continuous hydrogenation of soybean oil using copper catalyst can be improved economically by reusing the catalyst. A hydrogenated oil with an approximate iodine value drop of 25 was attained by regulating the conditions and size of the reactor. Catalyst was removed by centrifuge and recycled. Reaction products were evaluated to determine catalyst activity, linolenate selectivity and *trans* formation. By adding 0.2–0.4% fresh catalyst each time, the activity was retained. Linolenate selectivity ranged from 6 to 11 and *trans* formation, expressed as specific isomerization, ranged from 0.63 to 0.78.

INTRODUCTION

Copper chromite works well as a hydrogenation catalyst to improve the flavor stability of soybean oil through selective reduction of linolenate (1-3). Problems associated with copper catalysts are their difficult removal from the oil and their low activity compared to nickel. Higher pressures, larger amounts of catalyst, and longer reaction times are needed to compensate for the low activity (4, 5). One effective way to reduce catalyst consumption is by reuse of the catalyst (6). Soybean oil processors use this technique with nickel-catalyzed hydrogenation. This paper establishes the principle that, in a continuous reactor, the total catalyst requirement can be decreased by reuse of a portion of copper catalyst.

EXPERIMENTAL PROCEDURES

A single lot of soybean oil was used for all hydrogenations. Harshaw copper chromite (CU1106P) was the catalyst used.

Hydrogenations were accomplished in a pipe-line continuous reactor (1/16 in. × 40 ft) described earlier (7). Conditions were controlled to hydrogenate the soybean oil so that the iodine value decreased about 25 units. Hydrogen flow rate was maintained at 100 mL/min by a metering valve and oil flow rate was 2.2 mL/min or 3.5 mL/min. Temperature at 190 C and pressure at 200 psig were held constant throughout the study to eliminate their effects on the reactions. An oil-catalyst slurry was metered by a high pressure pump concurrently with hydrogen through the reactor, the hydrogenated product was collected, centrifuged and the oil was decanted from the catalyst. Fresh oil was added to the used catalyst for each subsequent reaction.

Methyl esters of the products were prepared by transesterification of the oil with sodium methoxide (8) and were analyzed by gas liquid chromatography (GLC) using a 6 ft 1/8 in. stainless steel column of 10% EGSS-X. Iodine value and linolenate selectivity (LnSel) were calculated from GLC data (9) and the amount of *trans* was determined by infrared using AOCS methods (10). Specific isomerization (S_i) represents the amount of *trans* formed/unit drop in iodine value (IV). The hydrogenated samples

TABLE I

Continuous Hydrogenation of SBO[a]-CuCr Catalyst Reuse

	Run no.									
Experiment no.	1	2	3	4	5	6	7	8	9	10
I.[b] (1% cat. 0% make-up)										
ΔIV	24	21	16	10	8	4				
% Ln	0.4	0.3	0.3	0.6	0.5	1.3				
LnSel	8.4	9.4	8.2	7.4	7.1	4.8				
% *trans*	16.1	14.3	10.7	7.2	5.7	0				
S_i[c]	0.67	0.68	0.67	0.72	0.71					
II.[b] (1% cat. 20% make-up)										
ΔIV	24	20	22	24	24	25	24	26	24	25
% Ln	0.4	0.5	0.9	1.0	1.1	1.0	0.9	0.7	0.9	1.2
LnSel	9.3	9.0	7.3	6.0	6.1	6.1	6.4	6.5	6.4	5.7
% *trans*	15.9	13.8	15.6	16.1	16.4	16.6	15.3	18.3	16.7	16.3
S_i	0.66	0.69	0.70	0.67	0.68	0.66	0.64	0.70	0.69	0.65
III.[d] (2% cat. 10% make-up)										
ΔIV	24	20	21	20	21	18	20	21	19	20
% Ln	0.3	0.6	0.5	0.5	0.5	0.6	0.5	0.6	0.5	0.5
LnSel	9.7	10.9	9.8	11.1	9.9	11.3	11.9	9.4	11.3	11.2
% *trans*	15.8	13.6	14.1	13.1	13.7	12.7	13.4	13.5	13.3	12.6
S_i	0.68	0.68	0.67	0.66	0.65	0.70	0.67	0.64	0.70	0.63
IV.[e] (4% cat. 10% make-up)										
ΔIV	27	22	23	22	25	28	25	26	26	26
% Ln	0.2	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.3
LnSel	8.8	11.0	10.8	9.8	8.3	10.0	9.3	9.0	9.4	9.4
% *trans*	20.8	17.1	16.5	16.9	18.8	21.6	17.5	20.4	20.0	20.3
S_i	0.77	0.78	0.72	0.77	0.75	0.77	0.71	0.78	0.77	0.78

[a] Conditions—temp. 190 C, pressure 200 psig.
[b] Reactor length—40 ft; oil flow rate—2.2 mL/min.
[c] Specific isomerization = % *trans*/ΔIV.
[d] Reactor length—20 ft; oil flow rate—2.2 mL/min.
[e] Reactor length—20 ft; oil flow rate—3.5 mL/min.

were examined for conjugation by ultraviolet absorption at 232 nm (10).

RESULTS AND DISCUSSION

Initially we tried to maintain a product composition throughout repeated hydrogenations without adding fresh catalyst. In experiment I (Table I), the initial catalyst concentration was 1%. After each cycle, the catalyst was removed and fresh oil was added without added fresh catalyst. The catalyst was recycled six times, and the activity and linolenate selectivity of the catalyst decreased with each reuse.

Subsequent experiments were done by replacing small amounts of spent catalyst with fresh catalyst. Using 1% initial catalyst concentration, the catalyst activity was retained if 20% of the catalyst was replaced in experiment II. The amount of *trans* unsaturation remained constant, but linolenate selectivity decreased from 9 to 6 by the fourth cycle. In experiment III, the initial catalyst concentration was increased to 2%; the reactor length was decreased to 20 m to maintain the 25 IV drop. When recycled, only 10% new catalyst was needed to retain the activity. Specific isomerization values remained the same and linolenate selectivity was high throughout the 10 hydrogenations.

When the catalyst concentrations was increased to 4%, the oil flow rate was increased to 3.5 mL/min to reach the desired degree of hydrogenation. The addition of 5% make-up catalyst was not enough to retain the activity needed and it was necessary to replace 10% of the catalyst. Linolenate selectivity remained high, but the specific isomerization values (S_i) increased at the 4% catalyst level (experiment IV).

Data in Table I (experiments II, III and IV) indicate that, after the first or second run, steady-state conditions with respect to catalyst activity are reached. With 1% catalyst and 20% replacement (experiment II) or with 2% catalyst and 10% replacement (experiment III), the catalyst needed is thus only 0.2%. In experiment IV, with 4% catalyst and 10% replacement, the value is 0.4%. Comparison of experiments II and III shows that, with proper choice of catalyst concentration and make-up percentage, a greater activity may be obtained without greater consumption of catalyst. This makes possible use of a shorter reactor or greater throughput.

As reported previously, conjugated diene was not present in the hydrogenated product when the pressure was 200 psig or higher (7). We found no conjugation in any of the reduced samples obtained from hydrogenations with fresh or recycled catalyst.

Our data in a small laboratory reactor illustrate that the concept of partial replacement and reuse of copper catalyst is valid. Optimal values of catalyst concentration and percentage replacement, as well as other parameters, will vary with the nature of the equipment, and it does not seem useful to optimize them further in the laboratory apparatus.

Higher hydrogen pressures than those used with nickel have been proposed for copper catalysts to increase the reaction rate and prevent occurrence of unreacted conjugated fatty acid isomers in the oil (4, 5). For these higher pressures, the desirability of a continuous reactor has been suggested (7). On the basis of this work, we evision a reactor in which catalyst is continuously removed from the hydrogenated product, and part of the catalyst is recycled continuously back to the reactor. In our work, a batch centrifuge was used to remove the catalyst, but other methods might be suitable on a larger scale.

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