Hydrogenation of Soybean Oil with Copper Catalysts Containing Small Amounts of Nickel Catalysts

K.J. MOULTON, R.E. BEAL and E.L. GRIFFIN, Northern Regional
Research Laboratory,[2] Peoria, Illinois 61604

ABSTRACT

Reaction rates, linolenate/linoleate reaction selectivity, *trans* formation, and conjugated diene formation were determined for mixed commercial catalysts containing 0.5, 1, 2, 10, and 20 parts nickel catalyst (25% nickel) per 1000 parts copper chromite catalyst (ppt) and at catalyst concentrations in the oil of 1.0, 0.5, and 0.25%. The rate of hydrogenation increased as the amount of nickel increased. Addition of 0.5, 1, and 2 ppt nickel catalyst to copper chromite catalyst resulted in a small decrease in selectivity compared with straight copper chromite. When soybean oil was hydrogenated with these mixed catalysts sufficiently to reduce linolenate to 0, iodine values were 102-108 compared to 109-112 for straight copper chromite and to less than 80 for straight nickel.

INTRODUCTION

Copper-containing catalysts, such as copper chromite (1-3) and copper on silica gel (4), selectively and completely reduce linolenate in soybean oil with only a small decrease in linoleate.

These catalysts have been investigated with the objective of substituting them for nickel catalysts to produce improved liquid salad and cooking oils by partial hydrogenation and winterization. Although soybean oil can be hydrogenated rapidly with a nickel catalyst, selectivity is poor and a winterized liquid oil with 0 linolenate content cannot be produced economically. We previously found (1) that with a copper chromite catalyst, soybean oil could be partially hydrogenated selectively to 0 linolenate and winterized, with a yield equal to that of a nickel-hydrogenated oil containing 3% linolenate. These liquid oils with 0 linolenate content have high temperature stability as shown by room odor tests. They are less susceptible to the development of strong odors when heated to frying temperatures (5), compared to commercial nickel-hydrogenated, winterized soybean oil.

Unfortunately with copper catalysts, activity is lower than for nickel catalysts. At the same concentration that nickel is commonly used, they give a much slower reaction; and, at higher concentrations, they increase hydrogenation cost. Catalyst cost can be reduced by reusing the catalyst, a method which has been demonstrated to be possible (4). In the present study, we investigated hydrogenation of soybean oil with mixed copper chromite and nickel catalysts (CuCr-cat and Ni-cat) to determine the effects of small amounts of nickel on the hydrogenation rate and the composition of the partially hydrogenated oil. Toyama (6,7) reported on catalysts with 10-100 parts nickel per 1000 parts (ppt) copper prepared by coprecipitating copper and nickel on keiselghur. With respect to the linolenate/linoleate selectivity, these catalysts performed similar to a nickel catalyst.

Swern (8) and Paterson (9) described similar results from hydrogenations using nickel catalysts with copper added. Paterson's catalysts might have performed better had the copper chromite been activated (10). No literature could be located on active copper catalysts containing amounts of nickel smaller than 10 parts per 1000 parts copper catalyst nor on oil hydrogenated with a copper-nickel catalyst to 0

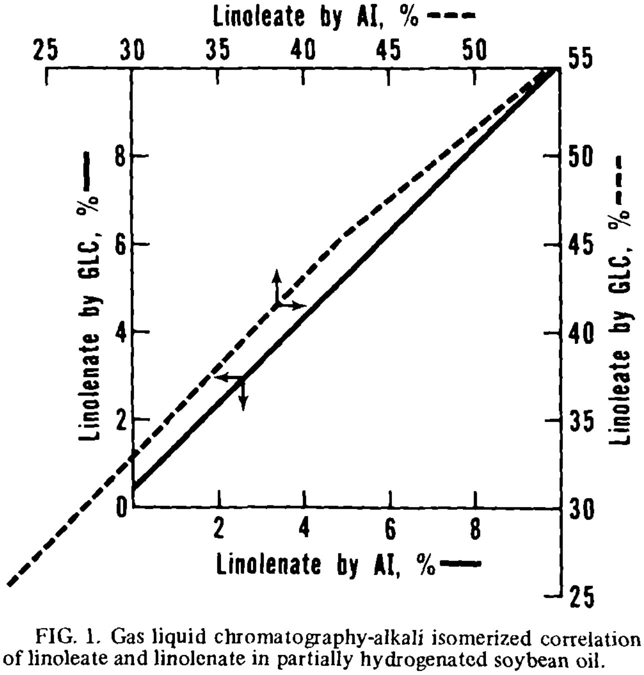

FIG. 1. Gas liquid chromatography-alkali isomerized correlation of linoleate and linolenate in partially hydrogenated soybean oil.

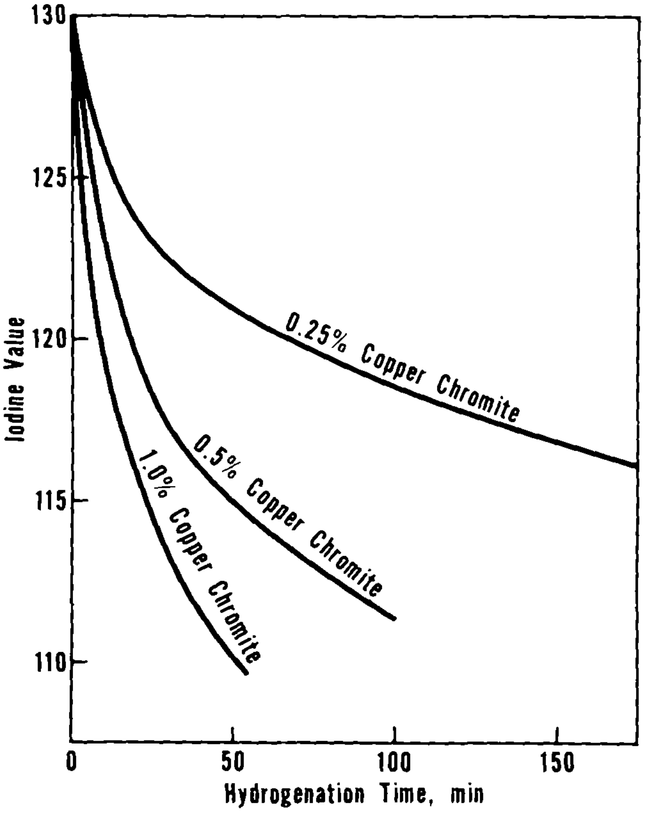

FIG. 2. Activity of copper chromite at catalyst concentrations of 0.25, 0.5, and 1.0% in the oil.

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[1] Presented at the AOCS Meeting, New Orleans, April 1973.

[2] ARS, USDA.

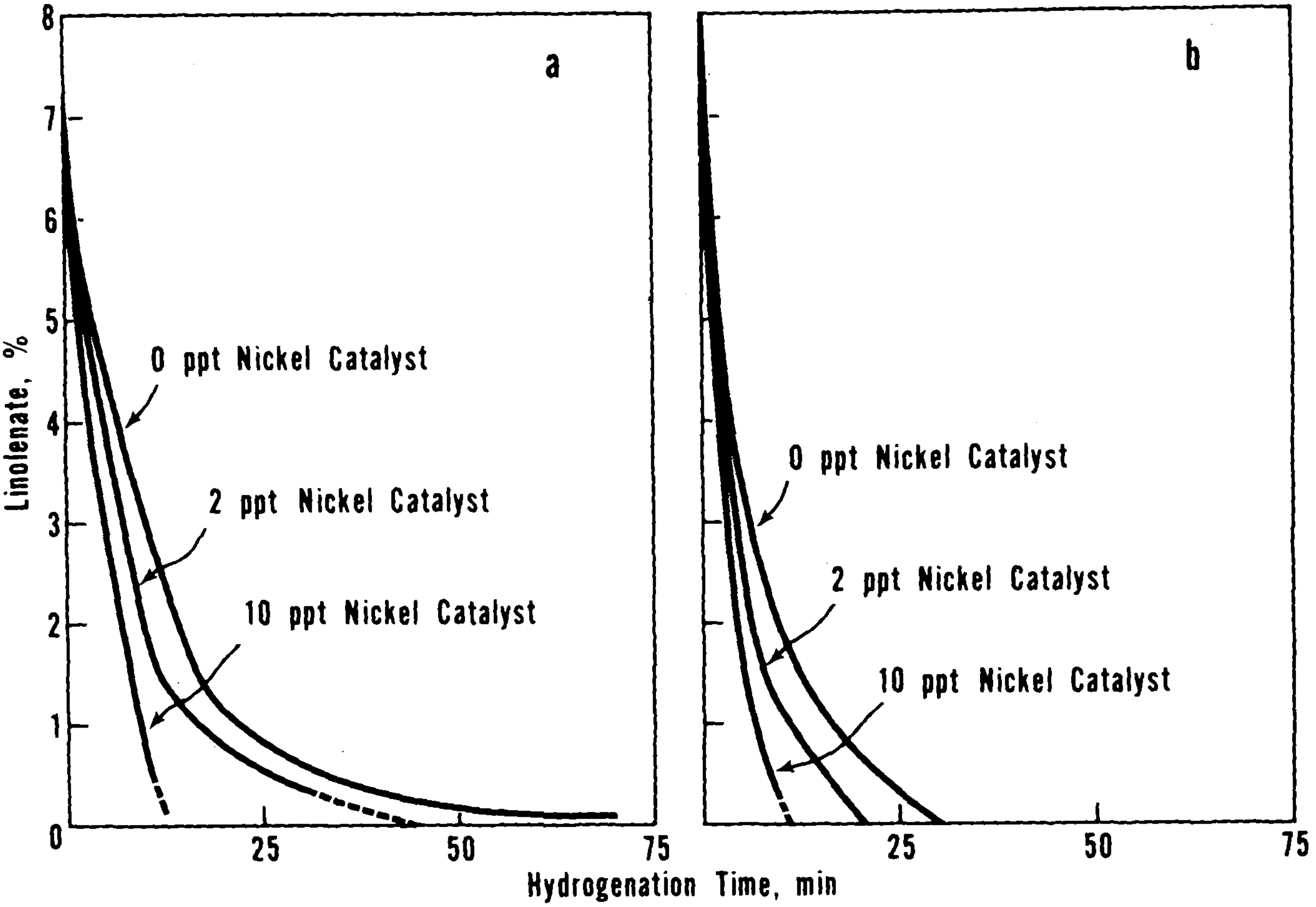

FIG. 3. Effect of 0, 2, and 10 parts per thousand nickel catalyst in copper chromite catalyst on time to hydrogenate soybean oil. Mixed catalyst concentration in oil: (A) 0.5%; (B) 1.0%.

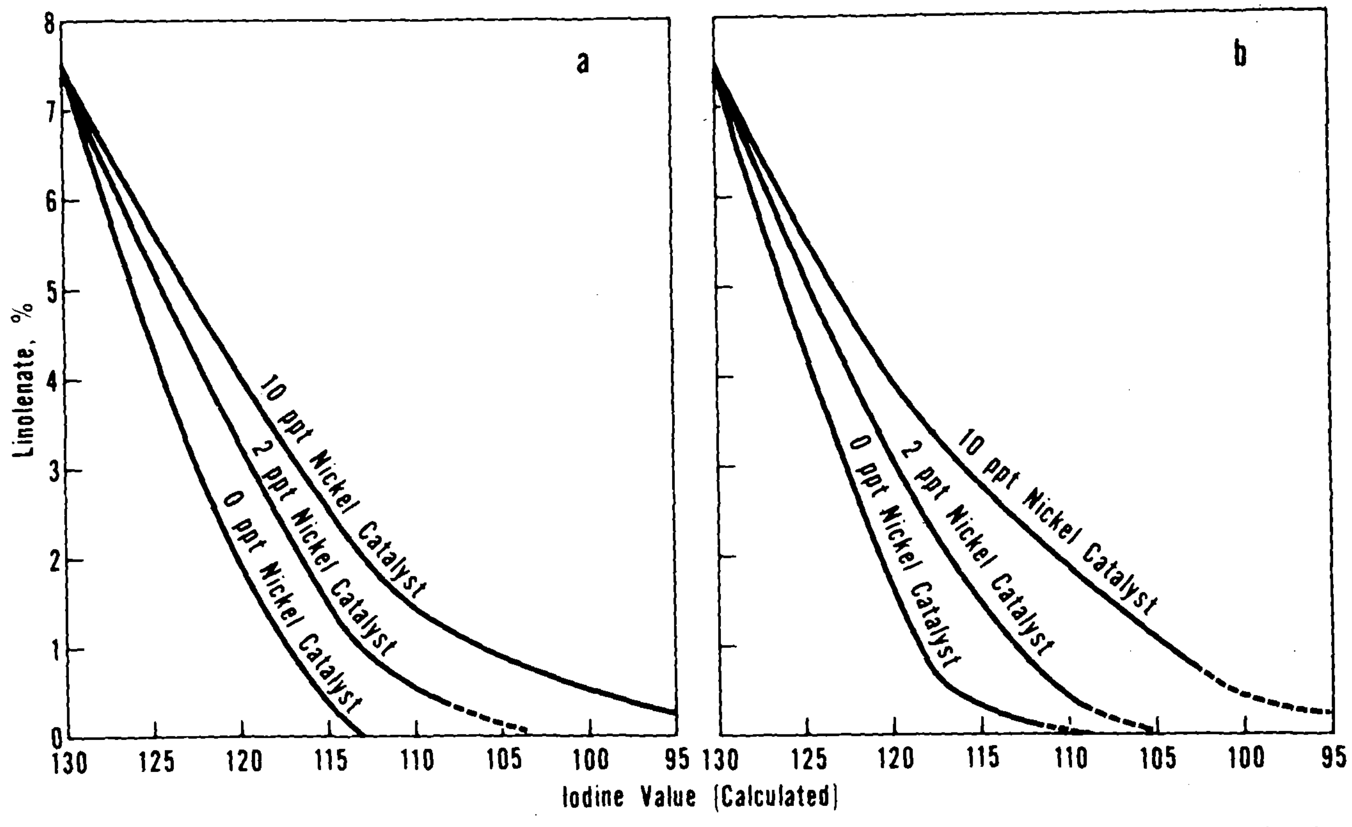

FIG. 4. Selectivity of copper chromite containing 0, 2, and 10 parts per thousand nickel catalyst in copper chromite. Mixed catalyst concentration in oil: (A) 0.5%; (B) 1.0%.

TABLE I

Composition of Selected Partially Hydrogenated Soybean Oil

Ni catalyst in copper chromite, ppt[a]	Calculated IV[b]	Saturated		Monoene, $C_{18:1}$[c]	Diene			Triene, $C_{18:3}$[d]	*trans*	Selectivity, K_{Le}/K_{Lo}	Hydrogenation time, min
		C_{16}[c]	$C_{18:0}$[c]		Conjugatable $C_{18:2}$[d]	Conjugated $C_{18:2}$[e]	Nonconjugatable $C_{18:2}$[f]				
Original SBO[g]	130	11.2	4.9	25.8	50.7	0.4		7.4	0	—	—
Catalyst concentration in oil: 1.0%											
0	122	11.3	4.8	29.7	48.5	1.2	1.4	3.1	4	8	5
0	117	11.2	4.7	33.5	47.0	0.8	1.8	1.1	7	11	15
0	113	11.1	4.6	37.3	43.5	0.6	2.9	0	10	—	30
1.0	120	11.3	4.8	30.8	47.7	1.4	1.4	2.6	5	8	5
1.0	112	10.9	5.1	39.1	41.0	0.7	2.7	0.5	11	8	15
1.0	107	11.0	4.9	44.2	(38.5)	0.6	0.8	(0)	13	—	20
2.0	120	11.2	4.9	32.2	45.5	1.2	1.9	3.1	5	5	5
2.0	114	11.1	4.8	37.7	41.5	0.8	3.0	1.1	9	6	10
2.0	108	11.3	5.3	41.9	(38.1)	0.6	2.5	(0.4)	11	7	15
10.0	114	11.2	5.2	37.2	40.3	0.8	2.8	2.5	7	4	3
10.0	106	11.1	5.4	44.9	(34.3)	0.6	2.9	1.0	11	4	6
10.0	94	11.4	6.3	56.1	(22.8)	0.3	2.9	0.2	17	4	10
Catalyst concentration in oil: 0.5%											
0	119	11.0	4.9	31.7	48.0	1.1	1.5	1.8	6	10	15
0	115	11.6	4.8	35.0	45.5	0.7	2.2	0.2	9	17	40
0	111	11.1	4.9	39.5	(41.2)	0.5	1.7	0.1	12	14	100
0.5	120	11.3	4.9	30.7	48.5	1.0	1.5	2.1	5	10	15
0.5	114	11.4	5.0	38.2	41.2	0.5	3.1	0.6	11	8	45
0.5	108	11.4	5.3	41.3	(39.4)	0.5	2.1	(0)	14	—	65
1.0	124	11.6	5.0	27.8	48.6	1.1	1.3	4.6	2	7	5
1.0	114	11.6	5.3	35.3	43.7	0.7	2.6	0.8	9	9	25
1.0	111	11.8	5.3	38.3	40.5	0.6	2.9	0.6	11	6	35
1.0	107	11.4	5.6	42.2	(38.7)	0.7	1.4	(0)	14	—	50
2.0	126	10.7	4.6	28.4	49.4	1.1	1.2	4.6	3	7	5
2.0	117	11.0	4.9	34.8	44.0	0.9	2.4	2.0	8	6	15
2.0	112	11.1	5.1	39.1	40.2	0.6	3.3	0.6	11	7	25
2.0	109	11.2	5.4	41.0	(38.9)	0.5	2.7	(0.3)	12	8	32
10.0	119	11.6	5.3	31.7	44.5	0.9	2.3	3.7	4	4	3
10.0	112	11.5	5.4	38.5	(39.2)	0.7	2.3	(2.4)	10	4	6
10.0	102	11.4	5.9	47.5	(30.1)	0.5		(0.7)	14	4	10
Catalyst concentration in oil: 0.25%											
0	121	11.1	4.7	30.1	49.5	1.0	1.2	2.4	5	11	45
0	115	11.1	4.5	35.3	46.0	0.7	2.2	0.2	8	17	195
0	111	10.8	4.7	40.6	(39.4)	0.5	4.0	(0)	13	—	405
1.0	121	11.1	4.5	31.3	47.0	0.8	2.0	3.3	6	6	180
1.0	115	11.4	4.8	35.7	44.0	0.7	2.3	1.1	10	8	330
1.0	111	11.3	5.0	39.5	39.5	0.7	3.0	1.0	12	6	420
2.0	122	11.0	4.7	30.7	47.3	1.0	1.8	3.5	4	6	15
2.0	116	11.2	4.7	35.0	44.5	0.7	2.5	1.4	8	8	45
2.0	111	11.2	5.5	38.1	41.0	0.6	3.2	0.4	12	9	75
10.0	123	11.2	5.0	30.7	45.5	0.6	2.2	4.8	4	3	10
10.0	118	11.1	5.2	34.5	42.2	0.6	2.8	3.6	8	3	20
10.0	111	11.1	5.7	40.3	(37.8)	0.4	2.3	(2.4)	11	3	40
20.0	119	11.3	5.4	33.0	42.5	0.7	2.8	4.3	5	3	5
20.0	116	11.0	5.3	36.1	40.3	0.6	3.0	3.7	8	2	10
20.0	111	11.0	5.8	41.3	(36.4)	0.4	2.7	(2.4)	11	3	15

[a] ppt = parts per thousand.

[b] Iodine values calculated from gas liquid chromatography (GLC).

[c] Determined by GLC.

[d] Alkali isomerization (AI) values were determined from Figure 1, except those in parentheses which are analytical values.

[e] Determined by UV.

[f] Determined by difference between total diene value (by GLC) and conjugatable diene.

[g] SBO = soybean oil.

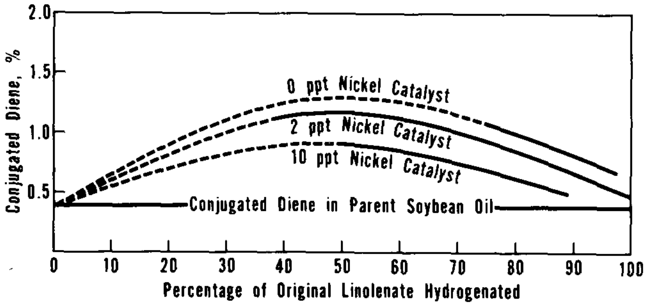

FIG. 5. Effect of nickel (0, 2, and 10 parts per thousand) in mixed catalyst on conjugated diene formed during hydrogenation of soybean oil. Catalyst concentration in oil of 0.5%.

linolenate.

We studied mixed commercial nickel and copper chromite catalysts in combinations where the nickel catalyst (25% Ni) amounted to 0.5, 1, 2, 10, and 20 ppt copper chromite catalyst. The mixed catalysts were used at three levels: 1.0, 0.5, and 0.25% based on oil wt. Selectivity, activity, *trans* formation, and conjugated diene formation were studied. Our findings indicate that small amounts of Ni-cat enhance the copper chromite catalyst's activity without greatly altering the character of the hydrogenated oil.

ANALYTICAL METHODS

The parent soybean oil and partially hydrogenated soybean oil products were esterified with methanolic BF_3 reagent according to Metcalfe et al. (11) and analyzed as follows: (a) Percentage fatty acid composition was determined by gas liquid chromatography (GLC) with an F&M Model 720 gas chromatograph. The 9 ft x 1/4 in. stainless steel column was packed with 20% diethylene glycol succinate (Hi Eff 1 BP) on 80-100 mesh Gas Chrom P (Applied Science Laboratories, Inc., State College, Pa.). The conductivity detector had a bridge current of 150 ma. A 1 μl sample was inserted at an injection temperature of 300 C into the column at 200 C. The helium carrier gas rate was 75 cc/min and detector temperature, 320 C. (b) Percentage *trans* isomer was determined with a Perkin-Elmer Model 337 IR spectrophotometer according to AOCS Tentative Method Cd 14-61 (12). (c) Percentage linoleate and linolenate (conjugatable) were determined by reading values from a GLC alkali isomerized (AI) correlation graph (Fig. 1) for products containing more than 42% linoleate (by GLC) and analyzed by AOCS Official Method Cd 7-58 (12) for products containing 42% (by GLC) linoleate and less. Figure 1 plots actual GLC and AI values determined on more than 100 samples of partially hydrogenated soybean oil. These curves eliminate a time-consuming analysis, which is not an official method for hydrogenated oils but which is most beneficial for evaluating data. The accuracy of this method was described by Moulton et al. (1). (d) Percentage conjugated diene was determined by AOCS Official Method Cd 7-58 (12) with a Beckman DU-2 spectrophotometer.

Iodine values (IV) were calculated from fatty acid composition, as determined by GLC and as adjusted for certain conjugated dienes with the same retention time as linolenate.

Selectivity ratios (K_{Le}/K_{Lo}) were calculated according to the method described by Butterfield et al. (13).

EXPERIMENTAL PROCEDURES

For each set of conditions, 2500 g from a single lot of commercially refined and bleached (IV 130) soybean oil was hydrogenated in a 1 gal autoclave equipped with auxiliary electric strip heaters and an internal coil for either steam heating or water cooling. Provisions were incorporated in the design of the convertor for either hydrogen or nitrogen admission up to 100 psig and vacuum to 30 in. Oil and catalyst were stirred rapidly by a gas dispersion agitator, described earlier by Beal et al. (14), which dispersed head space gas into the oil.

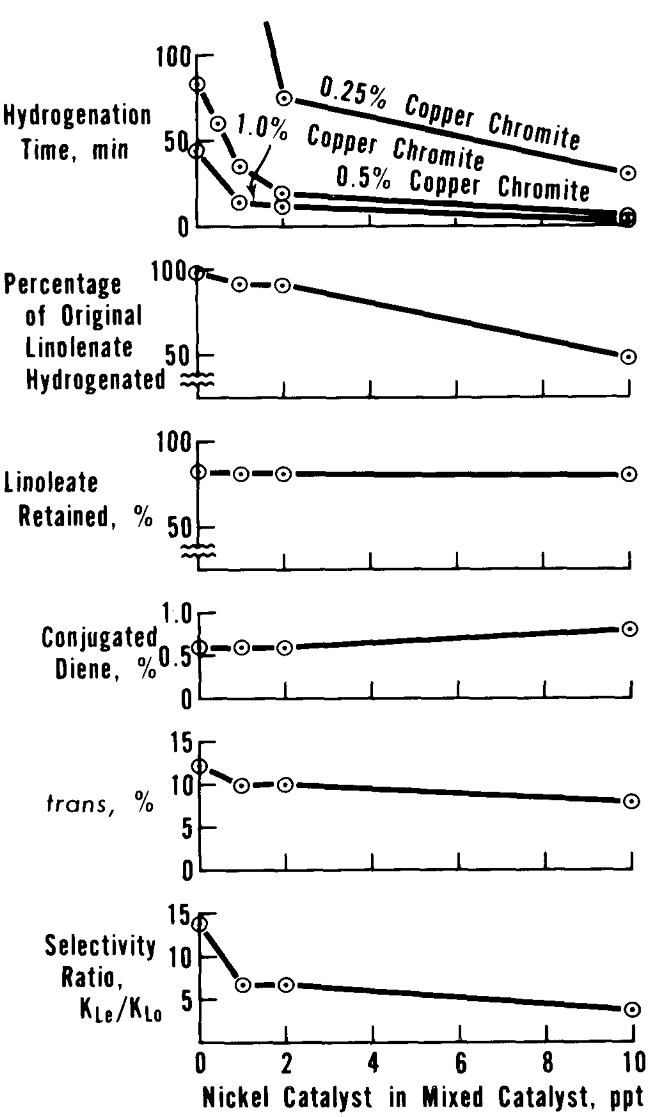

FIG. 6. Influence of added nickel catalyst to copper chromite upon hydrogenation time, amount of linolenate hydrogenated and linoleate retained; selectivity and amount of conjugated diene and *trans* isomer formed. Comparison of hydrogenated soybean oils with an IV of 112.

Catalysts were prepared by mechanically mixing an active nickel catalyst (Girdler G 15, 25% Ni) with an active copper chromite catalyst (Harshaw Cu 1106P, 39% Cu O). Mixed catalysts were prepared containing 0, 0.5, 1, 2, 10, and 20 ppt Ni-cat (equivalent to 0, 0.125, 0.25, 0.5, 2.5, and 5 ppt nickel) in CuCr-cat. These mixed catalysts were compared by hydrogenating soybean oil with them at CuCr-cat concentrations in the oil of 1.0, 0.5, and 0.25%. Testing was conducted in order of increasing Ni-cat content in the mixed catalyst starting with 0 and finishing with 20 ppt. This procedure prevented a catalyst low in nickel from possibly being contaminated by one containing more nickel. Multiple runs with catalysts of the same Ni-cat content were conducted before moving to those having higher Ni-cat content.

Soybean oil and catalyst were charged to the convertor; the convertor was alternately purged with nitrogen and evacuated 3 times, and then its contents were stirred vigorously while heating under vacuum to a constant 175 C at which time hydrogen was admitted and maintained at a pressure of 50 psig. Samples (20 ml) were withdrawn from the convertor periodically onto solid carbon dioxide to cool and protect the hydrogenated product from oxidation and filtered through filter aid. These samples were analyzed immediately by refractive index at 40 C and later by GLC, UV, and IR spectroscopy according to the methods described. After hydrogenation to the desired degree as indicated by refractive index, the convertor was evacuated; the remaining oil was cooled to 80 C under vacuum and filtered. The filtered product was collected under nitrogen, packaged under nitrogen, and stored at 0 C. The convertor was scrupulously cleaned with filtered soybean oil to remove catalyst traces and kept under positive nitrogen pressure between hydrogenation tests to prevent oil oxidation.

RESULTS AND DISCUSSION

Hydrogenation and composition data for each run are compiled in Table I. Only a few values are tabulated to illustrate the progress of hydrogenation. A plot of data for straight copper chromite and straight nickel catalyzed (at 150 C) hydrogenations was published previously (1).

The relative activity of straight copper chromite at various concentrations in the oil is illustrated by Figure 2. When copper chromite concentration was 0.25% in the oil, hydrogenation was slow. Catalyst concentrations of 0.5 and 1.0% gave progressively faster reactions. Addition of Ni-cat at any level to the CuCr-cat also increased the reaction rate. The improvement was a direct function of the amount of Ni-cat added. Figure 3 (3a and 3b) illustrates the relative activity of copper chromite and copper chromite nickel catalysts at concentrations in the oil of 0.5 and 1.0%. With 0.25% catalyst in the oil, a 0 ppt Ni-cat produced an oil with an IV of 111 in 405 min (Table I). A mixed catalyst with 2 ppt Ni-cat reached the same IV in 75 min. Although the reaction was more than 5 times faster with the mixed catalyst containing 2 ppt Ni-cat, the difference in linolenate content for the two 111 IV oils was but 0.4%. Rate increases were also very significant at catalyst levels in oil of 0.5 and 1.0% for a mixed catalyst containing 2 ppt Ni-cat.

Complete reduction of linolenate in soybean oil is desired if the stability of soybean oil is to be increased to the maximum extent (2). Figure 4 (4a and 4b) graphically illustrates the progress and selectivity of the hydrogenation of soybean oil at catalyst concentrations of 0.5 and 1.0%. With a straight copper chromite catalyst, a linolenate-free partially hydrogenated soybean oil was produced at an IV of 109-112; with addition of 1 ppt Ni-cat at an IV of 107, and with 2 ppt Ni-cat, at an IV of 102-107. The addition of 10 ppt and more Ni-cat to CuCr-cat produced a linolenate-free, partially hydrogenated oil with an IV ca. 80, approaching that with a straight nickel catalyst. CuCr-cat with this amount of Ni-cat then gives little or no improvement over straight nickel.

Addition of 2 ppt or less Ni-cat to CuCr-cat had only a small effect on linoleate content of hydrogenated soybean oil. At the 0.5% catalyst level (Table I), CuCr-cat with 0, 0.5, 1, and 2 ppt Ni-cat gave partially hydrogenated oils with 41.2, 39.4, 38.7, and 38.9% conjugatable C:18 diene at 0.1, 0, 0, and 0.3% linolenate levels, respectively. Conjugatable diene is principally linoleate although there is the possibility of some *trans* bond isomers being included. Adding either 1 or 2 ppt Ni-cat to copper chromite greatly improved the rate of hydrogenation with little change over straight copper chromite in the composition of the partially hydrogenated product.

The parent soybean oil contained 0.4% conjugated diene. With straight nickel catalyst, the conjugated diene does not increase appreciably, if at all, during hydrogenation due, in part, to the low selectivity of nickel (6). Soybean oil partially hydrogenated with straight copper chromite at 175 C and 50 psig produced up to 1.0% more conjugated diene than present in the parent oil when ca. 65% of the linolenate in the oil had been converted (Fig. 5). Koritala (15) found that conjugation precedes hydrogenation when copper chromite is the catalyst. The conjugated diene present may be that formed but not yet hydrogenated. However, after more than 95% linolenate was reduced during the same hydrogenation, only 0.3% additional conjugated diene was found in the hydrogenated oil. This amount of conjugated diene is independent of the copper chromite catalyst concentration in the oil. For 0.5% mixed catalysts containing 0.5, 1, and 2 ppt Ni-cat, an increase of only ca. 0.1% conjugated diene was produced when 95% linolenate was converted. With higher hydrogen pressures, less conjugated diene reportedly is produced with straight copper chromite catalyst (16).

Mixed copper chromite nickel catalysts containing 10 and less ppt Ni-cat are compared in Figure 6. The data were collected at 112 IV by interpolation or extrapolation of actual data. Addition of 0.5 to 2 parts Ni-cat per thousand parts CuCr-cat significantly improved the catalytic activity of straight copper chromite especially at 0.5 and 1.0% levels. Oils hydrogenated with these mixed catalysts retained 80% of the original linoleate when 90% of the original linolenate was reduced. Oils hydrogenated with straight copper chromite catalyst retained 83% of the linoleate and with straight nickel catalyst retained only ca. 50% at this same linolenate level. The amounts of *trans* isomer and conjugated diene formed in the oil during hydrogenation with these mixed catalysts were ca. the same as for soybean oil partially hydrogenated to an IV of 112 with straight copper chromite. Considering these data, with respect to the quality of the partially hydrogenated oil, a decrease in selectivity from 14 for straight copper chromite to 7-8 for 0.5 to 2 ppt Ni-cat in CuCr-cat may not have great significance for a practical operation.

These mixed catalysts are much more selective than a straight nickel catalyst and may be more acceptable for industrial use because of their significantly improved activity over a straight copper chromite catalyst.

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