

Effects of Minor Compounds on Hydrogenation Rate of Soybean Oil

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The poisoning effects of minor compounds in soybean oil on the activity of nickel-based catalysts during hydrogenation was investigated. Several soybean oils prepared by different processes were used as the starting oils for hydrogenation. Soybean oil prepared by combining neutralization with degumming and then followed by bleaching leads to a slower hydrogenation rate than an oil prepared by sequential degumming, neutralization and bleaching with activated clay. The selection of bleaching earth used in the bleaching process affected the hydrogenation rate. Soybean oil bleached with neutral clay showed a slower hydrogenation rate. Higher amounts of phosphorus compounds, oxidation products, β -carotene and iron in these oils accounted for the slower hydrogenation rate. Storage of refined and bleached soybean oil greatly affected the hydrogenation rate. An increase in the oxidation products of RB soybean oil during storage was the major reason for the decrease in the hydrogenation rate.

KEY WORDS: β -Carotene, hydrogenation, iron, nickel catalyst, oxidation products, phosphorus.

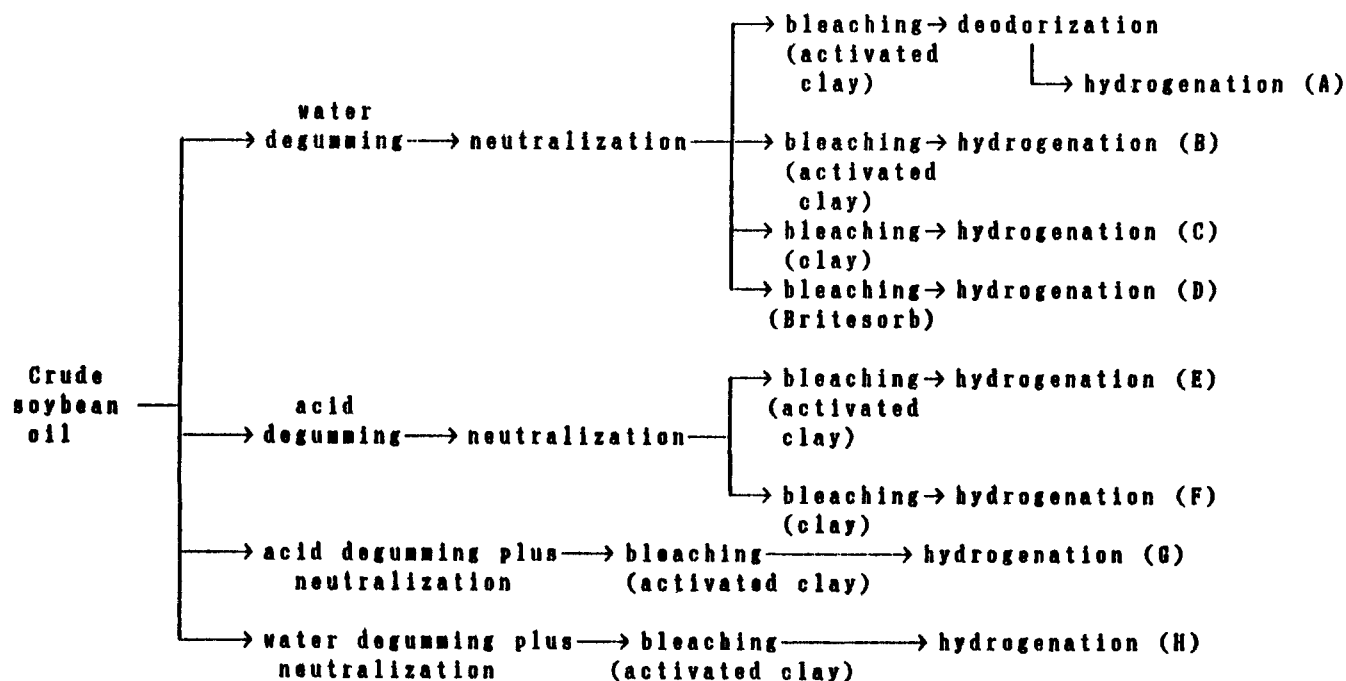
The effects of catalyst poisons on the hydrogenation of oils and fats have been studied previously (1-4). Generally, catalyst poisons have been identified as oil impurities, which reduce the catalyst's activity. These impurities are either decomposition products or residual compounds present after

refining and bleaching processes. Koritala (5) indicates that crude oil subjected to hydration, neutralization and bleaching before hydrogenation contains considerable amounts of poisons that inactivate catalysts to varying degrees. These poisons, including sulfur, phosphorus compounds, free fatty acid, oxidized fatty acids and sodium soaps, have an inactivating effect on nickel catalysts (3,6). In this study, the effects of minor compounds of soybean oil obtained from different refining processes on the hydrogenation rate were investigated. In addition, the extent to which compounds act as catalyst poisons during hydrogenation also was determined.

EXPERIMENTAL PROCEDURES

Materials. Crude soybean oil was purchased from a local soybean oil plant. Nickel catalyst used in this experiment was Resan 22 (22% Ni) obtained from Engelhard Co. (Cleveland, OH). Neutral clay (Celite) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and Britesorb was supplied by PQ Co. (Valley Forge, PA).

Refining and hydrogenation processes. Crude soybean oil was subjected to various refining processes, as can be seen in Scheme 1. For water degumming, 2% deionized water, based on oil volume, was added to the oil at 60°C and agitated for 30 min. For acid degumming, 0.25% concentrated (85%) phosphoric acid, based on oil weight, was



SCHEME 1

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first added to the oil at 60°C and agitated for 10 min. Then, 2% deionized water, based on oil volume, was added to the oil and agitated for 20 min. For neutralization, all the oil batches were refined by 18 Be' caustic soda with 0.20% excess based on the content of free fatty acid in the oil. For the combination of degumming and neutralization, degumming was performed for the first 10 min and followed by neutralization for 20 min. For bleaching, the oils were bleached with 2% neutral or activated clay under vacuum at 110°C for 20 min. For deodorization, the conditions were as in the commercial process (240°C, 1 h, 3 mm Hg). The refined and bleached (RB) or refined, bleached and deodorized (RBD) oil was then subjected to hydrogenation with 0.03% nickel catalyst based on nickel content at 180°C and 2.5 Kg/cm² hydrogen pressure.

Analyses. The analyses carried out on the RB or RBD oils from each oil batch included AOCS methods for peroxide value, Cd 8-53; acid value, Cd 3a-63; total phosphorus content, Ca 12-55; color, Cc 13b-45; and Fe content, Ca 18-79 (7); as well as anisidine value (8) and β -carotene (9).

RESULTS AND DISCUSSION

Refining and bleaching processes. Crude soybean oil was subjected to different refining and bleaching processes as shown in Scheme 1. The hydrogenation rates of these bleached or deodorized oils were determined during the reaction. In Table 1, RB soybean oils from oil batches C and F bleached with neutral clay (Celite) showed a lower hydrogenation rate than the other oil batches bleached with activated clay. A higher content of total phosphorus, oxidation products, Fe and β -carotene apparently caused the lower hydrogenation rate. The neutral clay did not efficiently remove these minor compounds during bleaching. However, the hydrogenation rate from oil batch D (RB soybean oil), which was bleached with the other neutral clay (Britesorb supplied by PQ Corp.), was similar to the rates from the oil batches A, B and E. The higher reaction rate of oil batch D, compared to those of oil batches C and F, was ascribed to the lower total phosphorus, oxidation products and Fe content. Britesorb, a selective adsorbent, was more effective than Celite for the removal of Fe, phosphorus compounds and oxidation products.

The crude oils of batches A, B and E, which were degummed by either water or phosphoric acid followed by

centrifugation and then neutralization, had hydrogenation reaction rates above 2 Δ IV/min. The combination of degumming and neutralization followed by centrifugation (oil batches G and H) gave a lower hydrogenation rate. Oil batch H, a combination of water degumming and neutralization, showed a slight decrease in the reaction rate. However, oil batch G, an RB oil prepared by a combination of acid degumming and neutralization and containing high amounts of total phosphorus, oxidation products, free fatty acids, Fe and β -carotene, showed a greater decrease in the hydrogenation rate.

Catalyst inhibitors. Sulfur, phosphorus compounds, free fatty acids, soaps and oxidation products of the oil have been reported to be poisonous to catalyst activity (3,5). In this study, phosphorus compounds and oxidation products of the oil showed significant effects on the inhibition of catalyst activity. In Table 2, the increase in the total phosphorus content and oxidation value (OV) (OV = 2 peroxide value + 1 anisidine value) of oils correlate well with the decrease in the hydrogenation rate, while the increase in free fatty acid and carbonyl values were not well correlated with reducing reaction rate. As shown in Figures 1 and 2, when the total phosphorus content and the oxidation value of bleached oil were more than 20 ppm and 8 ppm, respectively, the reaction rate was reduced below 2 Δ IV/min. In addition to total phosphorus compounds and oxidation products, several authors (4,9) note that catalysts are strongly poisoned by alkali soaps. In our experiment, the soap content of all the oil batches was not detectable due to the repeated washing of neutralized oil with warm, deionized water.

Addition of iron, either to the oil as soap or to the catalyst during preparation, are reported to diminish catalyst activity during hydrogenation (5). In our study, iron content was well correlated with the hydrogenation rate, and the rate was reduced to 2 Δ IV/min when the iron content of RB soybean oil was above 0.4 ppm (Fig. 3). β -Carotene is reported to have an inhibitory effect on copper catalyst during hydrogenation of soybean oil (5). Most of the β -carotene is decomposed after refining, bleaching and deodorization. Among the oil batches studied here, only oil batches A (RBD oil), B and E (RB oil), the β -carotene contents of which were below 1 ppm, had a Δ IV of above 2/min. When the β -carotene content was more than 2 ppm, the hydrogenation rate was reduced to below

TABLE 1

Analytical Results^a of Soybean Oils Prepared from Different Processes in Relation to the Hydrogenation Rate

Batch ^b	Rate ^c (Δ IV/min)	PV/AnV	OV ^d	COV	AV	TP (ppm)	Fe (ppm)	β -carotene (ppm)
A	2.285 \pm 0.001	0.24/3.50	3.98	7.78	0.09	10.56	.18	.33
B	2.440 \pm 0.091	0.31/4.10	4.72	7.83	0.26	14.46	.25	.50
C	1.662 \pm 0.036	3.96/6.03	13.95	8.59	0.26	28.10	.62	2.78
D	2.251 \pm 0.031	1.43/3.17	6.03	4.74	0.26	19.28	.28	2.16
E	2.243 \pm 0.091	0.22/4.28	4.72	5.54	0.14	8.52	.29	.84
F	1.584 \pm 0.004	3.00/8.55	14.56	9.13	0.22	69.31	.88	3.16
G	1.764 \pm 0.058	0.85/8.97	10.67	7.84	1.01	34.10	.54	2.65
H	2.012 \pm 0.002	0.38/5.43	6.19	7.17	0.17	16.66	.36	2.13

^aMeans are triplicate samples.

^bBatch types are according to Scheme 1.

^cMeans \pm SE.

^dOV = 2 PV + AnV.

Abbreviations: AV, acid value; AnV, anisidine value; COV, carbonyl value; PV, peroxide value; TP, total phosphorus; OV, oxidation value.

TABLE 2

Correlation r Between Hydrogenation Rate and the Respective Chemical Analysis.^a

Total phosphorus content	0.8777 ^b
Oxidation value	0.9489 ^b
Fe content	0.9353 ^b
β -Carotene	0.9107 ^b
Carbonyl value	0.6602 ^c
Acid value	0.4000 ^c

^aSample size is 25.

^bSignificant at the 1% level.

^cSignificant at the 5% level.

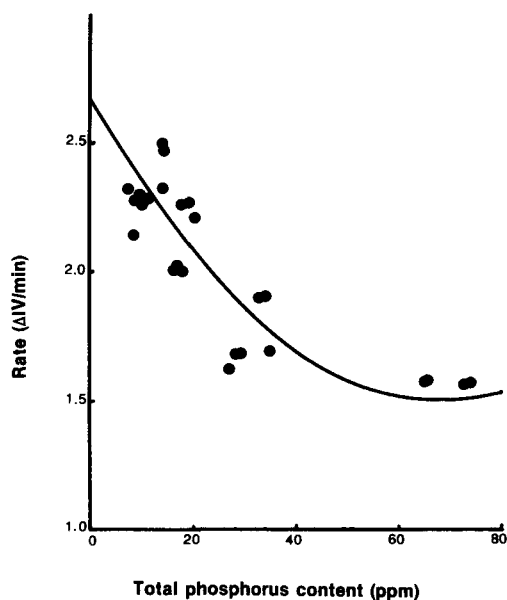


FIG. 1. Relationship between the rate of hydrogenation and the total phosphorus content of soybean oil.

2 Δ IV/min (Fig. 4). Although the β -carotene of oil batches D and H were above 2 ppm, the lower amount of total phosphorus and oxidation products were responsible for the higher hydrogenation rate compared to oil batches C, F and G.

Storage of RB soybean oil. Hydrogenation was performed on RB soybean oil of batch E after storage at different intervals. The reaction rate was reduced from 2.243 to 1.256 Δ IV/min after 24 d of storage (Fig. 5). The results of analysis are shown in Table 3. The peroxide, anisidine and carbonyl values of the RB soybean oil increased as oil storage was prolonged. The acid value increased after two days of storage and remained at 0.20–0.26 mg/g during storage. The total phosphorus content was not changed during storage. Comparison of the reaction rate at each day of storage with the individual analytical results indicated that the reduction of reaction rate was highly correlated with the increase in carbonyl ($r = -0.923$), oxidation ($r = -0.904$) and acid values

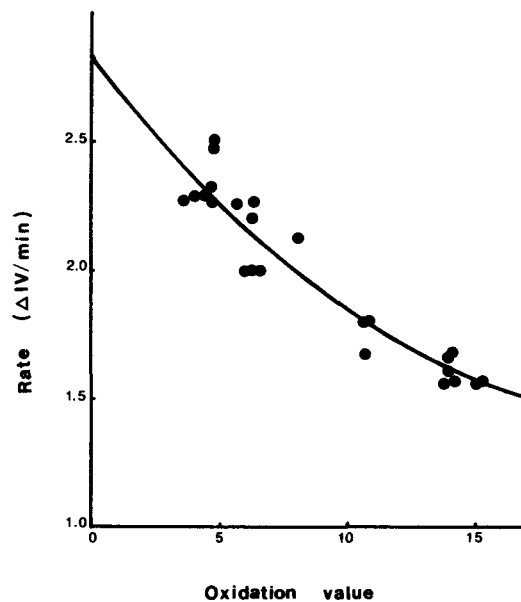


FIG. 2. Relationship between the rate of hydrogenation and the oxidation value of soybean oil.

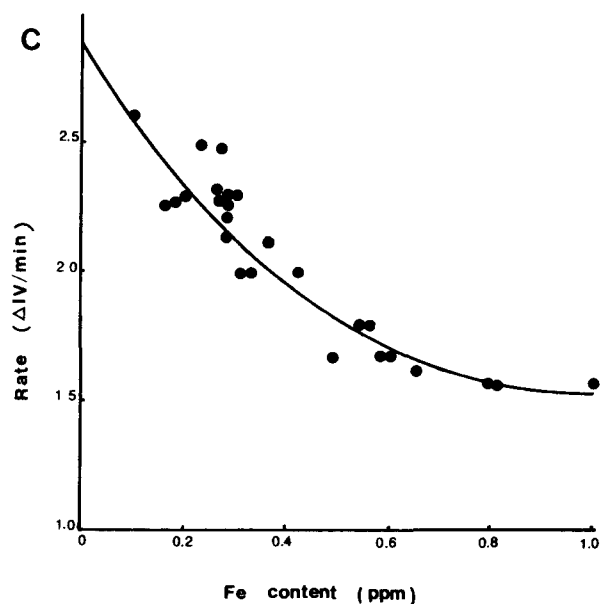


FIG. 3. Relationship between the rate of hydrogenation and the iron content of soybean oil.

($r = -0.839$). As a consequence it was concluded that during hydrogenation of RB soybean oil, the oxidation products of soybean oil produced during storage had a strong influence on the reduction of the hydrogenation rate.

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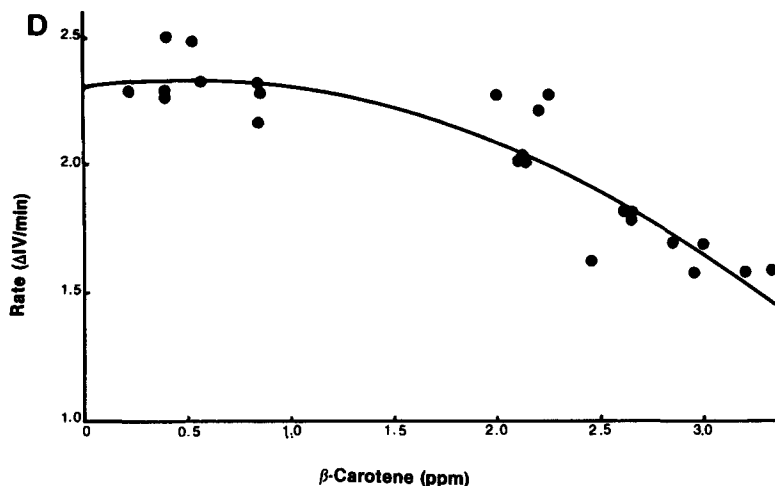


FIG. 4. Relationship between the rate of hydrogenation and the β -carotene content of soybean oil.

TABLE 3

Effect of Chemical Change of Bleached Soybean Oil^a During Storage on the Hydrogenation Rate

Storage Days	PV ^b	AnV	OV ^c	COV	AV	TP
0	0.21	4.5	4.92	5.32	0.11	8.92
2	0.54	5.0	6.08	5.38	0.20	8.90
4	0.70	5.2	6.60	6.38	0.21	8.32
7	0.79	5.2	6.78	6.30	0.24	8.11
9	0.90	5.4	7.20	7.32	0.23	7.32
11	0.91	5.6	7.42	7.32	0.24	8.01
13	1.52	6.2	9.24	8.10	0.23	8.31
17	2.00	7.0	11.0	8.92	0.25	8.30
20	2.32	7.2	11.84	8.72	0.26	8.31
24	2.54	7.3	12.38	9.15	0.24	8.31

^aBatch E, Scheme 1.

^bAbbreviations: AV, acid value; AnV, anisidine value; COV, carbonyl value; OV, oxidation value; PV, peroxide value; TP, total phosphorus.

^cOV = 2 PV + AnV.

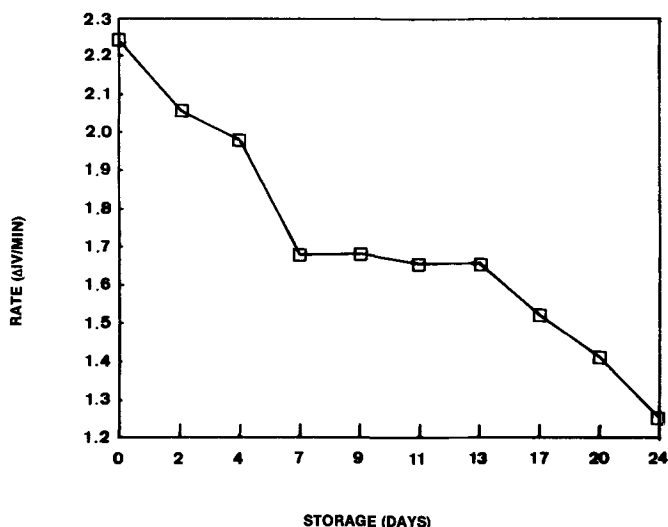


FIG. 5. Change of hydrogenation rate of refined and bleached soybean oil due to storage.

ACKNOWLEDGMENTS

This research was supported by both the Council of Agricultural in Taiwan, R.O.C., and the Office of International Cooperation and Development, USDA, U.S. (project no. TWARS-9). The authors thank T.L. Mounts for providing valuable assistance.

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[Received January 28, 1992; accepted June 28, 1992]