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REFERENCES

1. Lea, C.H., J. Sci. Food Agric. 8:1 (1957).
2. Wilson, B.R., A.M. Pearson and F.B. Shorland, J. Agric. Food Chem. 24:7 (1976).
3. Sessa, D.J., K. Warner and D.H. Hong, J. Food Sci. 39:69 (1974).
4. Sessa, D.J., K. Warner and J.J. Rackis, J. Agric. Food Chem. 24:16 (1976).
5. Roubal, W.T., JAOCS 44:325 (1967).
6. Hornstein, I., P.F. Crowe and M.J. Heimberg, J. Food Sci. 26:581 (1961).
7. Crossley, A., T.D. Heyes and B.J.F. Hudson, JAOCS 39:9 (1962).
8. Endres, J.G., V.R. Bhalerao and F.S. Kummerow, Ibid. 39:118 (1962).
9. Endres, J.G., V.R. Bhalerao and F.S. Kummerow, Ibid. 39:159 (1962).
10. Selke, E., W.K. Rohwedder and H.J. Dutton, Ibid. 52:232 (1975).
11. Selke, E., W.K. Rohwedder and H.J. Dutton, Ibid. 54:62 (1977).
12. Nawar, W.W., J.R. Champagne, M.F.Dubravcic and P.R. LeTellier, J. Agric. Food Chem. 17:645 (1969).
13. Nakanishi, R., and K. Suyama, Agric. Biol. Chem. 38:1141 (1974).
14. Pokorny, J., P. Rai and G. Janicek, Z. Lebensm.Unters. Forsch. 153:322 (1973).
15. Tai, T., J. Pokorny and G. Janicek, Ibid. 156:256 (1974).
16. Nichols, P.C., and R.T. Holman, Lipids 7:773 (1972).
17. Brodnitz, M.H., W.W. Nawar and I.S. Fagerson, Ibid. 3:59 (1968).
18. Thaler, H., and W. Saumweber, Fette Seifen Anstrichm. 63:945 (1961).
19. Pokorny, J., P. Tai and G. Janicek, Nahrung 20:149 (1976).

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Evaluation of Hydrogenation Catalyst Activity

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ABSTRACT

The AOCS Recommended Practice for testing activity of hydrogenation catalysts was used to compare activity and properties of a number of commercial catalysts with the AOCS standard catalyst. Four of five commercial catalysts tested were similar to the standard but one commercial catalyst was markedly more active and more selective. It also was very difficult to filter after hydrogenation. Selectivity of the catalysts in hydrogenation of soybean oil was determined from change in fatty acid composition. The most selective catalyst produced the highest level of *trans* isomers and the highest dropping point. Solid fat contents measured after 30 and 40 min of hydrogenation time were determined by wide-line nuclear magnetic resonance. The Recommended Practice and standard catalyst were useful tools in evaluating activity and selectivity of hydrogenation catalysts.

INTRODUCTION

During the hydrogenation of oils, the progress of the reaction is influenced by process conditions as well as the characteristics of the catalyst used (1). A catalyst can be described in terms of activity, which refers to the amount of catalyst needed to hydrogenate a batch of oil in a reasonable time, and its selectivity, which refers to the ratio of the reaction constants of 2 of the participating fatty acid species (2). According to Allen (1), activity may be defined as the decrease in iodine value (IV) per unit of time under specific conditions of hydrogenation. To enable easier comparison of different catalysts, the American Oil Chemists' Society has issued a Recommended Practice (3) for evaluation of the activity of catalysts. This involves hydrogenation of soybean oil with a standard catalyst and comparison with the results obtained with other catalysts. The effect of particle size of the catalyst on the activity has been studied by Dafler (4), who concluded that the catalysts with the smallest particle size are not necessarily the most active. Catalyst particle size is important in filtration of the hydrogenated oil as oils containing extremely small particles are difficult to filter and result in high nickel content.

This study was undertaken to evaluate a number of commercial hydrogenation catalysts using the recommended practice and the AOCS standard catalyst.

EXPERIMENTAL

Refined and bleached soybean oil was supplied by Canada Packers Ltd. of Toronto, Ontario. The hydrogenation catalysts were commercially available and were the dry-reduced type, except one was wet-reduced. The standard hydrogenation catalyst was obtained from the American Oil Chemists' Society. Hydrogenations were carried out in a Parr pressure reaction apparatus, series 4500, using a 2-ℓ bomb and a charge of 1 ℓ of oil. The hydrogenation conditions selected were: temperature 176 C, hydrogen pressure 200 kPa (15 psig) and catalyst concentration 0.2% (corresponding to 0.05% nickel). Agitation speed in the reactor was 610 rpm; an IV of 80 was reached with soybean oil and the standard catalyst within 40 ± 4 min as required by the AOCS recommended practice.

Iodine values were determined by the Wijs method (AOCS Cd 1-25). *Trans* fatty acids were determined by the infrared spectrophotometric method (AOCS Cd 14-61). Fatty acid composition was determined by gas liquid chromatography (GLC) of the methyl esters on a 125-cm column packed with 15% DEGS on Chromosorb RZ-60/80 mesh operated at 185 C and using a model 402 Hewlett Packard instrument with dual flame ionization detectors. Dropping point of hydrogenated fats was determined with the Mettler FP3 automatic dropping point apparatus as described by Mertens and deMan (5). Ease of filtration was evaluated by heating the hydrogenated oils with 0.1% diatomaceous earth for 10 min at 150 C and filtering them under vacuum (1.35 kPa or 10 mm Hg) through a Whatman No. 40 filter with a filter area of 12.5 cm^2. The time required for 250 ml of oil to pass through the filter

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was recorded.

Color of the filtered oil was determined by the AOCS photometric method (Cc 13c-50) using a Bausch and Lomb 700 spectrophotometer. The estimation of color was done on the second 250 ml of filtrate so that some filter cake would be present on the filter.

The content of nickel soaps in the filtered oil was estimated by the Cocks and Van Rede method (6) using α-furildioxime in hexane as reagent and measuring the absorbance at 458 nm.

Solid fat content of the hydrogenated oils was determined by wide-line nuclear magnetic resonance using a Newport Analyzer Mk 3 with temperature controlled magnet assembly. The samples were kept at 60 C for 30 min, then immersed in a 0 C bath for 15 min and in a 25 C bath for 30 min and again at 0 C for 15 min. Readings were then taken with the analyzer at 0, 5, 10, 15, 20, 25 and 60 C. Olive oil was used as a reference material. The percentage of solid fat was calculated as described by Mertens and deMan (7).

RESULTS AND DISCUSSION

The activity of the five catalysts was fairly close to that of the AOCS standard (Table I). Only catalyst D was markedly more active with a ΔIV of 1.39/min, whereas the other catalysts had a ΔIV in the range of 1.10-1.20. The fatty acid composition of the original oil and the products hydrogenated with the various catalysts is presented in Table II. From these data, the catalyst selectivity was calculated using Allen's method (1) as originally proposed by Albright (2). The selectivity ratio is defined as K_2/K_3, where $K_2 = 1 - L/L_0$ and $K_3 = S - S_0$ (L_0 and S_0 represent the linoleic and stearic acid contents in the original oil, L and S in the hydrogenated sample). These selectivity ratios are listed in Table III, and from our data, a graph was constructed from which the selectivity ratio can be determined from known values of L/L_0 and S-S_0. This graphical representation is presented in Figure 1, and this is similar to graphs prepared by Allen (1) and Albright (2). The data presented in Table III relate to the experimental results obtained with the 6 different catalysts. Catalyst D had the highest activity and also had the highest selectivity ratio. The other catalysts, although very similar in activity, had widely differing selectivity ratios.

TABLE I

Hydrogenation of Soybean Oil (IV-127.4) with Different Catalysts

Catalyst	IV	Hydrogenation time (min)	ΔIV/min
A	80.2	40	1.18
B	83.5	40	1.10
C	79.5	40	1.20
D	79.0	34	1.39
E	80.6	40	1.18
Standard	81.2	40	1.16

TABLE II

Fatty Acid Composition of Soybean Oil and Soybean Oil Hydrogenated with Different Catalysts (hydrogenation time as in Table I)

	Fatty acids (wt %)				
Sample	16:0	18:0	18:1	18:2	18:3
Soybean oil (SO)	10.2	4.4	25.3	50.4	9.8
SO-cat. A	10.1	7.8	66.1	16.0	0.5
SO-cat. B	10.4	9.5	65.9	13.5	0.6
SO-cat. C	10.3	13.9	61.7	12.5	1.6
SO-cat. D	10.0	6.3	66.8	15.0	0.5
SO-cat. E	10.7	10.5	66.0	12.6	0.2
SO-St. cat.	10.3	7.9	71.7	10.1	tr

TABLE III

Catalyst Selectivity in the Hydrogenation of Soybean Oil (hydrogenation time as in Table I)

Catalyst	S-S_0	L/L_0	Selectivity ratio
A	3.41	0.255	21.8
B	5.10	0.208	15.5
C	9.56	0.180	8.6
D	1.90	0.300	36.8
E	5.71	0.222	13.6
Standard	3.53	0.123	24.8

During hydrogenation, *trans* isomers are formed which contribute to the increased melting point of partially hydrogenated oils. *Trans* isomer formation was influenced by the nature of the catalyst used. Table IV lists the *trans* contents of the oils hydrogenated with the various catalysts and the range was from 28.4 to 36.7%. Catalyst D resulted in a markedly higher *trans* content and this is reflected in the dropping points listed in Table IV. The filtration characteristics of the oils after hydrogenation are presented in Table V. Filtration was relatively easy for all but the oil hydrogenated with catalyst D. This sample filtered so slowly that the time required for obtaining 250 ml filtrate was excessive. This sample also had the highest color in the filtrate. The slow filtration of catalyst D has been the subject of investigation by El-Shattory and deMan (8) and apparently is related to the small particle size of this catalyst after hydrogenation. The nickel content of the filtrate was below 1 mg/kg for all samples, with the exception of sample E, which had a nickel concentration of 2.1 mg/kg in the filtrate.

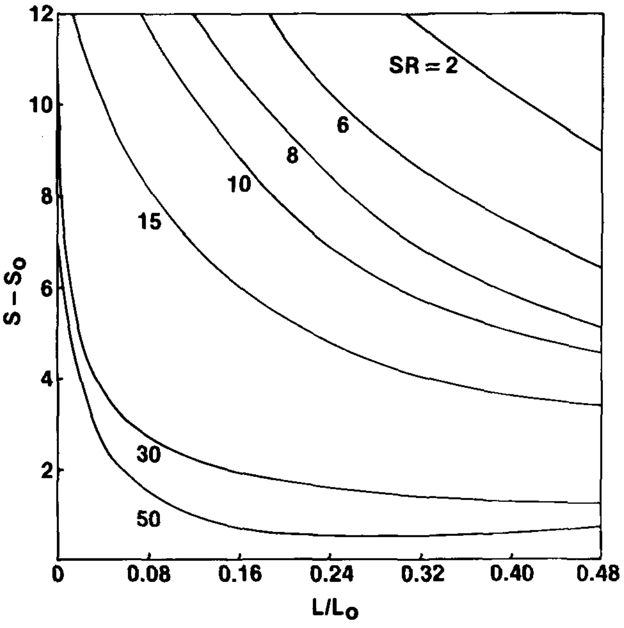

FIG. 1. Graph for the calculated selective ratios (SR) from the change in fatty acid composition during hydrogenation of soybean oil.

TABLE IV

Trans Content and Dropping Point of Soybean Oil Hydrogenated with Different Catalysts (hydrogenation time as in Table I)

Catalyst	*Trans* (%)	Dropping point (°C)
A	28.9	30.5
B	30.3	32.1
C	28.4	29.4
D	32.2	25.4
E	29.1	31.7
Standard	31.4	31.5

TABLE V

Filtration Characteristics of Soybean Oil Hydrogenated with Different Catalysts (hydrogenation time as in Table I)

Catalyst	Filtration time for 250 ml (min)	Color of filtrate	Ni in filtrate (mg/kg)
A	8.4	2.31	0.8
B	6.3	0.27	0.7
C	1.6	0.70	0.2
D	34.0[a]	4.98	0.6
E	8.1	2.39	2.1
Standard	4.0	2.02	0.7

[a] For 140 ml only.

The solid fat contents of the hydrogenated oils at temperatures from 0 to 25 C were determined after 30 min and 40 min of hydrogenation. The results of these measurements are given in Figures 2 and 3. The use of catalysts A, B and E resulted in closely similar solid fat contents at 30 as well as 40 min of hydrogenation. Sample C has the flattest solid contents curve, and this is the sample with the lowest *trans* content and the lowest dropping point.

The availability of a standard catalyst has been found useful in comparisons of properties of various catalysts and their effect on the properties of the hydrogenated oils.

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REFERENCES

1. Allen, R.R., JAOCS 55:792 (1978).
2. Albright, L.F., Ibid. 42:250 (1965).
3. AOCS Official and Tentative Methods, Recommended Practice No. 17-76.
4. Dafler, J.R., JAOCS 54:17 (1977).
5. Mertens, W.G., and J.M. deMan, Ibid. 49:366 (1972).
6. Cocks, L.V., and C. Van Rede, Laboratory Handbook for Oil and Fat Analysts, Academic Press, London and New York, 1966.
7. Mertens, W.G., and J.M. deMan, Can. Inst. Food Sci. Technol. J. 5:77 (1972).
8. El-Shattory, Y., and J.M. deMan, submitted for publication (1980).

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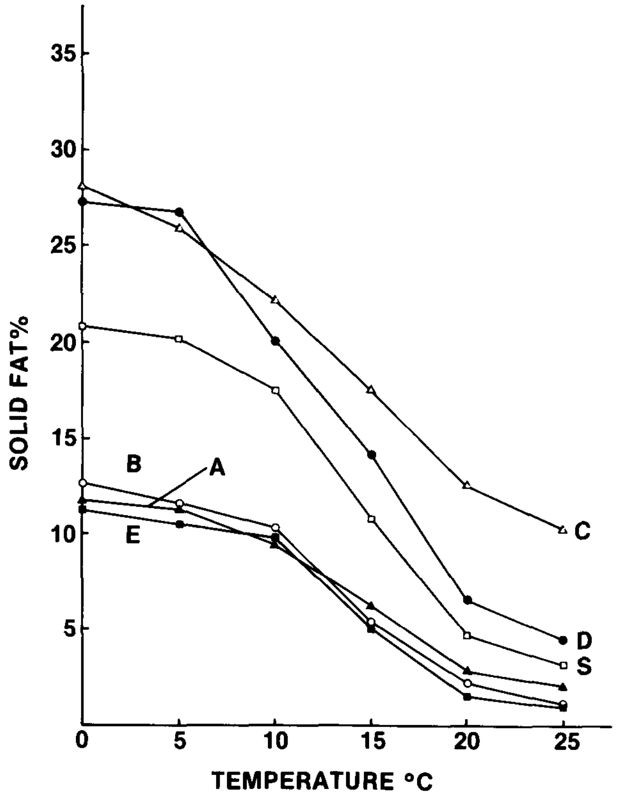

FIG. 2. Solid fat content of hydrogenated soybean oil after 30 min hydrogenation time, using catalysts A-E and standard catalyst.

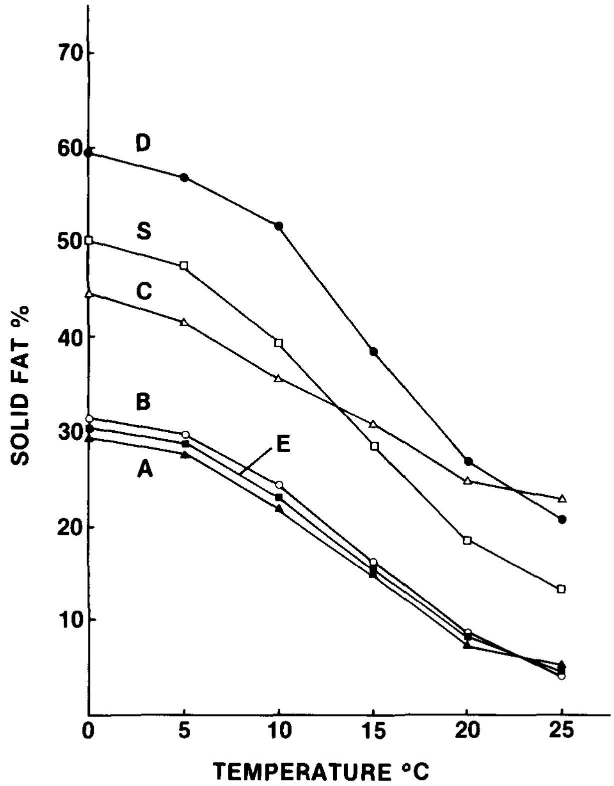

FIG. 3. Solid fat content of hydrogenated soybean oil after 40 min hydrogenation time, using catalysts A-E and standard catalyst.