Effect of Agitation on Selectivity in the Hydrogenation of Soybean Oil[1]

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THE relation of catalyst, temperature, and pressure to the selectivity of the hydrogenation reaction for vegetable oils has been studied extensively (1). The effect of agitation on selectivity has been investigated, but it is not yet thoroughly understood, particularly when considered in combination with other factors. Increasing the degree of agitation is generally considered to favor non-selectivity and to suppress the formation of higher melting *trans* isomers (2, 3). This report summarizes the results of a pilot-plant study of agitation in relation to the hydrogenation of soybean oil. The gross findings require, at the least, an extension of previous conceptions. Moreover they have practical implications which may be of immediate value for commercial operations.

Agitation can be defined in several ways. Quantitatively, agitation may be expressed in revolutions per minute with a given rotating agitator. Unfortunately, speed of agitation leaves unspecified the quality of agitation achieved, except within a very restricted physical environment. The measurement of qualitative occurrences such as turbulence and gas dispersion is difficult although some attempts have been made in this direction (6). The effect of surface contact between gas and oil during hydrogenation has received first consideration in this study.

Many devices have been described for effecting the hydrogenation of vegetable oils under conditions of intimate contact between the gas and oil phases. Among these are systems for continuously recirculating the oil through the hydrogen in the form of a fine spray, and others for recirculating the headspace gas through the oil as small bubbles. A patent granted to Ittner in 1918 describes an agitator with a hollow shaft whose action is to draw headspace gas downward and rapidly disperse it in the oil in sufficient quantity to increase the apparent volume of the liquid phase (11). He noted increased selectivity with respect to polyunsaturates by this method over processes in which sprays or films were used but presented no supporting data. Subsequently other mixing devices for accomplishing a similar effect have been described (12, 16).

At the Northern Utilization Research Branch a small, gas-dispersing agitator was constructed, and tests were performed in the laboratory to evaluate its effectiveness in small-scale hydrogenations. Figure 1 demonstrates typical performance of this agitator and, for comparison, that of a conventional turbine agitator, each under two possible conditions of operation. In general, the turbine agitator without baffles provides a surface presented by the formation of a vortex which is relatively small and extremely localized when compared with the gas-dispersion type with baffles. However, at the same speed, the simple turbine is likely to provide greater oil velocity with, presumably, a higher interchange of oil at the interface between the oil and catalyst. The essential comparison, then, between the two agitators, if baffles are used, is the comparison between high oil velocity with low gas interface and its opposite, low oil velocity with high interface.

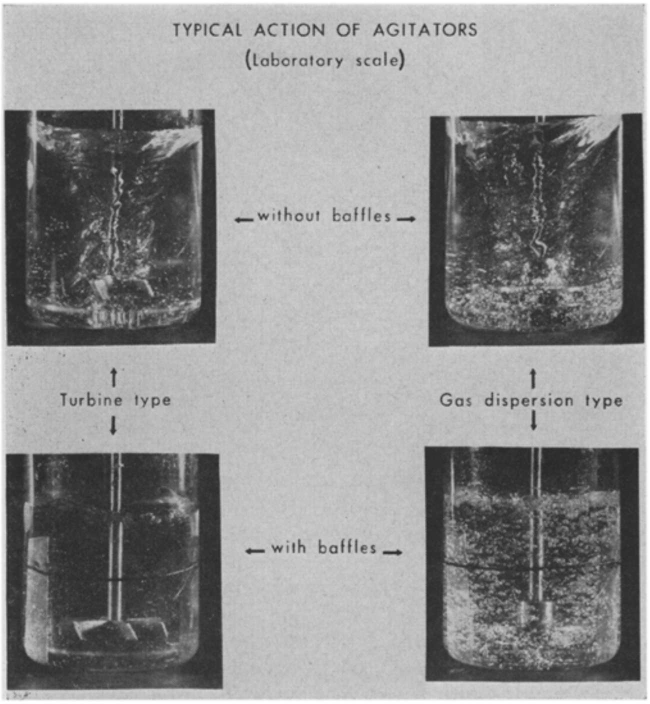

FIG. 1. Typical action of turbine and gas-dispersion agitators.

The results of preliminary experiments in the laboratory were promising, but the decision to carry out more complete experiments in the pilot plant was made for two other reasons. First, physical dimensions were believed to exert a significant influence on the manner in which various other factors affect the course of the reaction (14). Thus study of hydrogenations conducted in the pilot plant should furnish more valid estimates of the effect of agitation than experiments on a smaller scale. Secondly, several large samples from a run were desired, and these could be obtained in the pilot plant without appreciably reducing the size of the batch and thereby affecting the subsequent course of the reaction.

Experimental

Figure 2 shows the two agitators which were used in our studies of the hydrogenation of soybean oil. One of these is a simple turbine agitator, and the other is, primarily, a simplification of the one described by Ittner, differing from his in that there is no liquid flow through the impellers and in that it may be easily installed on an existing agitator shaft without requiring alterations to the shaft. The circular plates shown in the picture of the conversion parts for the gas-dispersion agitator are bolted together and are fastened to the existing shaft with set

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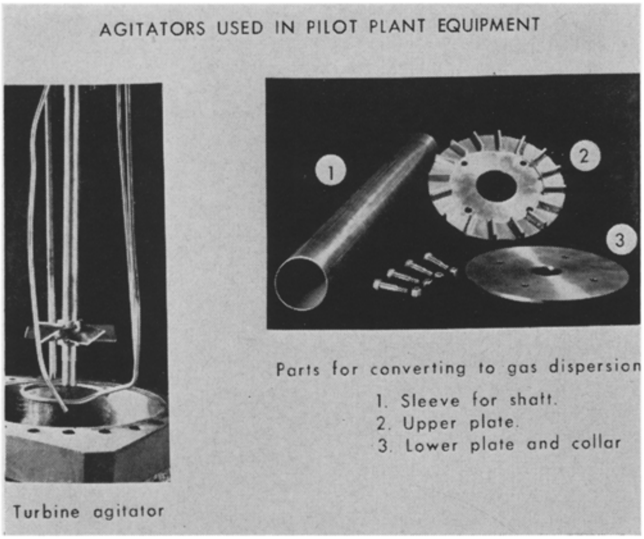

FIG. 2. Turbine and gas-dispersion agitators for pilot-plant hydrogenator.

screws. The tube shown in the same picture rests on top of the upper plate and is held in position by a groove in the upper plate and by a retaining clamp at its upper end, which is not shown. The path of the gas is downward from the top of the vessel through the annular space between the tube and shaft, and outward into the oil between the upper and lower plate. The action produced is similar to that shown in Figure 1, but the size of the bubbles relative to the size of the liquid medium is much reduced, giving the mass a creamy appearance.

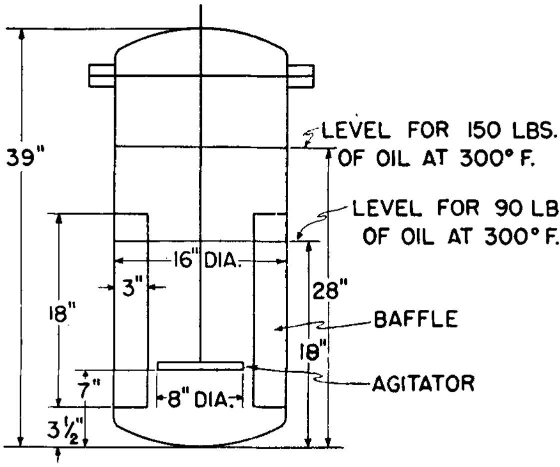

FIG. 3. Diagram of pilot-plant hydrogenator.

The diagram of the hydrogenator, in Figure 3, gives the dimensions of the hydrogenator and the two baffles which were installed in it, as well as the relative position of the agitator with respect to the bottom of the vessel and the surface of the oil at each of the oil batch sizes.

To make a comparison of the performances of the turbine and gas dispersion agitators, 5 additional variables, each at 2 levels, were considered. These included temperatures of 250° F. (121° C.) and 350° F. (177° C.), pressures of 5 and 50 p.s.i.g., catalyst concentrations of 0.025 and 0.05% nickel, batch sizes of 90 and 150 pounds of oil, and agitator speeds of 720 and 1,775 r.p.m. The catalyst was a commercial flake type containing 25% reduced nickel in hard oil. Relatively high agitator speeds were selected since the gas-dispersion agitator would not draw gas from the headspace into the oil at low speeds.

It may be calculated that to compare completely 6 variables, at 2 levels each, in all possible combinations the performance of 64 separate hydrogenations would be required. However, since the supply of a homogeneous lot of oil was limited, an arrangement which required but 12 hydrogenations to obtain estimates of the effects of all 6 variables was employed. The method in which 3 variables, at 2 levels each, are arranged in a Latin square so that but four experiments are needed to compare them is described by Gore (8). Table III shows the 12 hydrogenation runs arranged in three Latin square designs. It is evident that the experiments in squares 1 and 2 permit a direct comparison of the turbine and gas-dispersion agitators at each of four operating conditions and the runs in square 3 permit an additional estimate of the effect of gas dispersion.

The soybean oil used for the hydrogenation experiments was a uniform lot of refined, bleached oil prepared in the pilot plant. All runs were made with the same oil and catalyst. A series of samples having iodine values in a range of 60 to 100 were taken during each hydrogenation, but from practical considerations only those with iodine values between about 70 and 85 were selected for extensive analyses.

Linolenic and normal linoleic acids were determined by the A.O.C.S. Tentative Spectrophotometric method. The saturated acid content was determined by the neutral permanganate oxidation method reported by Hilditch (9). For this purpose approximately 25-g. samples of hydrogenated oil were converted to the corresponding methyl esters by alkaline methanolysis. After determining the iodine value and free fatty acid content of the undistilled esters, 2.5-g. samples were oxidized in dry acetone with potassium permanganate in accordance with details given by Schuette and Nogare in their application of the method (15). Following neutralization of the excess permanganate, the aqueous solution was extracted 3 times with 50 cc. portions of ethyl ether. The ether solution was washed several times with 2% aqueous potassium hydroxide solution until the wash solution remained alkaline to phenolphthalein and finally with water until excess alkali was removed. The remaining ether solution of saturated esters was dried, filtered, and evaporated, and the esters were heated to constant weight in a vacuum oven at 80° to 85° C. After the residual esters were weighed, they were dissolved in 10 cc. of carbon tetrachloride, 5 cc. of which were used for an iodine-value determination and 5 cc. for a free fatty acid analysis. A correction was applied for unsaponifiable matter in the saturated ester fraction by making analyses thereof on a number of samples. The total oleic acid and isolinoleic acid content for each sample were calculated from fatty acid material balances and from iodine-value balances, using the theoretical iodine values from the A.O.C.S. Tentative Method for polyunsaturated acids, for oleic, linoleic, and linolenic acids. Micropenetration measurements were made by the method of Feuge and Bailey (4). Capillary melting points were determined by the Official A.O.C.S. Method.

TABLE I

Conditions for Hydrogenating Soybean Oil in the Pilot Plant with Two Types of Agitators and Analyses of Hydrogenated Oils

Run	Agitator type	Temp.	Pressure	Catalyst	Agitator speed	Batch size	Iodine value (Wijs)	Saturated	Total[a] oleic	Isolinoleic[a]	Linoleic	Linolenic	Induction time	Micropenetration[b]		Capillary[b] m.p.	Hydrogenation time[b]
														25° C.	30° C.		
		° F.	*psig.*	*% Ni*	*rpm.*	*lbs.*							*Hrs.*	*mm.*	*mm.*	*°C.*	*Min.*
Orig. oil							129.5	15.0	24.8	....	49.2	6.6	....	......	......	....	......
1	G.D.	250	5	0.05	720	90	82.3	23.5	53.3	4.0	14.3	.52	23	225	365	38.5	145
							78.3	24.5	55.7	4.1	11.0	.34	36	135	205	41.5	161
							74.7	26.0	56.5	4.1	8.8	.22	47	70	150	45.7	175
							70.1		......	....	....	......	....	50	105	47.7	191
							66.1	......	......	....	....	......	111	30	65	49.4	210
2	G.D.	350	5	0.05	1775	90	81.8	17.5	65.6	3.8	8.4	.26	44	390	......	31.7	17
							70.4	21.6	69.6	3.3	1.1	.03	210	75	185	39.7	23
							65.4	......	......	....	....	......	....	35	65	44.1	27
3	G.D.	250	50	0.05	1775	90	83.6	25.9	47.9	3.6	17.2	1.05	22	115	215	49.0	39
							78.1	27.8	49.8	3.0	14.3	.75	27	80	145	50.3	44
							72.3	30.4	50.7	2.9	11.2	.48	34	55	104	52.8	50
4	G.D.	350	50	0.05	720	90	83.4	17.8	63.5	3.4	10.5	.39	33	325	......	32.6	12
							73.0	21.2	67.7	3.3	3.4	.05	99	125	265	38.0	15
							67.7	23.9	68.2	2.2	1.3	.01	153	60	118	44.5	16
5	G.D.	350	5	0.05	720	90	81.6	17.2	66.2	4.4	7.7	.06	44	360	......	32.0	30
							70.0	20.5	72.3	2.1	.66	.01	226	70	172	39.0	39
							64.6	......	......	....	....	......	....	25	54	44.1	45
6	G.D.	350	5	0.025	720	150	81.9	16.8	66.7	4.5	7.5	.12	48	380	......	29.1	60
							70.7	20.5	71.7	2.7	.72	.01	230	72	170	38.1	81
							64.5	......	......	....	....	......	....	25	58	43.7	96
7	T.	250	5	0.05	720	90	81.8	23.8	53.4	3.0	14.8	.65	26	150	280	33.0	121
							70.1	28.6	56.3	3.2	7.3	.16	50	68	145	41.4	152
							64.1	......	......	....	....	......	....	37	74	50.2	172
8	T.	350	50	0.05	720	90	79.2	18.3	66.9	3.0	8.1	.31	38	180	375	34.5	5
							73.3	20.2	69.5	1.4	4.4	.12	79	100	195	38.2	6
							69.3	......	......	....	....	......	....	50	110	42.0	7
9	T.	350	5	0.025	720	90	77.7	19.8	65.5	4.5	5.7	.16	58	212	......	33.5	23
							72.5	21.8	66.9	4.1	2.7	.06	86	90	194	37.9	28
							66.9	......	......	....	....	......	....	40	85	42.5	34
10	T.	350	5	0.05	720	150	76.7	17.4	71.3	3.7	3.2	.03	95	245	......	33.0	36
							71.2	19.8	72.4	2.9	.54	.01	218	85	245	38.1	42
							65.1	......	......	....	....	......	....	25	70	41.2	51
11	T.	350	5	0.05	1775	90	80.3	18.6	65.4	2.3	8.9	.44	34	205	......	39.2	15
							74.8	20.1	68.0	2.2	5.1	.16	65	135	270	41.2	19
							68.6	......	......	....	....	......	....	55	110	42.0	23
12	T.	250	50	0.05	1775	90	83.1	28.2	44.2	2.7	19.0	1.47	16.5	59	93	52.2	58
							76.9	30.5	46.0	2.5	15.6	1.03	23	40	......	54.5	65
							71.6	......	......	....	....	......	....	35	47	55.2	71

G.D.—Gas dispersion. T.—Turbine. [a] Calculated from iodine value and material balance. [b] Additional data at other iodine values are available on penetration, melting point, and time, but are omitted in this tabulation.

TABLE II

Conditions for Hydrogenating Soybean Oil and Properties of Hydrogenated Oils at Iodine Values of 70 and 80[a]

Run	Agitator type	Temp.	Pressure	Catalyst	Agitator speed	Batch size	Iodine Value (Wijs)	Saturated	Total[b] oleic	Iso-[b] linoleic	Linoleic	Linolenic	Induction time	Micropenetration		Capillary m.p.	Hydrogenation time
														25° C.	30° C.		
		° F.	*psig.*	*% Ni*	*rpm.*	*lbs.*							*Hrs.*	*mm.*	*mm.*	*° C.*	*min.*
1	G.D.	250	5	0.05	720	90	80	24.0	54.9	8.9	12.4	.41	29	160	290	40.5	155
							70	28.6	56.4	4.4	6.1	.12	77	50	100	47.5	193
3	G.D.	250	50	0.05	1775	90	80	27.1	49.1	3.1	15.4	.85	25	90	170	49.5	43
							70	31.9	50.1	3.3	9.9	.38	37	50	85	53.0	52
2	G.D.	350	5	0.05	1775	90	80	17.9	66.8	4.0	6.75	.19	55	250	550[c]	33.0	17
							70	21.9	69.6	3.1	.96	.02	220	70	140	40.5	23
4	G.D.	350	50	0.05	720	90	80	18.6	65.4	3.6	7.8	.21	47	250	550[c]	34.0	12
							70	22.6	68.2	2.7	2.05	.03	130	70	140	42.0	15
5	G.D.	350	5	0.05	720	90	80	17.4	67.6	4.3	6.25	.05	55	250	550[c]	33.0	31
							70	20.5	72.4	2.0	.67	.01	220	70	140	40.0	40
6	G.D.	350	5	0.025	720	150	80	17.1	68.3	4.3	5.85	.085	60	250	550[c]	30.5	64
							70	20.6	72.2	2.2	.60	.01	240	70	140	39.0	83
7	T.	250	5	0.05	720	90	80	24.3	54.4	3.0	13.4	.54	28	150	290	34.5	124
							70	28.7	56.2	3.2	7.3	.16	51	55	110	42.5	152
12	T.	250	50	0.05	1775	90	80	29.1	45.6	2.3	17.4	1.23	20	50	75	53.5	61
							70	34.3	45.6	3.3	11.7	.66	31	30	45	55.5	73
8	T.	350	50	0.05	720	90	80	18.1	66.7	1.6	8.95	.35	33	250	550[c]	34.0	4
							70	22.1	69.2	1.3	2.9	.065	120	70	140	42.0	6
9	T.	350	5	0.025	720	90	80	19.1	64.5	4.4	7.4	.24	49	250	550[c]	31.5	22
							70	22.9	67.6	3.4	1.65	.03	105	70	140	40.0	30
10	T.	350	5	0.05	720	150	80	16.5	69.4	3.7	5.9	.066	60	250	550[c]	30.5	32
							70	20.2	73.0	2.2	.25	.004	240	70	140	39.0	44
11	T.	350	5	0.05	1775	90	80	18.6	65.5	2.4	8.6	.43	33	250	550[c]	38.5	16
							70	21.9	69.6	1.2	2.75	.06	120	70	140	42.5	22

G.D.—Gas Dispersion. T.—Turbine. [a] Obtained by graphical interpolation of data in Table I. [b] Calculated from iodine value and material balance. [c] Too soft to measure.

The stability of samples of hydrogenated oil was measured by the induction time in an oxygen uptake apparatus similar in principle to that of Gilmont *et al.* (7). For that purpose they were first deodorized for 2 hours at 200° C. in the laboratory in a glass deodorizer, after which 0.01% of citric acid in water was added to the oil and it was heated to 100° C. under vacuum to remove excess moisture. The induction time was then measured at 220° F. (104.5° C.). It was observed with several samples that no rancid odor was detectable prior to the induction point but that a strong odor developed shortly thereafter in accordance with the observation of Gilmont and co-workers.

Results

A summary of the conditions for hydrogenating soybean oil in the pilot plant and the analyses of samples taken during the runs is given in Table I. The logarithms of compositional data were plotted against the corresponding iodine values and interpolated or extrapolated, as required, to estimate compositions at iodine values of 70 and 80 which are given in Table II. Capillary melting points and hydrogenation times and the logarithms of oxidative stability and of micropenetration were similarly plotted from Table I to obtain data for Table II.

To estimate the effect of a variable on a given characteristic of the product, numerical vlues for the selected characteristic at a given iodine value are entered in Table III. The values are averaged over a uniform condition, and the difference, due to change in degree of that condition, may be expressed as a numerical difference or as a ratio. A logarithmic relationship between the condition and effect is believed to exist in some of the relations studied in this report, but arithmetic averages are used in all the tables for the sake of simplicity.

The effect of operating conditions on oxidative stability of the hydrogenated oils is shown in Table III, items *a*. As an example of the method by which data arranged in Latin squares are analyzed, the data entered in square 1 may be considered. The average induction period in hours for T_1, or 250° F. (121° C.), is 41, and that for T_2, or 350° F. (177° C.), is 120. The preliminary conclusion is that an increase in temperature of 100° F. (55.5° C.) has caused an increase in the stability of about 80 hours, or threefold. Similarly, an increase in pressure of 45 p.s.i.g. has decreased the average induction period from 85 to 75 hours. After the gross effects have been estimated in this fashion, attention to the actual values in the face of the table may result in refinements of the conclusion. In this particular instance it is readily observed that, whereas there is a difference between P_1 and P_2 in the T_1 row, there is none in the T_2 row. This result may be due either to lack of effect of either pressure or speed at the higher temperature or to the combined effect of agitator speed and pressure acting in opposite directions but of equal magnitude. The true situation is likely to be at some point between these

TABLE III
Effect of Operating Conditions on Stability, Penetration, Melting Point, and Hydrogenation Time for Soybean Oil Hydrogenated to an Iodine Value of 70

Square 1 Constant Conditions: A_1,B_1,C_1			
	P_1	P_2	
	Run 7 (T_1P_1) R_1	Run 12 (T_1P_2) R_2	Av. for T_1
T_1	a. 51 b. 55 c. 42.5 d. 152	31 30 55.5 73	41 42 49.0 112
	Run 11 (T_2P_1) R_2	Run 8 (T_2P_2) R_1	Av. for T_2
T_2	a. 120 b. 70 c. 42.5 d. 22	120 70 42.0 6	120 70 42.2 14
	Av. for P_1	Av. for P_2	Overall Av.
	a. 85 b. 62 c. 42.5 d. 86	75 50 48.7 39	80 56 45.6 63
	Av. for R_1	Av. for R_2	
	a. 85 b. 62 c. 42.2 d. 79 e. 0.35	75 50 49.0 47 1.80	

Square 2 *Constant Conditions:* A_2,B_1,C_1			
	P_1	P_2	
	Run 1 (T_1P_1) R_1	Run 3 (T_1P_2) R_2	Av. for T_1
T_1	a. 77 b. 50 c. 47.5 d. 193	37 50 53.0 52	57 50 50.2 122
	Run 2 (T_2P_2) R_2	Run 4 (T_2P_2) R_1	Av. for T_2
T_2	a. 220 b. 70 c. 40.5 d. 23	130 70 42.0 15	175 70 41.2 19
	Av. for P_1	Av. for P_2	Overall Av.
	a. 146 b. 60 c. 44.0 d. 108	83 60 47.5 33	116 60 45.6 70
	Av. for R_1	Av. for R_2	
	a. 103 b. 60 c. 44.7 d. 104 e. 0.14	128 60 46.7 37 0.52	

Square 3 Constant conditions: P_1,T_2,R_1			
	C_1	C_2	
	Run 5 (B_1C_1) A_2	Run 9 (B_1C_2) A_1	Av. for B_1
B_1	a. 220 b. 70 c. 40.0 d. 40	105 70 40.0 30	162 70 40.0 35
	Run 10 (B_2C_1) A_1	Run 6 (B_2P_2) A_2	Av. for B_2
B_2	a. 240 b. 70 c. 39.0 d. 44	240 70 39.0 83	240 70 39.0 63
	Av. for C_1	Av. for C_2	
	a. 230 b. 70 c. 39.5 d. 42	172 70 39.5 56	
	Av. for A_1	Av. for A_2	
	a. 172 b. 60 c. 39.5 d. 37	230 70 39.5 61	

Key:

Hydrogenation temperature
T_1—250 F. (121° C.)
T_2—350° F. (177° C.)

Hydrogenation pressure
P_1—5 p.s.i.g
P_2—50 p.s.i.g.

Type of agitator
A_1—Turbine
A_2—Gas dispersion

Catalyst concentration
C_1—0.05% Ni
C_2—0.025% Ni

Batch size
B_1—90 lb. oil
B_2—150 lb. oil

Agitator speed
R_1—720 r.p.m.
R_2—1775 r.p.m.

a. Induction period, hours
b. Micropenetration (mm.) at 25° C.
c. Capillary melting point, °C.
d. Hydrogenation time, minutes
e. Power requirements, kilowatts

two alternatives. If pressure and speed act in opposite directions, the magnitude of the depressing effect of pressure on the stability would be expected to be greater than the effect of speed in increasing it. If this were true, one would expect a somewhat lower value as the lower right item of square 1. The most reasonable first conclusion, then, is that the effect of pressure tends to disappear at the higher temperature and that the effect of speed of agitation is negligible with this agitator. The general conclusion that the effect of speed alone is small as compared with the effect of pressure is substantiated for the dispersion agitator by the relatively small difference due to the effect of speed as shown in square 2, and more clearly by comparing the lower left item in square 2 with the upper left item in square 3. Here any difference in stability is due only to speed of agitation. No difference is observed.

Continuing the analysis of the data in Table III, items *a*, an item-by-item comparison of squares 1 and 2 clearly demonstrates the superior stability of oils produced by using the gas-dispersion agitator. The degree of over-all effect can be estimated by comparing the over-all averages in the lower right-hand corner of the squares. A 50% gain can be attributed to the change in type of agitation. Since the items in the two squares are comparable except for the type of agitator, a direct comparison is possible and indicates that the greatest advantage of the gas-dispersion type is at low pressure and high temperature, the effect of speed with the dispersion agitator having been ruled out as described previously. From square 3, by comparison of averages within the square and comparison of items with those in squares 1 and 2, the conclusion is obtained that an increase in batch size has caused an appreciable increase in the stability of the oil and that a decrease in catalyst concentration caused the opposite effect, particularly with the turbine agitator. A second estimate is obtained from square 3 of the difference between the two types of agitation, and the results again demonstrate the general superiority of the dispersion type by a margin which is quite close to the estimate from squares 1 and 2.

The stability, as measured by induction time, has been found by other workers (5) to be related to the fatty acid composition. The data for the present work have been inter-related by plotting induction period in hours against a linear function of composition in which the coefficient of the individual acid content is in proportion to the rate of reaction with hydrogen under selective conditions which has been reported for it (1). Bailey implied that this selection of coefficients may be justified since he stated that the relative rates for oxidation have been found by Hilditch to be "strikingly similar" to those for hydrogenation. The relation of composition to stability when plotted on logarithmic scales is linear over the range of values studied. In Figure 4, data from Table I are represented graphically. The scatter of points about the line may be due either to analytical error, to incorrect coefficients in the composition function, or to lack of data concerning such acids as elaidic, which may be less reactive than oleic. Despite this Figure 4 demonstrates that, at least with the more unstable oils, the measure of stability used in this work can be interpreted as being representative of the amount of polyunsaturated fatty acids; and the increases in stability mentioned in the preceding paragraphs can be interpreted roughly as being due to factors which selectively reduce the amount of these acids during the hydrogenation process.

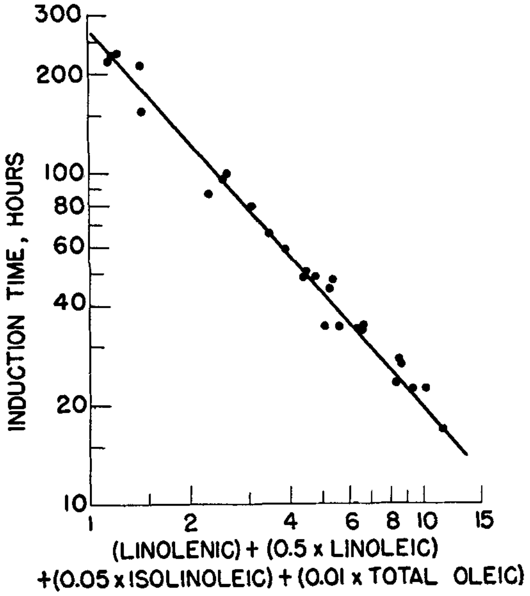

FIG. 4. Relation of stability to composition of hydrogenated soybean oil.

From Table III, items *b*, one finds that the primary effect is that increasing the temperature leads to production of a softer material. As with stability, agitator speed is seen to have little influence on consistency. The remaining, but somewhat minor, differences are due to increased pressure at 250° F. (121° C.) and the specific condition of high pressure, and low temperature, with the turbine agitator. The dispersion agitator is responsible for a softer product only under the most favorable conditions for producing a hard product, that is, at low temperature and high pressure. Batch size and catalyst concentration have no appreciable effect on the penetration at 25° C. of the hydrogenated oil.

In Table III, items *c*, however, one finds fairly significant differences in the performance of the two agitators relative to their effects on the melting point of the product. Although the over-all averages in squares 1 and 2 are identical, the magnitude of the average effect of pressure is greater while the effect of temperature is smaller when the turbine agitator is employed. Considering the data in square 1, the only appreciable effect observed at this particular iodine value with the turbine agitator is the production of material with extremely high melting point at the high pressure and low temperature. As was found with stability and consistency, the chief effect is that of temperature. The relation of melting point to conditions of hydrogenation is more complicated than in the case of penetration and can probably be explained only by means of a study of the fatty acid composition, particularly in respect to isomers of oleic acid. Speed, batch size, and catalyst concentration appear to have a role in determining the melting point of the hydrogenated oil.

The data in Table III, items *d*, illustrate the only advantage of higher speeds which is to increase the rate of hydrogenation. Although the apparent effect of increased speed with the turbine agitator may be actually due to pressure, the direct comparison available between lower left item in square 2 and upper left item in square 3 leaves little question that a significant increase in rate of hydrogenation was accomplished by increasing the speed of the dispersion agitator. The finding that the relation of speed and rate is dependent on the type of agitation suggests an extension of previous conceptions (10, 13). The advantage of the latter type is somewhat offset by an inherent slowness at slow speed, as is best demonstrated by comparing the R_1 items in square 1 with those of square 2. The expected increase in speed of hydrogenation with both pressure and temperature and the decrease with increasing batch size and reduction in amount of catalyst is noted.

The figures in Table III, items *e*, are average values in kilowatts of the power required by the two agitators at the two speeds. These were obtained with an indicating wattmeter. The power required to turn the agitator in the empty hydrogenator was subtracted from the power readings taken during actual hydrogenations, thus eliminating the friction load. The dispersion agitator required only about 50% more power at the high speed than the turbine agitator required at the low speed.

All of the criteria for the effect of agitation on selectivity, rate, and power have been interpolated to give values which would have been obtained with oils of 80 iodine value (Table II) and studied at that degree of hydrogen uptake. The gross effects of the variables examined are in the same direction. Also the consistency at 30° C. reflects the results found at 25° C. (Table II). Hydrogenation to an iodine value of 80 results in a softer, less stable, lower melting product requiring less time for production, and at either 70 or 80 iodine value the consistency at 30° C. is softer than it is at 25° C. Obviously, the values for stability, consistency, and melting point at 80 iodine value may be compared in tables similar to Table III.

Discussion

Three aspects of agitation have been studied. The first, a matter of degree, was speed, and its effect is to increase the rate of hydrogenation, especially with the gas-dispersion agitator. The second aspect was a matter of kind and showed that the dispersion of hydrogen increases the stability of the product significantly over a wide range of conditions without changing either the penetration or the melting point markedly, particularly at the higher temperatures. The dispersion of the gas can be accomplished economically with the conversion parts described. The third aspect of agitation was a combined factor, the properties of which are difficult to estimate. This factor, batch size, seems to have no effect on the rate of hydrogenation, if computed only on the basis of iodine value decrease per unit time per pound of oil; but, together with extending the total time for hydrogenation of the batch to a given iodine value, increasing the batch size increases the stability of the hydrogenated product appreciably, again without changing the physical characteristics to a major degree. This is particularly true with the turbine agitator.

The most useful aplication of these observations is that appreciable savings of time and power input can be achieved with the dispersion agitator if it is operated at high speeds. Under these conditions a high degree of selectivity with regard to removal of linoleic and linolenic acids may be obtained. The conclusion that batch size has a larger effect than agitator speed in determining the course of the reaction emphasizes the importance of the relationship between the physical dimensions of the system and the manner in which agitation influences the chemical changes involved (14). Although this observation justifies the decision that was made to carry out the experiments in the pilot plant, it also implies that the situation may even be changed again when hydrogenations are carried out on a commercial scale.

If, as has been suggested previously, the use of the dispersion agitator leads to better dispersion of the gas and greater interfacial area for the gas-oil mixture, it is then evident that selective removal of linoleic and linolenic acids is better accomplished by providing for intimate mixtures of gas and oil than by attempting to obtain better agitation for the catalyst in the oil. If, in contrast, a high speed of agitation provides for a high rate of interchange of reactants at the catalyst surface, an increased interchange does not appreciably affect the relative rates of reaction of the various component acids but within certain limits may affect the rate of hydrogen uptake of the mixture (10, 14).

The question as to the relation of composition to physical properties is both interesting and important. It is believed that the data on composition should be extended to include estimates of elaidic acid before an attempt is made to explain through composition the complex relationship between penetration, melting point, and stability. In fact, since all the properties depend upon composition, a more fundamental method of analysis would be to enter such data in the squares so that the effects of the treatments on the composition could be estimated. Also the questions as to the reality of some of the effects observed in these experiments, such as the apparent disappearance of the influence of pressure at the higher temperature, can be answered only by additional work.

The Latin square arrangement, besides providing estimates of the effect of other variables, has enhanced the comparison of the two agitators by comparing them over a less restricted range than could have been possible in the same number of runs carried out in the usual manner. It is believed than in this case the choice, a fortunate one, has contributed greatly to the knowledge of the process with a minimum of experimentation.

Summary

A total of 12 hydrogenations were conducted in the pilot plant. The conditions were such that analyses of the data would furnish information as to the effect of 6 variables on the course of the reaction. The most reliable estimates were obtained for the effect of increasing, by agitation, the dispersion of hydrogen in the oil. The dispersion was accomplished by converting from a simple turbine agitator to a gas dispersing type with easily fabricated parts. This change resulted in a more selective reaction with respect to unsaturates. The change can also result in a shorter reaction time, or in the consumption of less power. Judging from its effects on the course of hydrogenation, agitation cannot simply be defined in terms of speed.

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The Influence of Dietary Fat on the Glyceride Structure of Animal Fat[1]

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In recent years there has been increasing interest in the glyceride structure of animal depot fats. Unfortunately there is a pronounced tendency to develop unified theories to account for whatever structures are found, whether in plants or animals. Thus, Hilditch developed the concept of "even distribution" although, as he has recently emphasized (1, 2), he did not propose it as a "rigid" rule. Nevertheless, Hilditch has attempted to apply the "even rule" to animal fat, explaining the deviation from it in "stearic-rich" depot fats by the concept of "biohydrogenation" in the tissues (2, 3, 4).

Kartha has rejected the "even distribution" rule and substituted a unified rule which he believes can be used for calculating the glyceride structure of any natural fat (5, 6, 7). Kartha's concept is that all lipases have equal affinity for all fatty acids, and *vice versa.* He proposes the theory that glycerides are synthesized with random distribution of the fatty acids until any further production of saturated triglycerides would produce a solid fat. Subsequently saturated acids are distributed without the production of saturated triglycerides.

Morris and Mattil (9) pointed out several years ago that "the fat of the larger land animals, being derived from both animal and plant sources, would be expected to vary in glyceride structure, depending upon the diet of the animal and the extent to which the fat is absorbed as such or altered by interesterification, ester exchange and hydrolysis and resynthesis during metabolism." Nevertheless, Kartha, in a very recent contribution to this subject, stated that, "in adipose tissues as well as in mammary glands of animals, fat can be deposited from ingested foods without affecting the normal glyceride type distribution" (7).

Deuel has reviewed the various attempts, except Kartha's, to explain the distribution of fatty acids in natural glycerides (8).

Unfortunately few, if any, studies have been made of the structure of the glycerides produced by animals on fat-free diets. The theories developed have been highly speculative, based on data of glycerides obtained at random.

The present study is an effort to determine experimentally the divergence of endogenous animal glycerides from the "random" or "even" type distribution and the effect on it of exogenous fat.

Experimental

Groups of albino rats and New Hampshire-Delaware Cross chicks were reared on an essentially fat-free ration (Table 1). The neutral fats extracted from these animals were then fed at the 20% level to second groups receiving the same basal ration. Under these conditions the glycerides fed are identical to body glycerides.

TABLE I

Basal Ration

	%		%
Soybean protein	25.0	Methionine	0.8
Sucrose	58.6	Glycine	0.5
Salts	6.0	Choline	0.2
Dried whey	5.0	Inositol	0.2
Liver L[2]	4.0	Cottonseed oil	0.1
		Mixed tocopherols	0.1
mg/kg		mg/kg	
Niacin	100	Pyridoxine	8
P-aminobenzoic acid	100	Thiamine	6
Ca-pantothenate	40	Folic acid	4
Carotene	33	Menadione	0.5
Riboflavin	12	Biotin	0.3

Third groups were fed 20% cottonseed oil in the basal ration since this fat conforms very closely to the "even" type distribution (10). A fourth group of chicks received 10% cottonseed oil.

Rats

Low fat ration. Several gravid females were placed on the low fat ration until after the young were

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