The Hydrogenation of Soybean Oil

Experimental Investigation of Its Application to Lard-Substitute Production

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ALTHOUGH there are four varieties of soybean, only one, the yellow, or soybean as it is universally called, is used in the soybean mills. The mills, or soybean oil-pressing plants, rank foremost in the manufacturing industry in Manchuria which comprises the three Provinces: Fengtien, Kirin and Heilungkiang, having 20 million inhabitants and an area of 365,000 square miles. The output of the oil in 1923 was about 500,000 tons. In Dairen, the center of soybean mills, 390 tons of oil are produced daily.

Since soybean oil is between peanut and cottonseed oils in the uses and the qualities, and no hydrogenation plant is established in China, the commercial hydrogenation of this oil, especially for edible purposes, should be developed, to better feed the 400 million Chinese, as well as their neighbors of non-farming nations.

The oil used had the following characteristics:

Specific gravity at 15.5°....	0.925
Free fatty acid calculated as oleic acid	0.57%
Iodine number	140.0

The catalyst is 'poisoned' by free fatty acids and moisture in oil. The latter is removed by drying and the former with caustic soda solution.

The oil was agitated with an electrical stirrer and 80 percent of the theoretical amount of caustic soda solution (16° Be.) were added. After 30 minutes the oil was heated in a water bath to 50° until the emulsion was "broken." It was then allowed to settle and was filtered through filter paper. The oil thus obtained was dried in the same cup for ten minutes at 120°, being agitated during the operation and then being filtered again. It was stored for hydrogenation.

The hydrogenation took place in a bronze autoclave holding about 600 cc., provided with a stirrer and oil bath for heating.

Preparation of the Catalyst

There are two distinct methods of preparing the catalyst, one being known as the dry process and involving nickel salts in the dry state, and the other being known as the wet process, according to which the catalyst is prepared by reduction in oil. The latter process has been proved simpler and more reliable.

The catalyst was prepared by grinding nickel formate, the most commonly used material in the wet process, in the oil, and heating the oil emulsion thus obtained in the autoclave, hydrogen being passed in to displace the air in the autoclave until the reduction was complete. After the air had been completely displaced, (usually in five minutes), the burners were lighted and so regulated that the temperature was raised gradually and kept at 240°. When the bubbles of hydrogen became even and regular, usually after three to four hours, the nickel formate was considered to be completely reduced. The catalyst was now ready for use. It was newly prepared for every hydrogenation.

Hydrogenation

The oil to be hydrogenated was poured into the autoclave, the air displaced as before and the cap bolted on. The burners were lighted and regulated so as to get a definite temperature, and the valve admitting hydrogen was regulated so as to get a definite pressure indication on the gauge. Stirring was begun and after a definite time a sample of 20 to 60 cubic centimeters was withdrawn with a pipette, and filtered through a hot water funnel. The process from air-displacing to sample-filtering was repeated until several samples had been taken.

The conditions under which the oil was hydrogenated and the iodine numbers of the samples were as follows:

Run 1. Temperature 170°C., pressure 40 pounds, 100 revolutions per minute, 0.6% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	60	106.0
2	120	95.7
3	180	87.3
4	240	79.0
5	300	75.8
6	340	72.0
7	370	66.8

Run 2. Temperature 180°C., pressure 40 pounds, 100 r.p.m., 1.00% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	60	83.9
2	120	72.7
3	180	66.4
4	240	62.9
5	300	56.8

Run 3. Temperature 170°C., pressure 2 pounds, 406 r.p.m., 1.00% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	60	2.78
2	70	2.54

Run 4. Temperature 170°C., pressure 20 pounds, 406 r.p.m., 1.00% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	15	18.3
2	20	18.0
3	25	17.3

Run 5. Temperature 160°C., pressure 10 pounds, 400 r.p.m., 0.40% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	15	45.0
2	30	42.2
3	45	37.9

Run 6. Temperature 150°C., pressure 10 pounds, 400 r.p.m., 0.40% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	10	78.2
2	20	66.6
3	30	50.2

Run 7. Temperature 150°C., pressure 10 pounds, 320 r.p.m., 0.40% catalyst.

Sample	Elapsed Time Minutes	Iodine No.
1	30	82.1
2	60	56.6
3	90	43.9
4	120	40.5

The Effect of Pressure

The working pressure[1] of hydrogenation of cottonseed oil is below 40 pounds. No higher pressure seems to be necessary for hydrogenation of soybean oil. Moore[2] has pointed out that the hydrogenation rate of cottonseed oil is approximately proportional to the pressure. This fact will hold true for soybean oil.

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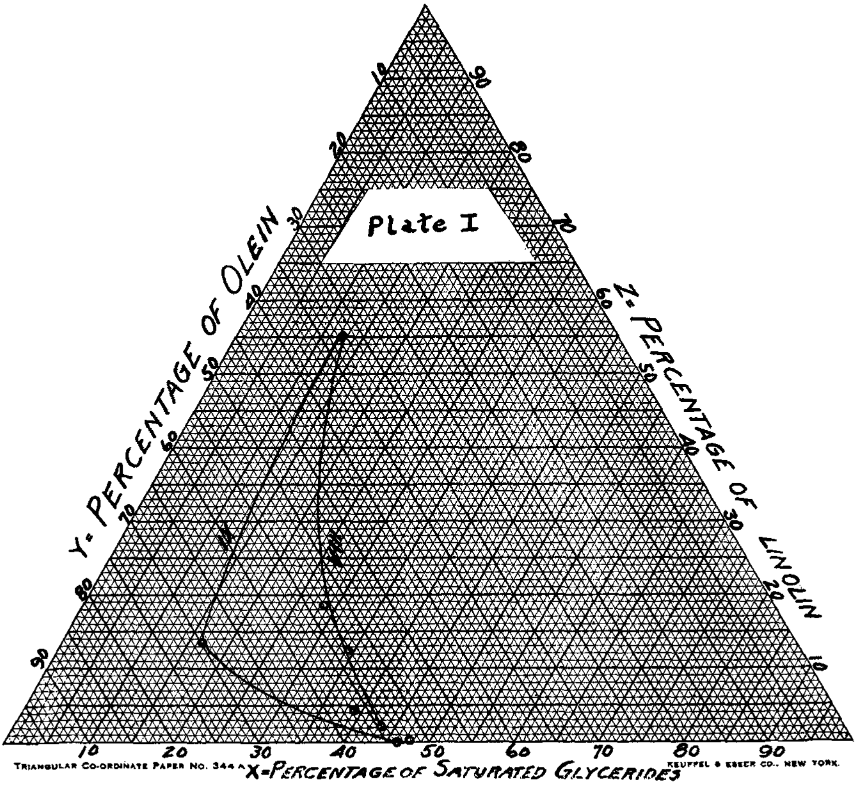
[1] Rogers "Industrial Chemistry" (1926) 764.

[2] Jour. I. and E. Chem. 9, 459 (1917).



Graphs showing progress of reaction in hydrogenation of soybean oil

The Effect of the Amount of Catalyst

As in practically all catalytic reactions, the hydrogenation rate[3] is increased as the percentage catalyst is raised. The fact[4] that no more than one percent of catalyst is necessary, is applicable to the hydrogenation of soybean oil, for no more than one percent of catalyst was used in the experiments and the results were satisfactory.

The Composition of Fats from Runs 6 and 7

The fats were analyzed in order to know how the reactions progressed in the course of the hydrogenation process. The Gusserow-Varrentrapp lead-salt-ether method was used here. It is in principle a separation of two groups of lead salts of fatty acids based on the difference in solubility of the two groups in ethyl ether. The detailed procedure of analysis has been fairly well mapped out by Tortelli and Ruggieri[5] and others.

The composition of the fats, together with the iodine numbers of the fats and the liquid fatty acids, were as follows:

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[3] Rogers, ibid.
[4] Moore, ibid.
[5] Lewkowitsch Analysis Oils, Fats and Waxes, I 560 (1921).

	Saturated Glycerides x	Per Cent Olein y	Linolin z	Fat A	Iodine Number Liquid Acids B
Run 6 (1)	28.5	53.5	18.0	78.2	114.1
(2)	34.2	53.7	12.1	66.6	100.0
(3)	43.4	54.5	2.1	50.2	92.7
Run 7 (1)	16.5	70.0	13.5	82.1	103.5
(2)	39.0	56.2	4.8	56.6	97.3
(3)	46.3	53.7	0.0	43.9	86.2
(4)	47.5	52.5	0.0	40.5	80.3

Graphs I and II, plate 1, show the composition of the fats during hydrogenation; taking the composition of the oil as x, (saturated glycerides) 12.5% y, (olein) 33.4% z, (linolin) 54.1%.

Both the figures show that linolin changed into saturated glycerides and, more quickly, into olein. The linolin disappeared when the saturated glycerides reached 45.6 percent, then olein changed into saturated glycerides very slowly. The agitation was higher in run six than in run seven, so the reaction was quicker in the former than in the latter.

The Melting Points of Fats from Run 7

As the hydrogenated fat is to be used for edible purposes, its melting point should approximate that of lard. It was determined with the Mulliken capillary tube apparatus[6]. The melting points of the fats, together with the corresponding iodine numbers were as follows:

Melting points °C	18.5	35.0	39.1	46.9
Iodine numbers..	82.1	56.6	43.9	40.5

The melting points of lard, "Crisco," and "Snowdrift" were determined with the same apparatus. They are 40.4°, 40.7°, and 42.3° respectively; 40° is taken as the melting point of the commercial hydrogenated soybean fat.

Conclusions

(1) An increase of temperature, pressure, agitation or amount of catalyst will increase the hydrogenation rate.

(2) In high agitation, at 320 r.p.m. or above, the change of 10° in temperature between 150° to 180° produces little or no effect.

(3) The hydrogenation rate is approximately proportional to the pressure, the amount of catalyst, and one half of the speed of agitation.

(4) No more than one per cent of catalyst is necessary.

(5) The course of the reactions of hydrogenation of soybean oil is the same as with cottonseed oil.

(6) The commercial hydrogenation of soybean oil can be a reality, for it is easily hydrogenated. As in run seven the time for obtaining the fat of 40° melting point was only one and one-half hours, although the time may be different on the commercial scale.

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[6] Woodman "Food Analysis" (1915) p. 154.

United States Bureau of Mines, Reno, Nev., has recently finished a study of native clays to be used as substitutes for fullers' earth in bleaching oils. The raw clays studied resemble sepiolite, and the clays requiring acid treatment resemble bentonite.