# Hydrogenation of Triglycerides Containing Linolenic Acids: II. Continuous Hydrogenation of Vegetable Oils

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## Abstract

In this study continuous hydrogenation of neutral oils, especially the selective hydrogenation of soybean oil, is described. The reactor is a column divided by a series of plates into a number of reaction chambers. Oil with suspended catalyst and hydrogen enters the column at the bottom and flows concurrently with hydrogen through it. The pressure in the reactor will adjust itself, depending on the activity and concentration of the catalyst and throughput of oil. The ratio of gas volume in the reactor to volume of the oil is very low, so that the iodine value of the hydrogenated product can be controlled to within 1.5 iodine unit.

## Introduction

World production of fats and oils is 35 million metric tons annually. Most of these are vegetable oils and are hydrogenated for production of semisolid or solid fats, which, in turn, are processed to margarine or used as shortenings. A little hydrogenation transforms less stable vegetable oils into more stable salad oils.

Although very large quantities of oils are hydrogenated by the edible oil industry, this is still carried out chiefly by the batch method in the same way as it was done 70 years ago when W. Normann (1) developed oil hydrogenation.

There is, however, a reason for this surprising fact. First, a variety of different oils are used for hydrogenation, such as soybean, sunflower seed, cotton seed oil and others, and secondly, different final products may have to be obtained from one and the same initial material. These different final products must not be mixed, a requirement which is easily fulfilled by batch hydrogenation but which constitutes an obstacle for continuous operation. The batch method moreover allows the operator to follow up the progress of hydrogenation by measurement of physical properties (e.g., refractive index, melting point) or of chemical characteristics (e.g., iodine value).

Today, however, a homogeneous crude stock is increasingly available, namely soybean oil. Its absolute quantity and relative share in total oil production have steadily risen over the last decades; also the final product of uniform melting point or constant iodine value is now turned out at large quantities.

Continuous hydrogenation is therefore gaining increasing interest. The exact degree of hydrogenation, too, is presently under control thanks to automation and control techniques so that any problems of uniformity no longer exist.

To date, few processess for the continuous hydrogenation of oils have been published in the literature, and these have not had wide acceptance by industry (2–4). Operation of these plants with respect to pressure was identical to the batch plants, i.e., the oil was hydrogenated at constant pressure with suspended or fixed-bed catalyst, with or without agitation. In these processes, the degree of hydrogenation was adjusted by the catalyst activity or catalyst concentration or by the residence time of the oil in the reactor.

## Continuous Hydrogenation

In contrast to the conventional hydrogenation processes, the process to be described works by a different principle. The reaction system is almost entirely filled with the oil to be hydrogenated and contains only as much gas volume as is indispensable to maintain a recycle of the hydrogen gas. The oil for hydrogenation with catalyst suspended in it is metered into the reaction system. The hydrogen is added proportionally to the quantity of oil and the desired degree of hydrogenation, i.e., the desired reduction of the iodine value, independent of the pressure in the reaction system.

The operation of the above cited principle is as follows. As oil and hydrogen are proportioned in terms of the desired degree of hydrogenation, oil difficult to hydrogenate, poor catalyst activity, or concentration will at once lead to the formation of a high hydrogen pressure in the reaction system. As reaction velocity increases with rising pressure, there will soon come about a pressure at which the hydrogen consumed by the reaction equals the hydrogen which is added. Vice versa, easily hydrogenable oil, high catalyst activity, or concentration cause the formation of a low pressure. As, moreover, the ratio of gas volume to liquid volume is very low, only very little hydrogen is consumed for the pressure increase or, vice versa, only very little hydrogen is set free for the reaction in the event of a pressure decrease. The volumes of hydrogen necessary to adjust the pressure are so little that they have practically no influence on the composition of the final product.

This process, if it were a simple reaction, could easily be carried out in an agitated vessel. Soybean oil contains several unsaturated fatty acids, viz., linolenic, linoleic and oleic acid, so that these particular conditions have to be taken into account for hydrogenation. In most instances it is desired that the linolenic and the linoleic acids be hydrogenated preferentially, because a high linolenic acid content has a specially unfavorable effect on the stability of hydrogenated soybean oil. These three unsaturated acids react with the hydrogen at different velocity, and the ratio of reaction rate constants of the individual reactions, the so called selectivity ratio, is mainly influenced by the hydrogenation catalyst used (5–13).

It can easily be demonstrated that in the hydrogenation of soybean oil the conversion of linoleic and, even more, the conversion of linolenic fatty acid, strongly decrease if instead of batch process the same reactor is operated continuously under identical reaction conditions and with identical hydrogen conversion. The reason for this is the back-mixing in a continuously operated agitated reactor: during the reaction already hydrogenated material remains in the reactor for a period longer than necessary and on the other hand part of the initial material runs
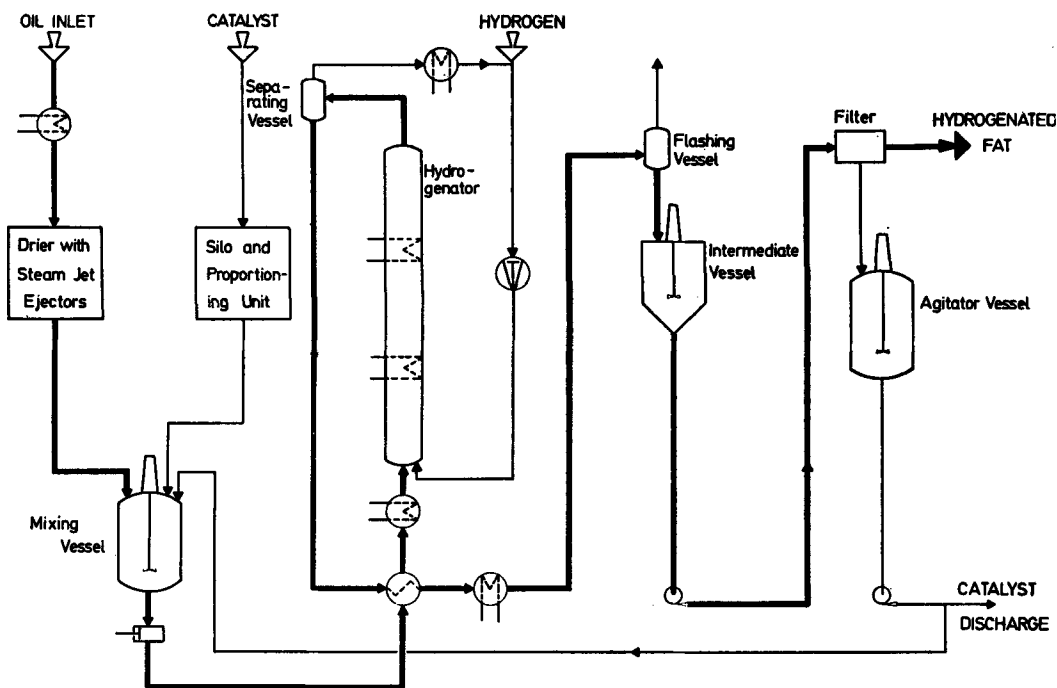
FIG. 1. Flow sheet of the continuous hydrogenation plant.

quickly through the reactor and is not converted at all. Such back-mixing can be avoided when several agitated vessels are arranged in series and the material for hydrogenation is run through them in succession. In these instances where real agitated vessels have to be employed as reactors, a plant with more than five or six agitated vessels is found uneconomical. In the hydrogenation of triglycerides containing linolenic fatty acid, i.e., soybean oil, the object is to reduce the linolenic acid to a concentration of, e.g., 0.1% or less. It can be proved by means of theoretical considerations and by tests that it is absolutely necessary to conduct the hydrogenation in more than 10, if possible in 15 or still more reaction stages. In order to ensure that a continuous hydrogenation plant is not too expensive and therefore uneconomical, it has been necessary to design reaction stages which are as simple and as low in cost as possible.

The hydrogenation reactor used for the present studies consists of a column through which both reaction components, hydrogen and triglyceride, are run concurrently from bottom to top. Except for the rising gas bubbles, the reactor is entirely filled with liquid, and trays with flow apertures divide it into 16 reaction chambers to avoid back-mixing. There has been no need to incorporate agitators, as the hydrogen is recycled and the volume of recycle gas is sufficient to thoroughly mix the contents of the individual reaction chambers and to keep the catalyst in suspension, besides, the velocity of the hydrogen is such to prevent back-flowing of the liquid through the apertures of the trays in the column.

Following is a description of the whole continuous hydrogenation process (Fig. 1).

First the neutral oil is freed of water in a vacuum drier and then mixed with fresh and used catalyst. This suspension and recycle hydrogen are fed to the multiple-stage reactor in which hydrogenation takes place. Unreacted hydrogen is separated from the hydrogenated fat in a separator. The fat is withdrawn continuously and filtered for removal of the catalyst. Hydrogen cycling is maintained by a cir-

culation pump. The volume of hydrogen required to obtain the desired degree of hydrogenation, is metered into the hydrogen cycle. In this manner the pressure in the reaction system adjusts automatically. Owing to this automatic pressure build-up in conjunction with the proportioning of the hydrogen into the reaction system, the desired degree of hydrogenation is exactly maintained for any desired length of time. Part of the used catalyst may be returned from the filter to the process. The remainder is removed and replaced by fresh catalyst.

The plant described also offers all advantages usually found in a continuous process. Particularly the gentle thermal treatment of the material to be hydrogenated because of the rapid heating, and the better heat utilization are worth mentioning. This is outlined by the heat exchangers shown in Figure 1. A further advantage is the constant hydrogen consumption.

## Pilot Plant Operation

The process has been tested in a pilot plant of the design described above. Mainly soybean oil has been hydrogenated using commercial catalysts. The capacity of the pilot plant could be varied between 0.5 and 1.2 metric tons per day.

TABLE I
Continuous Hydrogenation
of Soybean Oil With Nickel Catalyst

| Test No. | 1 | 2 | 3 |
|---|---|---|---|
| Temperature, C | 180 —200 | 200 | 200 |
| Throughput daytons | 0.65 | 0.86 | 0.86 |
| Iodine value in final product | 76.4 — 77.7 | 82.5 —84.0 | 82.7 —83.8 |
| Melting point, C | 37.5 — 38.2 | 34.8 —35.2 | 34.8 —35.2 |
| Dienoic fatty acids, % | 0.98 | 0.96 | 0.80 |
| Trienoic fatty acids, % | 0.01 | 0.04 | 0.02 |
| Average pressure, kg/sq. cm | 1.8 | 2.6 | 4.1 |
| Pressure range, kg/sq. cm | 1.5 — 2.4 | 1.8 — 3.2 | 3.6 — 4.8 |
| Test duration, hr | 25 | 48 | 25 |

TABLE II
Continuous Hydrogenation
of Soybean Oil With Different Catalysts

| Test No. | Initial material | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Catalyst | | Nickel flakes | Nickel flakes | Nickel on Kieselgur | Copper chromite |
| Catalyst concentration, % | ........ | 0.1 | 0.1 | 0.1 | 0.3 |
| Temperature, C | ........ | 190 | 170 | 190 | 190 |
| Throughput daytons | ........ | 1.2 | 1.2 | 1.2 | 1.2 |
| Iodine value | 130.8 | 103.7 | 104.4 | 104.8 | 111.0 |
| Dienoic fatty acids, % | 46.7 | 19.9 | 18.2 | 26.5 | 33.1 |
| Trienoic fatty acids, % | 7.6 | 1.9 | 1.4 | 3.0 | 0.4 |
| Pressure, kg/sq. cm | ........ | approx. 3 | approx. 3 | approx. 3 | 20–30 |
| Linolenate Selectivity | ........ | 1.35 | 1.49 | 1.34 | 5.77 |

TABLE III
Batchwise Hydrogenation
of Soybean Oil With Different Catalysts

| Test No. | Initial material | 1 | 2 |
|---|---|---|---|
| Catalyst | | Nickel on Kieselgur | Copper chromite |
| Catalyst concentration, % | ........ | 0.1 | 0.3 |
| Temperature, C | ........ | 190 | 190 |
| Iodine value | 131.0 | 104.0 | 109.0 |
| Dienoic fatty acid, % | 52.5 | 33.4 | 35.7 |
| Trienoic fatty acid, % | 8.5 | 4.5 | 0.5 |
| Pressure, kg/sq. cm | ........ | 1.9 | 16.0 |
| Linolenate Selectivity | ........ | 1.16 | 5.10 |

The object of the first test series was to produce a fat from soybean oil of a melting point of 35 and 38 C for further processing to margarine. A catalyst consisting of 50% nickel on kieselgur was used at the 0.1% level. Most of the catalyst had been used several times and 10% fresh catalyst added. The temperature was kept between 180 and 200 C. Table I shows some typical results of these hydrogenation tests.

It can be said generally that the consistency of the products obtained on this continuous pilot plant, e.g., as regards the melting point and the solid fat index, and the composition of the products do not differ practically from those products obtained by the batch process on an industrial plant and with the same catalyst. The low content of dienoic and trienoic fatty acids however, is especially remarkable.

Test 3 was run in order to demonstrate the performance of the design principle for this continuous hydrogenation plant. The set conditions, such as throughput, reaction temperature, ratio of hydrogen to oil, etc., were identical to those of Test 2, moreover, operation was not interrupted between these two tests. The only difference was that the addition of fresh catalyst was stopped after Test 2 had run for 48 hr. Since the used catalyst is no longer as active as the fresh one but the hydrogen to oil ratio remains the same, the pickup of hydrogen is enforced by a higher pressure in the plant, and the degree of hydrogenation remains identical to that of the preceding test. This is apparent from the practically unchanged iodine value of the final product. The fluctuations occurring in the melting point are only slightly beyond the limits of analysis accuracy. The variations of the pressure in the plant during a test are explicable by slight modifications of the catalyst concentration and by different hydrogenation properties of the crude stock.

The aim of another test series was to try to produce an oil retaining only very little trienoic fatty acids starting from soybean oil and applying little hydrogenation, i.e., a slight reduction of the iodine value

by 20 to 25 units. Table II shows the results obtained in this manner.

It can clearly be seen that one cannot obtain as good results from nickel catalysts as from Adkins copper chromite catalyst. Even if the iodine value is lower than in the test with copper catalyst (Test 4), the products hydrogenated with nickel (Tests 1–3) still contain much more linolenic acid. This property of the catalyst can be expressed numerically by indicating the linolenate selectivity. Table II shows this selectivity in the last line.

It must still be stressed that these tests have not been conducted in order to find or develop catalysts which have a very high selectivity. Catalysts with a very high linolenate selectivity as, e.g., 10 to 15 have already been described in the literature (8–9). The hydrogenations were carried out with a commercially available Adkins catalyst of the same type as was used earlier in the production of fatty alcohols from fatty acids. These tests were only carried out to show that hydrogenation by this continuous process is just as selective as hydrogenation by the batch process. To prove this, batch hydrogenation was carried out with nickel catalyst and with copper chromite catalyst under the same conditions. The results are listed in Table III. It follows from the calculated linolenate selectivity that no difference is perceptible between batch hydrogenation and hydrogenation in the continuous plant.

REFERENCES

1. Normann, W., DRP, Patent No. 141,029 (1902).
2. Bolton, E. R., E. J. Lush, EP 162, 270 (1920); Ibid. 203, 218 (1922).
3. Mills, V., AP 2 520 423–425 (1947).
4. Smith, F. G., JAOCS 25, 328 (1948).
5. Bailey, A. E., Ibid. 26, 644 (1949).
6. Albright, L. F., Ibid. 42, 250 (1965).
7. Butterfield, R. O., E. D. Bitner, C. R. Scholfield and H. J. Dutton, Ibid. 41, 29 (1964).
8. Koritala, S., and H. J. Dutton, Ibid. 43, 556 (1966).
9. Okkerse, C., A. de Jonge, J. W. Coenen and A. Rozendaal, Ibid. 44, 152 (1967).
10. Allen, R. R., Ibid. 44, 466 (1967).
11. Albright, L. F., Chem. Eng. 74(19), 197 (1967).
12. Butterfield, R. O., H. J. Dutton, JAOCS 44, 549 (1967).
13. Schmidt, H. J., Ibid. 45, 520 (1968).

[Received May 27, 1969]