Practical Features in Soybean Oil Hydrogenation

I. GARIBAY M., Aceitera "La Gloria," S.A., Apartado 1-229, Guadalajara, Mexico

ABSTRACT

Soybean oil differs from other oils in linolenic acid content. This causes variations in processing. Hydrogenation of soybean oil depends on catalyst selectivity, hydrogenation conditions and the final product desired. Oil, hydrogen and catalyst must meet certain conditions in order to attain successful hydrogenation. Batch equipment and processing are described.

INTRODUCTION

Soybean oil belongs to the linolenic group of oils. It shares with cottonseed, peanut, sunflower, corn and safflower oils two peculiarities: a low content of saturated (16:0 and 18:0) acids and high percentage of 18:1 and 18:2. Soybean oil has, in addition, a significant amount of linolenic, 18:3.

Oils from the oleic-linoleic group may be processed as cooking or salad oils, some of them without being winterized and others after dewaxing or winterizing. None of these oils shows flavor reversion, except for soybean. This flavor change results from the linolenic group, which has a very high reactivity. Soybean oil used as salad oil may be subjected to a light and very selective hydrogenation followed by winterization, to drastically reduce the linolenic acid.

GENERAL PRINCIPLES

Hydrogenation has two principal aims: to manufacture solid or semisolid products with certain plastic properties, and to increase the stability of the oil.

The hydrogenation reaction appears to be very simple; however, it is a complex reaction. Soybean oil is a mixture of different triglycerides, both saturated and unsaturated. When this oil is partially hydrogenated, it may form a very large variety of products, depending on which triglyceride is saturated, which double bond is saturated and what kind of isomers are formed among the molecules not saturated. Furthermore, it depends on the degree of progress of hydrogenation. These factors combined lead to the conclusion that, theoretically, it is possible for a single oil to yield thousands of different hydrogenated products.

The hydrogenation course and the composition and characteristics of the final product depend on the factors shown on Table I. The most important factor probably is the type of catalyst. Some catalysts promote formation of iso-oleic more than others. This can be useful in the hydrogenation of margarine stocks, provided the catalyst does not promote the formation of saturated products. If that happens, the catalyst is unsuitable for partial hydrogenation and should be used only for total hydrogenation where iso-oleic and saturated formation is desirable.

It is notable that in soybean oil hydrogenation, there are two distinct types of selectivity. One is that which allows the hydrogenation of linolenic groups to proceed before that of the linoleic and oleic groups. The other selectivity is for the preferable saturation of linoleic groups over oleic groups. Nickel catalyst is not very effective for the 18:3 over 18:2, but it can be very effective for the selective saturation of 18:2 over 18:1.

TABLE I

Hydrogenation Factors

	Activity	Selectivity	*trans*-Isomers
Temperature	+	+	+
Pressure	+	-	-
Agitation	+	-	-
Catalyst type	+/-	+/-	+/-
Catalyst conc.	+	+	+

Hydrogenation Requirements

In order to hydrogenate satisfactorily, it is essential that the oil, the hydrogen and the catalyst meet several conditions. Soybean oil should be well refined, bleached and dried, free of gums (phosphatides) and peroxides. The soap content must not exceed 20 ppm. The absence of gums is very important. If they remain in the oil, they may poison the catalyst and precipitate at hydrogenation temperatures, darkening the oil and clogging filters, thus making filtration almost impossible. Soap poisons the catalyst. It reacts with nickel, forming nickel soaps and reducing proportionally the available nickel. Moisture inactivates the catalyst and may promote free fatty acid formation by hydrolysis.

Hydrogen should be at least 99% pure. It should be dry and free of contaminant gases such as H_2S, CO, SO_2, and CS_2. Modern hydrogen plants which produce hydrogen from gaseous hydrocarbons and steam yield a very pure hydrogen, especially if the hydrogen is purified by molecular sieves. The purity may reach 99.97%. When hydrogen contains sulfur compounds, the S combines with nickel, poisoning the catalyst and reducing activity and selectivity drastically.

The catalyst is the critical element of hydrogenation. The course of the reaction depends on it, and the reaction speed depends on the activity of the catalyst. Durability is economically important because the catalyst may be used for several hydrogenations before it is discarded. Selectivity is the most important characteristic, because it determines the course of the reaction. Isomer formation is important to the hydrogenation of certain products. Filterability allows complete separation of the catalyst from the oil. Uniformity ensures the same performance of the catalyst, even if different lots are used.

In the hydrogenation of stearines, the only important characteristics for catalysts are activity, durability and filterability.

Products of Hydrogenation

The most important products prepared from soybean oil are shortenings, margarines and stearines.

Shortenings. Fairly selective conditions are used to avoid isomer formation: temp, ca. 150 C; pressure, high (40-60 psig); and catalyst concentration, 0.05-0.10%. A selective catalyst is used with low iso-oleic promotion properties. Main objective: plasticity.

Deep frying and biscuit shortening. Highly selective conditions are needed to obtain a low content of diunsaturates:

temp, ca. 180 C; pressure, low (5-10 psig); catalyst concentration, 0.12-0.15% (high). A very selective catalyst is used. Main objective: stability.

Margarines. Highly selective conditions are used to promote isooleic formation and to avoid saturated group formation. Thus, the product will melt below body temperature and will be firm at low temperatures to permit forming and packing operations. Conditions: temp, ca. 180 C; pressure, low (0-5 psig); and catalyst concentration, 0.10-0.15%. A highly selective catalyst is used with high iso-oleic promotion properties. Main objective: low saturated contents.

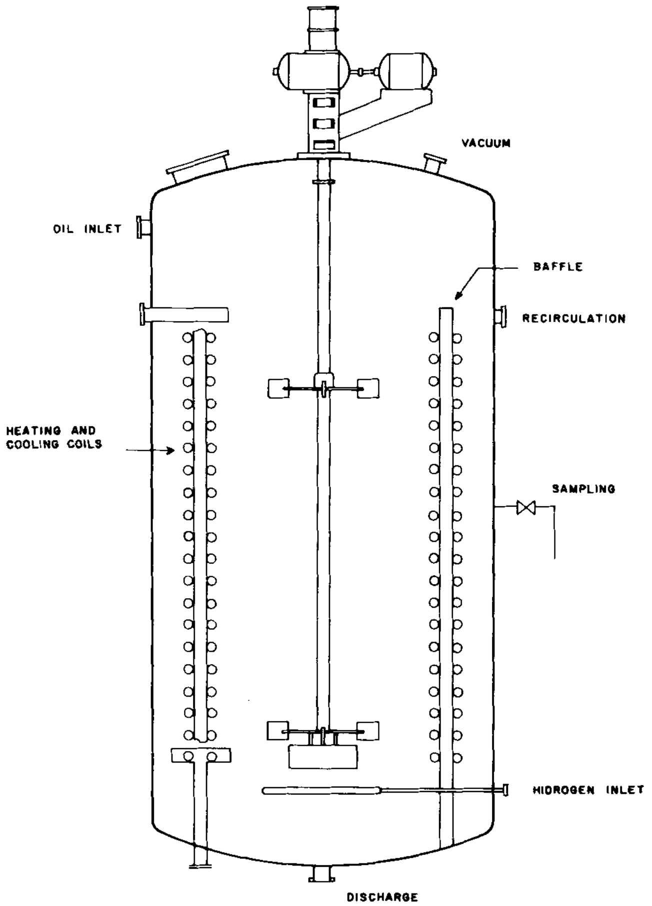

FIG. 1. Typical batch converter.

Stearines. Selectivity is unimportant and iso-oleic formation is insignificant: temp, ca. 220 C; pressure, 60-100 psig; very high catalyst concentration, preferably catalyst discarded from shortening or margarine hydrogenations, 0.5-1.0%. Main objective: activity for a fast hydrogenation.

HYDROGENATION EQUIPMENT

In spite of the tremendous amount of oils hydrogenated worldwide, many plants are using the same procedure developed by Normann almost 80 years ago. Many processors hydrogenate different oils because of geographic or economic reasons, or both. On the other hand, characteristics of hydrogenated products are very different. Continuous hydrogenating equipment has been developed, but it has limitations. It requires a unique raw material run day after day and crucial volumes of finished product with unchanged characteristics. For this reason, the most commonly used batch equipment will be described.

The reactor for hydrogenation is called a converter (Fig. 1). It is a carbon steel, vertical cylinder with coils for heating and cooling. A turbine agitator and a hydrogen distribution pipe provide the required agitation. There are provisions for changing oil and catalyst, for recirculating the oil coming from the filter press, for unloading the converter and for sampling the oil. There is also a connection for vacuum. The converter is designed for pressures of 150 psig. It is constructed with or without hydrogen and oil recirculation. The two types with recirculation are generally found in industry. Heating is supplied by high-pressure steam or a thermal fluid. Operation temperature range is 150-225 C. The reaction is exothermic, i.e., temperature rises 1.7 C for each unit of iodine value reduction; therefore, it is imperative to cool the oil to maintain the hydrogenation temperature specified.

In addition to the converter, there are two filter presses, several tanks, pumps, and appropriate instruments to measure, control and keep records of the operation.

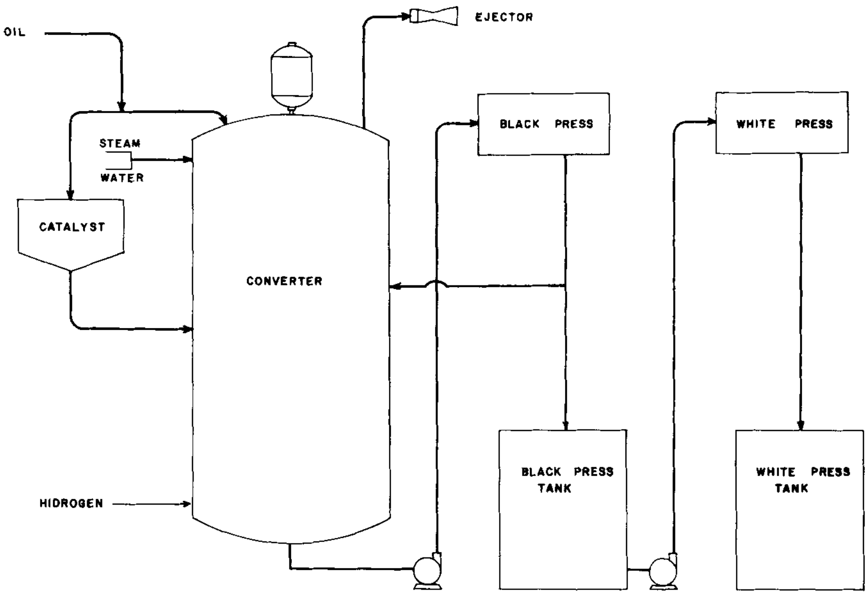

FIG. 2. Hydrogenation unit operation.

PROCEDURE

The operation is outlined in Figure 2. The converter is loaded with oil from a scale or a measuring device. The valve for the vacuum system is opened. The vacuum deaerates the oil and prevents it from oxidation. Steam for heating is turned on and the catalyst, previously suspended in oil, is added any time during the heating period. When the oil reaches the specified temperature, the vacuum is closed and hydrogen is added until the specified pressure is attained. Pressure is kept unchanged during hydrogenation. When the exothermic reaction raises the oil temperature close to the maximum temperature specified, water is introduced into the coils. Samples are withdrawn from time to time to determine the refractive index (related to the iodine value) for measuring hydrogenation progress. When the operator judges that the endpoint is very close, the agitation and or hydrogen circulation are suspended until laboratory results are ready. With some practice, operators may determine the endpoint proximity by the pressure drop in hydrogen storage tanks. Each plant has its preference for a method to determine endpoint. Iodine value, refractive index, congeal point, cloud point and C number are some methods used. If this analysis shows that the hydrogenation is over, hydrogen is vented to the atmosphere through the vacuum system, the agitator is run again and the oil is cooled or transferred to a cooling tank or heat exchanger. The cooling continues until a temperature of 65 C is attained. The oil is filtered through the "black press" that is precoated with oil, and then filtered to separate catalyst from oil. Generally, it is necessary to recirculate the oil several minutes to obtain a clear filtrate. Recently developed catalysts appear to have excellent filterability so that filter aid is not required. The oil is poured into a tank supplied with coils and agitator. This tank is used frequently to rebleach the oil or for the addition of other stocks. Citric or phosphoric acid is added to the oil before filtering it again. This acid inhibits any adverse effects that traces of nickel impart to the oil.

After the oil is filtered through this press, called the "white press," it is ready to be deodorized. It is not advisable to invert the order because hydrogenation gives the oil a peculiar and undesirable odor.

De Smet Process for Physical Refining of Soybean Oil

G.L. POSSCHELLE, De Smet USA Corp., 2625 Cumberland Parkway, Suite 200,
Atlanta, GA 30339

INTRODUCTION

Physical refining—also called steam-refining—is the combined neutralization and deodorization by steam distillation under high vacuum. The process will give, with the right equipment, a first class edible oil from a good quality crude.

However, to obtain a good final product, it is essential to make sure the crude oil entering the neutralizer/deodorizer is free of impurities. Considering the process of water-degummed soybean oil with 0.2–0.5% phosphatides content, the three steps of the physical oil refining process are discussed.

CENTRIFUGAL ACID DEGUMMING

Water-degummed oil contains remaining phospholipids and other gum-like impurities. The object is to eliminate them as much as possible. To accomplish this, centrifugal degumming using a small quantity of phosphoric acid is most recommended; the acid attacks the hydratable and nonhydratable phospholipids and eliminates trace metals. Centrifugal separation of the formed compounds reduces the phosphorous content of the oil to 10–20 ppm.

This process can be replaced by the degumming stage of an alkali centrifuge refinery, if this is available in the factory.

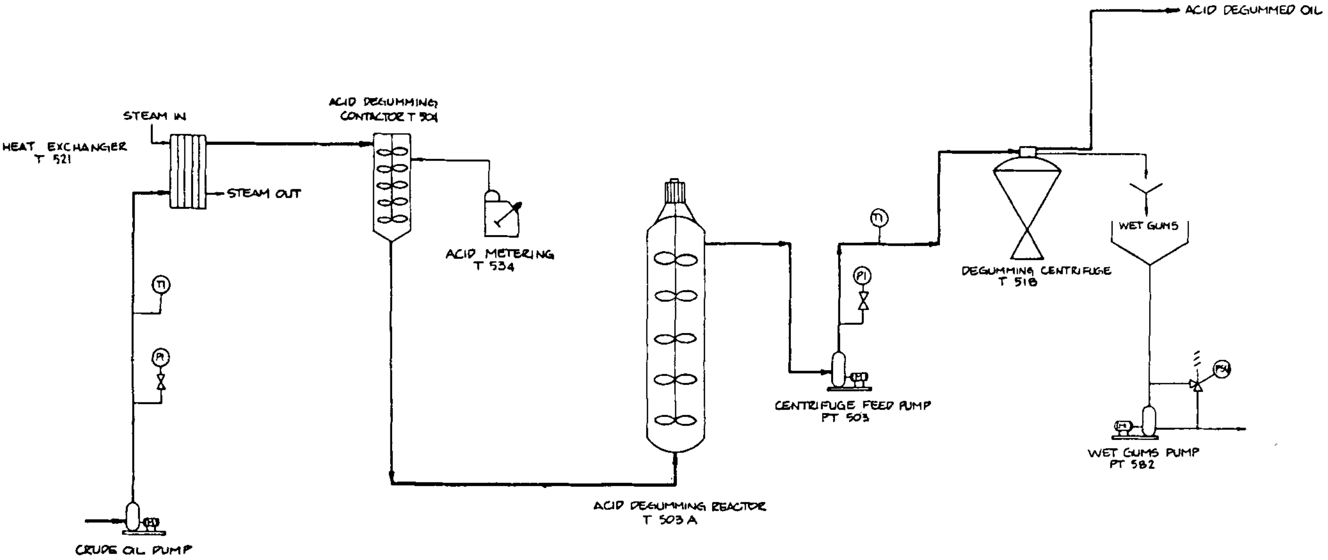

FIG. 1. Acid-degumming.