containing polyunsaturated acids with 4 or more double bonds, and, in fact, soybean oil of IV greater than about 140 (and containing 7–9% linolenic acid). For these oils, hydrolytic methods at lower temperatures are required.

Enzymatic Fat Splitting

Lipolytic enzymes such as those obtained from castor beans have been used in the past to split fats (14), but this technique is inefficient (best conversions approximate only 90%), sluggish and not especially easy to handle as a unit operation. In process, the method was a batch operation suited only for fats limited to a melting point of 40 C, and consumed from 24–48 hr for completion. However, this technique, in the case of very sensitive fats and oils such as conjugated components or those containing up to four or five double bonds (from fish oil) may be the only one of all the methods capable of generating fatty acids from triglycerides with minimal structural changes (see M.E. Stansby's paper). Although castor oil has been split in the past by this method, it is no longer split this way today, recourse being made to other less drastic hydrolyses than medium or high pressure splitting techniques.

Although enzymatic splitting has had little value in the past as an industrial method of fat splitting, its use in the laboratory for the determination of fat and oil structure has been very important. Pancreatic lipase has been discovered to preferentially hydrolyze the 1- (or 3-) positions of glycerides (15). Under controlled conditions the specificity may be made absolute (16,17). Already, hundreds of fats and oils have been investigated with this technique; much triglyceride structure definition has accrued. More recently, the discovery that the lipase from the seed of *Vernonia anthelmintica* is capable of preferentially hydrolyzing the 2-position of fats and oils, first established with trivernolin oil itself (18), appears to be a useful discovery. Immediately it was established that the unique keto structure of this oil was not responsible for the specific positional hydrolysis, for pancreatic lipase hydrolyzed it to the expected 1,2-diglycerides (19) indicating that the normal 1- or 3-hydrolysis had indeed occurred. It remains to determine if the 2-position specificity for this lipase is characteristic of other fats and oils.

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Hydrogenation of Fatty Acids

R.C. HASTERT, Catalyst Department, Harshaw Chemical Co.,
23800 Mercantile Rd., PO Box 22126, Beachwood, OH 44122

ABSTRACT

Catalytic hydrogenation is a vital process for both the edible fats and oil and the industrial fatty chemical industries. The similarities and differences between the fat and oil and fatty acid hydrogenations in equipment, processing conditions, and catalysts employed are of some importance since both are used in the various operations. Generally, the catalytic hydrogenation of fatty acids is carried out in corrosion-resistant equipment (316SS), whereas for fats and oils while 316SS is desirable, 304SS or even black iron suffice. The speed of hydrogenation varies radically with the content of impurities in both fat and oil and fatty acid feedstocks. Especially detrimental for both hydrogenations are soap and sulfur contaminants, proteinaceous materials left in the oils from poor refining, etc. Fatty acids from vegetable oil soapstocks are especially difficult to hydrogenate. Soybean-acidulated soapstock must usually be double-distilled for good results; cottonseed soapstocks frequently triple-distilled in order that they can be hydrogenated below iodine values of 1. Fatty acid hydrogenation effectiveness is measured by achieving a low iodine value as fast and as economically as possible. Variables that influence hydrogenation effectiveness are reactor design, hydrogen purity, feedstock quality, catalyst activity and operating conditions.

INTRODUCTION

History and Background

The origin of vapor phase hydrogenation is usually traced to Sabatier and his associates (1). In 1897 they were trying to make nickel carbonyl by the addition of ethylene to nickel. The experiment was "unsuccessful." Analysis of the gaseous residue revealed ethane rather than nickel carbonyl. The nickel had served as two catalysts. It first decomposed some of the ethylene to form carbon and hydrogen and then hydrogenated the remaining ethylene to ethane.

Hydrogenation in the liquid phase is generally credited

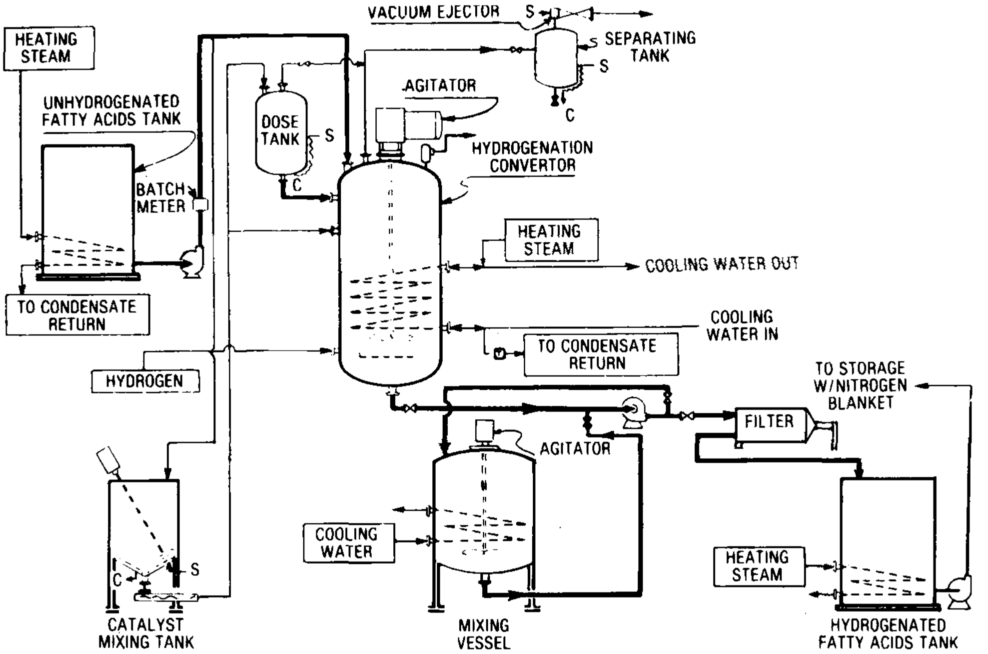


FIG. 1. Flowsheet for hardening plant.

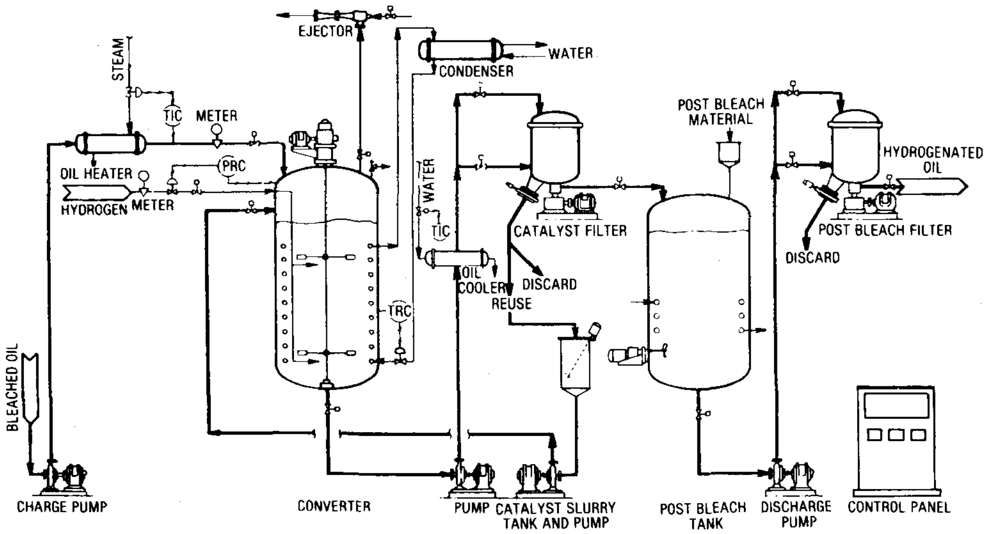


FIG. 2. Batch hydrogenation plant.

to William Normann, who obtained a British patent on the process in 1903 (2). The novelty of Normann's contribution was that the reaction not only was conducted in the liquid state but that it also employed a relatively inexpensive catalyst, nickel, instead of one of the precious metals, such as platinum or palladium. Commercial fatty acid hydrogenation in the United States became significant in the early 1930s. Vegetable oils were then coming into use as ingredients in the manufacture of shortening and margarine. The crude oils required caustic refining which produced a soapstock byproduct. While the soapstock could be acidulated into relatively pure fatty acids, it retained the high iodine value of the oil from which it had come. Enterprising observers quickly perceived that hydrogenation could turn his abundant and relatively cheap byproduct into a saturated fatty acid having a titer even higher than the familiar triple-pressed stearic. The first stainless steel converters, operating at pressures up to 150 PSIG (10 ATO), followed soon thereafter. Higher pressures did not become common until the late 1940s and then as a spinoff from the higher pressure equipment required to hydrogenate fatty nitrogen derivatives.

Hydrogenation of fatty acids to a very low iodine value is both simple in definition and readily measurable in effectiveness. The objective is to reduce the iodine value as low as possible, as fast as possible, as cheaply as possible. Variables that affect the reaction rate are: (a) reactor design; (b) hydrogen purity; (c) catalyst efficiency; (d) operating conditions; (e) feedstock quality.

Reactor Design

Before looking specifically at the hydrogenation reactor, let us review its position in the series of operations that constitute the hydrogenation process. Collectively, they are commonly referred to as a **hardening** plant.

Figure 1 (3) is a typical flowsheet for a hardening plant. The hydrogenation vessel (commonly called a converter) receives unhydrogenated oil, hydrogen and catalyst. It is serviced by electricity (for the agitator), a vacuum system (for drying and hydrogen evacuation), steam (for heating), and water (for cooling). Prior steps include hydrogen generation, feedstock purification and catalyst preparation.

Subsequent steps include cooling and catalyst removal.

Figure 2 (4) is a flowsheet of a different engineering company. While this print was prepared for an edible oil hardening plant, the operations are essentially the same. The only significant differences in the design of hardening plants for edible vs. fatty acid hydrogenation are the pressure requirements and the materials of construction. Edible oil converters are usually designed for a maximum of 100 PSIG (7 ATO), whereas 500 PSIG (34 ATO), or even higher, is common for fatty acid plants. Stainless steel is required for fatty acids. It is desirable but not essential for triglycerides. Specific materials of construction for fatty acid converters will be covered in another paper.

Figure 3 (5) is a hardening plant flowsheet from another engineering company. A distinctive feature of this flowsheet is that it includes a heat recovery tank. The heat exchange between the incoming cold feedstock and the hot hardened fat saves both steam and cooling water. It seems reasonable to assume that all hardening plants built in the future will include energy saving features.

Figure 4 (6) illustrates a variation in design for energy conservation. Instead of a drop tank for each converter, there is one external heat exchanger for two converters that are counter-cycled. In other words, hot hydrogenated oil exiting from one converter meets cold feedstock entering the other converter. Figure 5 (7) depicts this external spiral heat exchanger.

Figure 6 (8) shows the cross-section of a typical industrial fatty acid converter. The design is not dependent on reactor size. This particular example includes hydrogen recycle. The advantage of recycling is controversial. Whether recycling or not, hydrogen concentration in the headspace will gradually decrease during hydrogenation. This is caused both by volatiles coming from the oil and by the accumulation of inerts (primarily methane and nitrogen) that may be present in the fresh hydrogen. Some operators maintain constant hydrogen concentration by a small continual bleed of headspace hydrogen. Others vent at intervals. Obviously, the amount of inert accumulation coming from the hydrogen is directly related to iodine value reduction.

A radically different engineering approach to a hydrogenation reactor system is depicted in Figure 7 (9). It is based on entrainment of hydrogen by high velocity liquid-catalyst flow through a Venturi nozzle. This system has been used quite extensively, particularly in Europe, for a variety of organic chemical hydrogenations. Fatty acid plants are also operating in Europe and South America, and one designed for continuous hydrogenation of fatty acids is currently under construction in Japan.

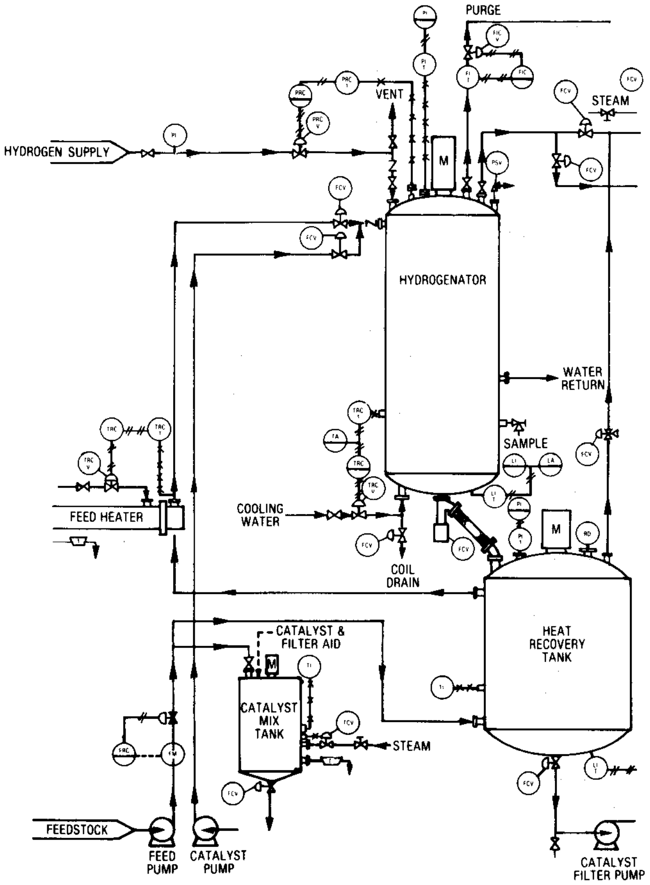


FIG. 3. Hardening plant with heat recovery system.

Another system, which is specifically engineered for continuous hydrogenation of fatty acids, is also available. Several such plants are in operation outside the United States. Figure 8 (10) is a flowsheet illustrating its design. The fatty acid is heated in heat exchanger E1 and sprayed into a vacuum vessel D2 for drying. A piston pump G2 conveys the dried feedstock through heaters E2 and E3 into

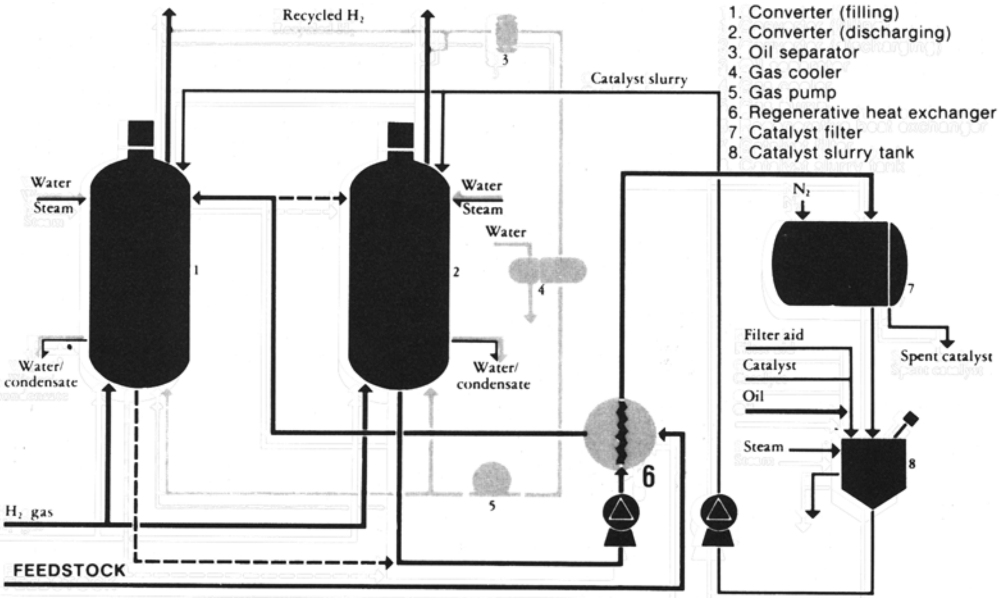
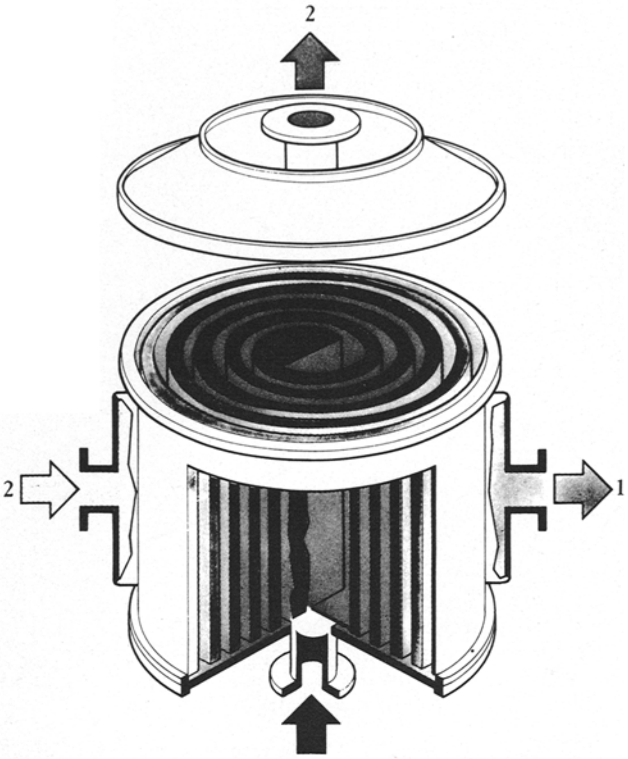


FIG. 4. Semicontinuous hydrogenation system.



1. Hydrogenated product.
2. Feedstock.

FIG. 5. External spiral heat exchanger.

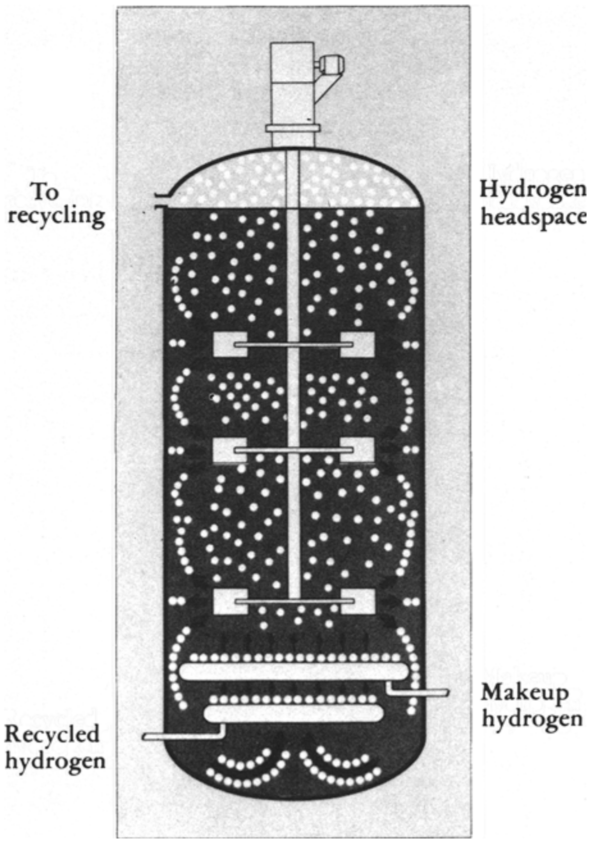


FIG. 6. Gas recycling system.

the hydrogenation reactor. Hydrogen and catalyst are added to the fatty acid feedstock before it enters the converter. Fatty acid, catalyst and hydrogen pass concurrently upward through reactor D1. Hydrogenation takes place at a constant pressure of ca. 370 PSIG (25 ATO) and at conventional temperatures. While the fatty acid and catalyst pass through the hydrogenator only once, a large excess of hydrogen over that needed for the reaction is recirculated through compressor G3. The hydrogenated fatty acid-catalyst mixture heat exchanges in E2 with the feedstock entering reactor D1. Heat exchanger E5 further cools the product. The fatty acid is then flashed (D4), temporarily stored (F2) and subsequently filtered for removal of the catalyst (D5).

Hydrogen Purity

Hydrogen is usually obtained either by steam reforming of hydrocarbons (methane or propane) or by electrolysis. Both methods produce hydrogen of high purity that is suitable for hardening fatty acids. Plants of proven design are available, scaled to whatever hydrogen requirement is desired. Both compressed and liquified hydrogen are also commercially available. The purity is excellent but the cost is higher. It is most often used where the requirement does not justify the investment for on-site generation. This may be for a primary need or to peak-load a generating facility that is being outgrown.

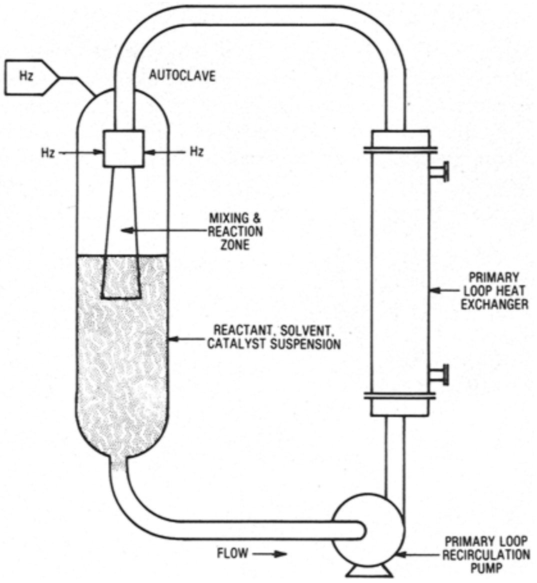


FIG. 7. Loop reactor operating principle.

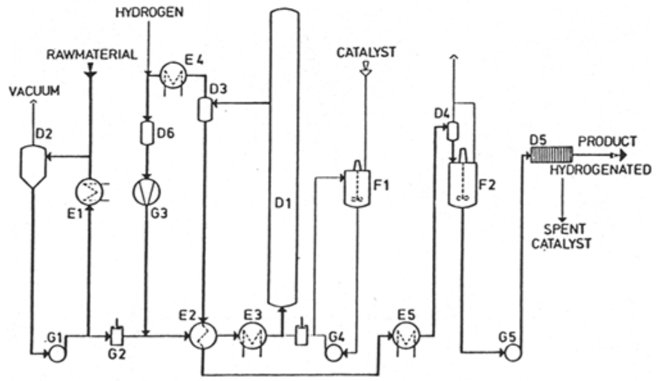


FIG. 8. Continuous hydrogenation system.

Catalyst Efficiency

Nickel catalysts of suitable quality for fatty acid hydrogenation are readily available from commercial manufacturers. This paper will not attempt to evaluate the differences among them. Most are of the dry reduced type, made by precipitation of nickel salts on silica or alumina supports. This is followed by washing, drying, reduction with hydrogen at elevated temperature and, because of their pyrophoricity, immersion in a protecting medium, usually a fully hardened vegetable oil or meat fat. Nickel catalyst made by the wet reduction of nickel formate is also sometimes used for hydrogenating fatty acids. While wet reduction is a classic reaction, done essentially the same by all manufacturers, dry reduced catalysts vary considerably in their composition and techniques of manufacture. Commercial catalyst companies are quite secretive concerning details of the manufacture of their products, and this paper will not delve into that subject.

Operating Conditions

The operating conditions that affect reaction rate are: (a) pressure; (b) temperature; (c) catalyst loading level; (d) agitation; (e) feedstock quality.

Figure 9 (11) illustrates reaction rate when hydrogenating distilled tallow fatty acids at pressures ranging from 50 PSIG (3.4 ATO) to 370 PSIG (25.2 ATO).

Figure 10 (12) illustrates the same phenomenon with a much less pure feed. As can be noted, there is a diminishing return with no further discernible advantage above ca. 450 PSIG (30 ATO).

Coenen (13) and others have shown that while raising the temperature greatly increases reaction rate at lower temperature levels, a diminishing return soon is evident, and at a certain level there is a negative effect. Figure 11 illustrates this phenomenon for sunflower fatty acids where the

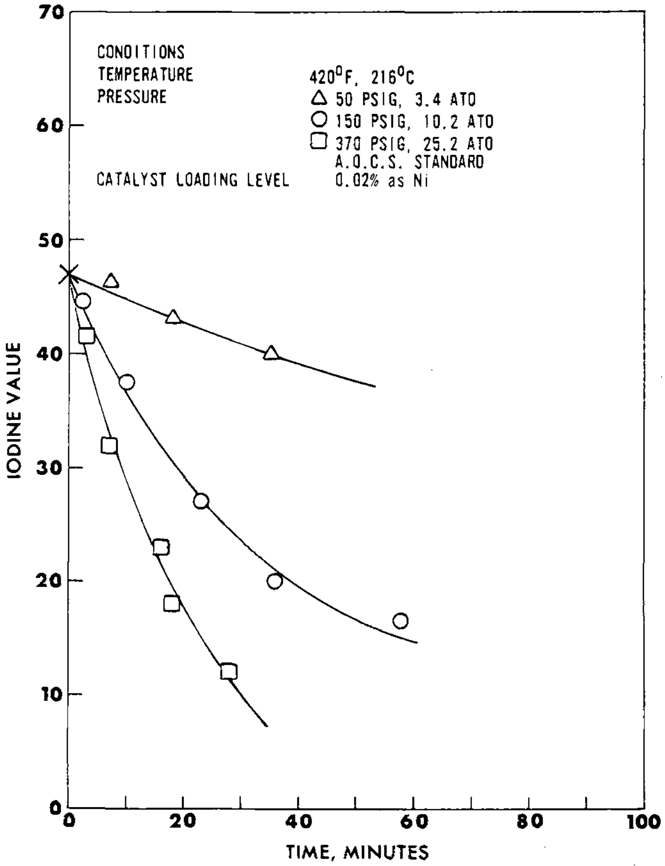


FIG. 9. Hydrogenation of distilled tallow fatty acids. Effect of pressure on reaction rate.

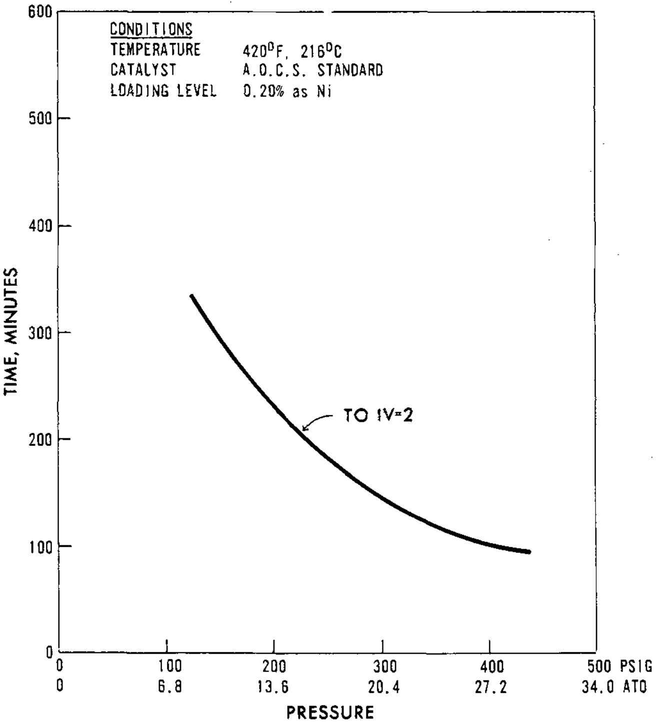


FIG. 10. Hydrogenation of undistilled oleic acid. Effect of pressure on reaction rate.

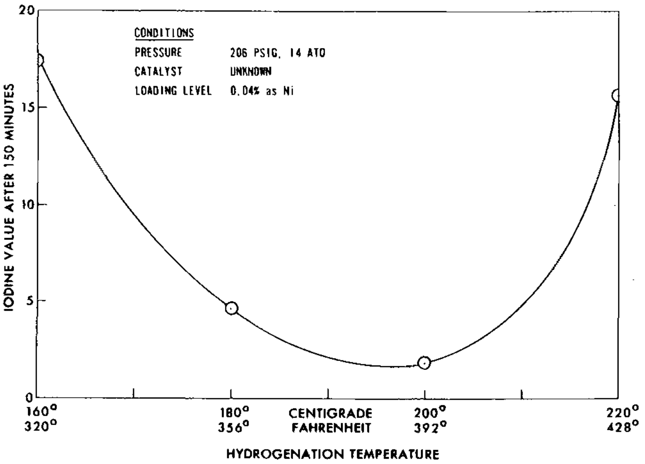


FIG. 11. Hydrogenation of sunflower seed fatty acids. Effect of temperature on reaction rate.

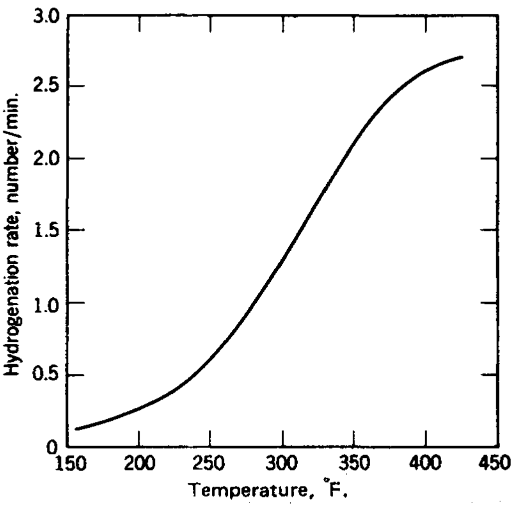


FIG. 12. Effect of temperature on rate of hydrogenation of cottonseed oil (14).

optimum is ca. 385 F (195 C). The optimum temperature varies for different fatty acids but is generally in the 360-410 F (180-210 C) range. This means that reaction cooling may be necessary to complete the hardening of a converter batch.

Bailey (14) had much earlier hinted at the same phenomenon when hardening cottonseed oil. Figure 12, taken from the third edition of his "Industrial Oil and Fat Products," illustrates his findings. These data show that the diminishing return effect for a triglyceride is at a considerably higher temperature than for a fatty acid.

Figure 13 (15) illustrates the acceleration in reaction rate achieved with an increased catalyst loading level when hydrogenating a high quality feedstock.

Figure 14 (16) also shows the reaction rate effect of catalyst loading level for a good quality feedstock but under somewhat different hardening conditions and is depicted in a different manner. The diminishing return phenomenon for catalyst loading level is more apparent in this graph.

The effect of agitation on reaction rate is the most difficult of the operating variables to illustrate because there are no means of measurement among converters comparable to temperature, pressure, etc. While variation can be introduced in the laboratory by changing stirrer speed, agitation in industrial converters is generally not variable.

Figure 15 (17) strikingly illustrates the effect of increasing stirring rate (i.e., agitation) when hydrogenating fatty acids in the laboratory at typical industrial conditions. Somewhere between 900 and 1000 rpm the maximum return for increased agitation is reached. It is my opinion that this maximum rate is not being achieved in industrial converters of current conventional design and hardware.

Figure 16 summarizes the effect of increasing the severity of individual operating conditions on reaction rate: (a) pressure diminishes but continues to give some return; (b) temperature levels off, peaks, and then decreases; (c) catalyst loading level starts slow, increases rapidly and then levels off; (d) agitation reaches an abrupt peak and then stays constant.

Accepted theory is that the only hydrogen capable of reaction are those molecules which have been solubilized in the oil. Therefore, if some technique were devised to increase this solubility, reaction rates could increase accordingly and new higher plateaus would be established for each of the operating variables. In my opinion, increasing the

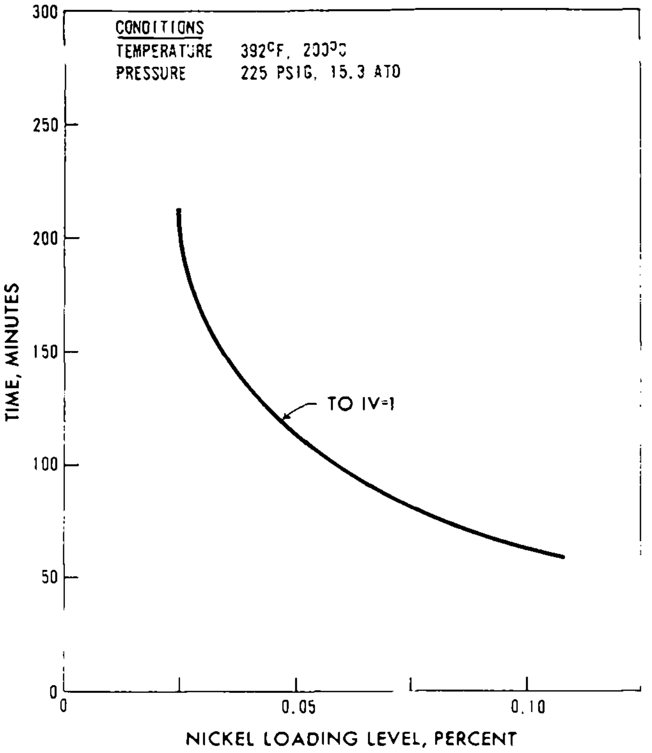


FIG. 14. Hydrogenation of distilled tallow fatty acids. Effect of catalyst loading level on reaction rate.

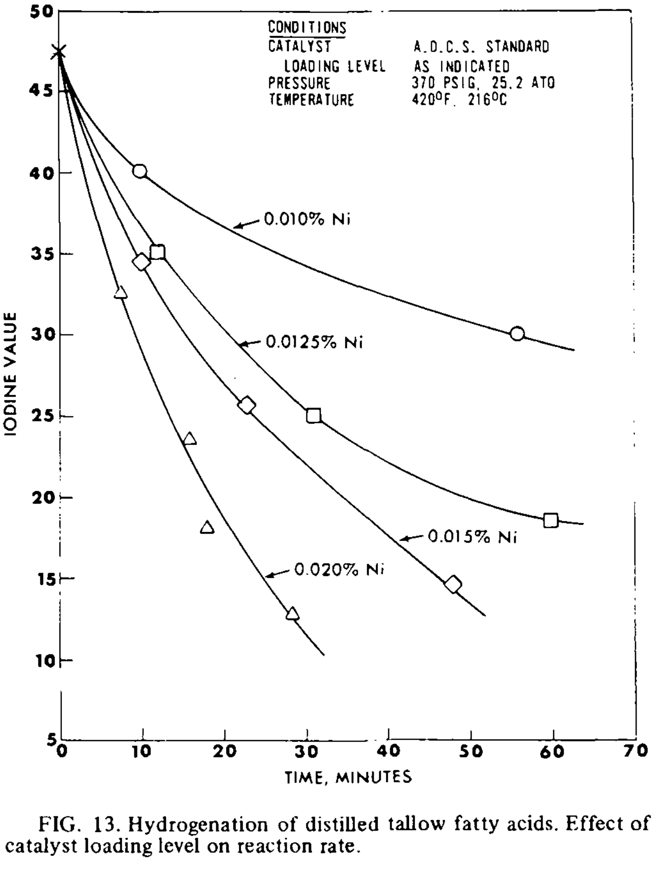


FIG. 13. Hydrogenation of distilled tallow fatty acids. Effect of catalyst loading level on reaction rate.

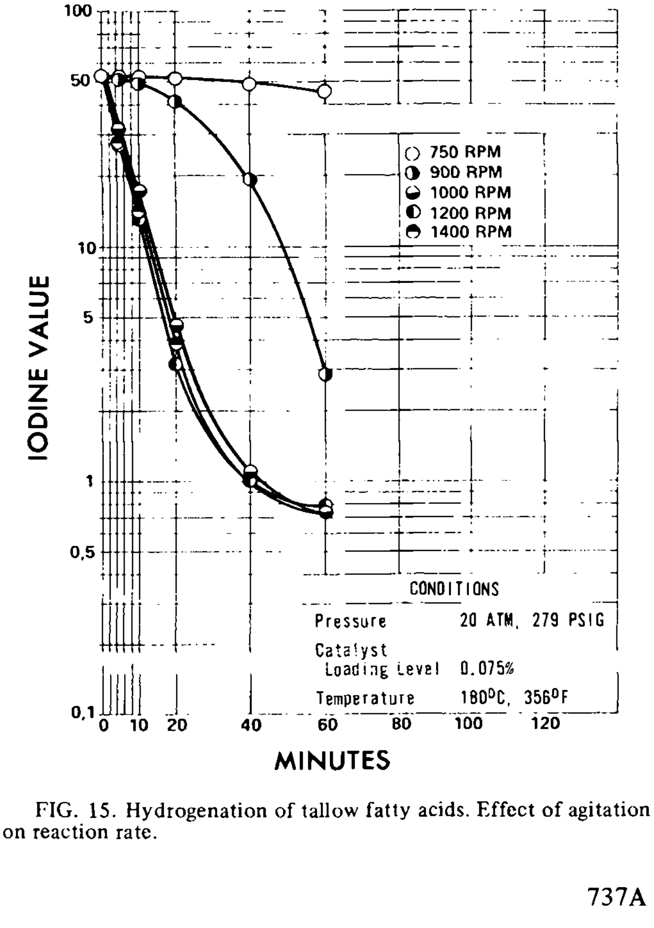


FIG. 15. Hydrogenation of tallow fatty acids. Effect of agitation on reaction rate.

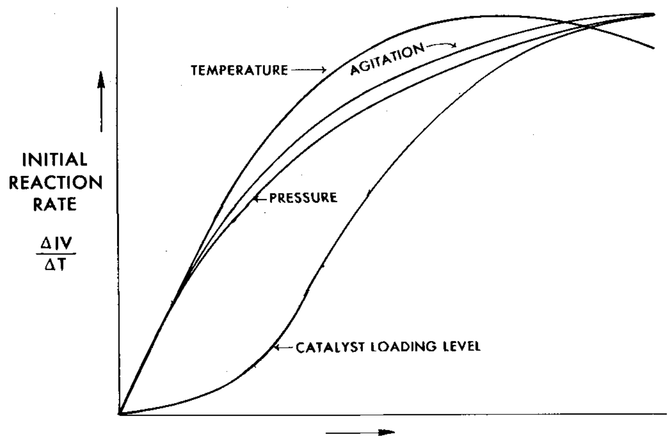


FIG. 16. Hydrogenation of fatty acids. Effect of operating variables on reaction rate.

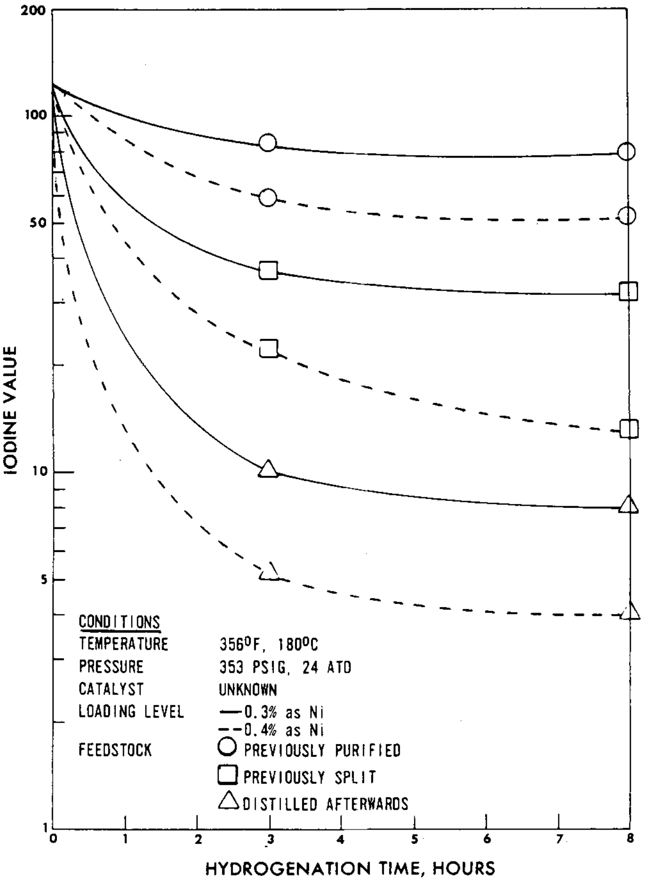


FIG. 17. Hydrogenation of marine fatty acids. Effect of feedstock quality on reaction rate.

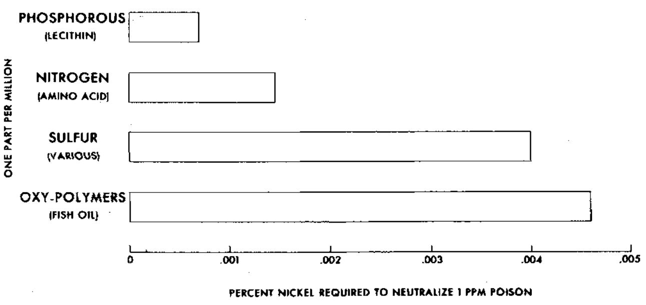


FIG. 18. Hydrogenation inhibiting effect of several catalyst poisons.

hydrogen bubble surface area through greater agitation should achieve the same result.

Figure 17 (18) illustrates the effect of feedstock purification on hydrogenation reaction rates. The same marine fatty acid was hardened under constant conditions with the only variable being the purification of the feed. The same phenomenon was observed at two catalyst loadings.

Ottessen (19) did an excellent piece of work several years ago attempting to define precisely the effect of several alleged catalyst poisons on catalyst effectiveness. Figure 18 depicts his findings for four such poisons. While choosing the optimum loading level of catalyst to be employed in a commercial converter depends on more than analyzing the feedstock for specific impurities, it is certainly true that known impurities neutralize catalyst to an exact degree. The threshold of this neutralized nickel must be exceeded before hydrogenation will take place.

Fatty acids react with nickel to form nickel soaps. Nickel soaps are not hydrogenation catalysts. Therefore, fatty acid hardening is essentially a race to get the reaction completed before the catalyst is inactivated. This is the reason the catalyst is not added to the converter until just before hydrogenation is to be begun. It is also the reason that catalyst employed to harden fatty acids cannot be reused. Some processors hydrogenate triglycerides before splitting them. Using this approach, catalyst can be reused.

Inedible Tallow Disposition

Tallow is a byproduct of the slaughter of cattle and sheep. In the United States it is mostly the former. About 10% of the tallow produced is utilized in direct manufacture of edible fats, principally shortening. The other 90% is disposed of in inedible applications as illustrated in Figure 19 (20)., Of the three billion pounds total inedible tallow in 1978, 23% (705 million pounds) was split into fatty acids. Of that portion, 41% (289 million pounds) was hydrogenated.

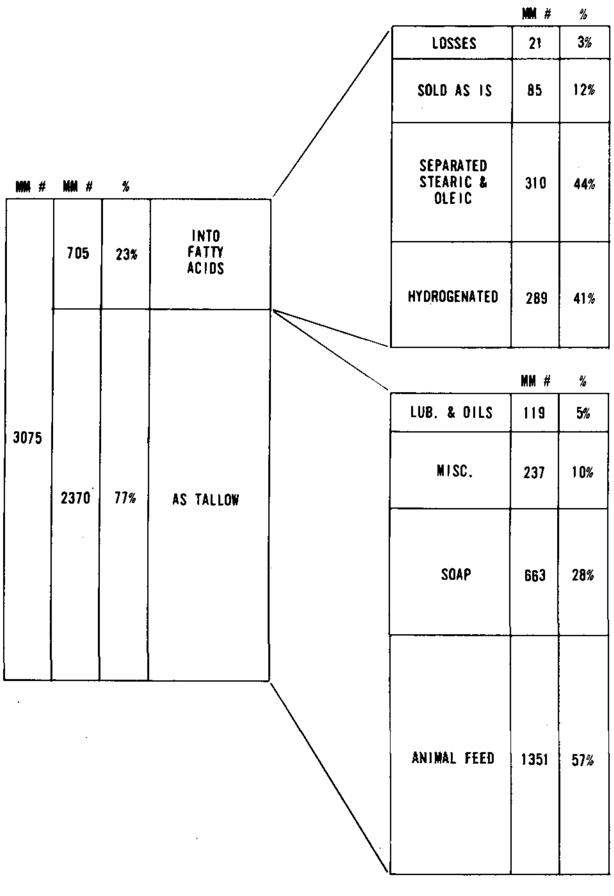


FIG. 19. Estimated 1978 U.S. disposition of inedible tallow.

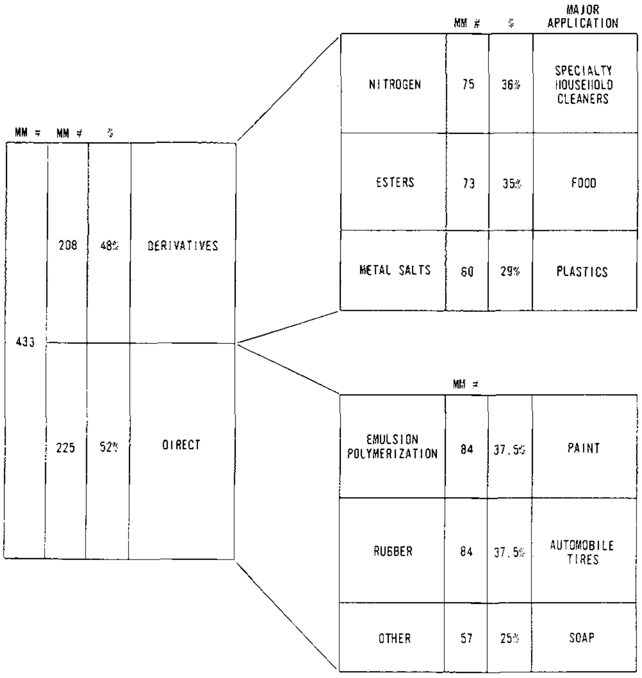


FIG. 20. Estimated 1978 U.S. consumption of hydrogenated tallow and soya fatty acids.

Total Hydrogenated Fatty Acids Consumption

Adding hydrogenated vegetable oil fatty acids (principally soya), plus some split edible tallow, to the inedible tallow source referred to above, brings the total of hydrogenated fatty acids to well over 400 million pounds annually. Their usage is depicted in Figure 20 (21). About half are used directly, with the paint and rubber industries accounting for 75% of this direct consumption. The other half are utilized in three major types of derivatives: nitrogen, esters, and metal salts. Their respective major applications are specialty household cleaners, food, and plastics.

Most of these applications will be discussed in detail in other papers. However, as is evident, hydrogenated fatty acids contribute to our technically based civilization in many and diverse ways.

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Separation of Fatty Acids

K.T. ZILCH, Technical Director, Emery Industries, Inc.,
4900 Este Avenue, Cincinnati, OH 45232

ABSTRACT

Fatty acid separations which do not involve fractional distillation are discussed. Various methods of separating fatty acids from a practical point of view and the most salient facts of each process are described.

HISTORICAL

The first reported separation of fatty acids that appeared in the literature was back in 1828 when a gentleman by the name of Gusserow (1) separated linear saturated fatty acids from linear unsaturated fatty acids by first preparing the lead salt derivative, dissolving the mixed salts in diethyl ether or ethyl alcohol, and then separating the less soluble saturated acids from the more soluble unsaturated acids. Because this method of separation was very efficient, many researchers since that time have prepared various salts of fatty acid mixtures and studied their fractionation in a number of solvent systems.

Separation of fatty acids by this procedure has never become a commercial reality because of process economics. However, before the advent of gas liquid chromatography, this method was frequently used as an analytical tool. In fact, the American Oil Chemists' Society Official Methods describes a lead salt separation procedure (2) for analyzing mixtures of fatty acids.

COMMERCIAL PROCESSES

There are basically five commercial processes for the separation of fatty acid products: panning and pressing; Solexol Process; Emersol Process; Armour-Texaco Process; and the Henkel Process.

Panning and Pressing

In the Panning and Pressing Process (3,4), saturated acids are separated from unsaturated acids by first melting the fatty acid mixture, pouring it into shallow, rectangular aluminum pans, and placing in a cool room to slowly solidify. The formed cakes are removed from the pans, wrapped in burlap or cotton cloth, stacked in vertical presses, and pressure applied to slowly exude the lower melting liquid fraction. In the case of separating tallow fatty acids, the final temperature of the pressed cake determines the titer of the oleic acid fraction and the iodine