

# Application of Partial Hydrogenation Theory to the Design of Commercial Reactors for Hydrogenating Triglyceride Oils<sup>1</sup>

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## ABSTRACT

Within the last 15-20 years, major advances have been publicized regarding the mechanism and general understanding of the partial hydrogenation of triglycerides, including soybean oil, cottonseed oil, corn oil and various animal fats (primarily hog and beef fats). Although edible shortenings, oleomargarine stocks and soap stocks are produced in large quantities, there is considerable doubt that the theory and fundamental information relative to hydrogenation is always applied to the fullest extent in designing and operating commercial reactors. This paper will review past accomplishments, the current state of the art and probable directions to be taken to obtain even further reactor improvements.

## APPLICATION OF FUNDAMENTALS OF HYDROGENATION

Partial hydrogenation of triglycerides as practiced commercially always involves a highly complicated series of consecutive and simultaneous steps, including transfer steps of reactants and products to and from the catalyst surface, adsorption and desorption steps on the catalyst surface, and surface hydrogenation and isomerization reactions (1,3,5,6,10,21,32,35,38). Both supported and unsupported nickel catalysts are employed commercially. The catalyst particles are just large enough to be filtered.

In commercial hydrogenators, three factors are of considerable importance in order to obtain the desired hydrogenation. These factors are the overall rate of hydrogenation (or the rate of decrease of the iodine value), the selectivity of hydrogenation defined as the preferred hydrogenation of polyunsaturated chains as compared to monounsaturated ones and the controlled production of isomers.

### Rates of Hydrogenation

Obviously a high rate of hydrogenation, expressed as the rate of decrease of the iodine value with respect to time ( $-d[IV]/dt$ ) is desirable since then the overall capacity of a given hydrogenation reactor is high. In reporting these overall rates of hydrogenation, the basic assumption is made that all unsaturated groups ( $-CH=CH-$ ) in the fatty acid chains are equal. An upper limit relative to rate of hydrogenation is that adequate control of the temperature must be maintained at all times. In general, however, removal of the exothermic heat of hydrogenation is not a controlling step.

In batch hydrogenation, which is currently the predominant commercial method employed, the average rate of hydrogenation is sometimes determined by dividing the total decrease in the iodine value by the time of the run; or, on occasion, only the time of the run, i.e., the inverse of the rate, is considered. Reporting these values is both convenient and easily understood. However the method has a major fault in that it does not really take into account the

two relatively distinct portions of a batch run. First, there is the start-up period during which the oil is heated to the desired operating temperature. Second, there is the main portion of the run during which hydrogenation occurs at rather uniform operating conditions including temperature. The factors affecting these two portions of a run can be quite different in nature. Considering first the main portion of the run, the rate of hydrogenation can be expressed in many cases for well purified refined and bleached oils as follows (19,35,38):

$$-d(IV)/dt = k(IV) \quad [1]$$

Hence the rate during this portion of the run is essentially first order with respect to the total degree of unsaturation, as measured by the iodine value. In the above equation,  $k$  is the pseudo first order reaction rate constant.

Results from laboratory dead-end reactors have shown that the above equation does not represent the overall rate of hydrogenation when many commercial nickel catalysts are used for the first time (35,38). During the initial portion of a run, the rate of hydrogenation is much slower than that predicted by the above equation. Calculations can be made to determine the increased length of time for completing a run that results from the initial slow rate. In general, the increased length of time defined as the induction period (IP) decreases with increased pressures and especially increased temperatures. At 100-120 C, induction periods as high as 20-30 min or even longer have been noted. At 160 C or higher, essentially no induction period is often noted.

At least for numerous catalysts and oil systems, the induction period is caused by an initially partly deactivated catalyst (35). During the induction period, the catalyst is "activated," and when the catalyst is reused, no induction period is noted. Whether or not a catalyst exhibits an induction period can sometimes be of significant importance relative to the length of the start-up period of a batch run. For catalysts that are already activated, hydrogenations start at lower temperatures during the start-up portion of the run. The exothermic heat of reaction then acts to decrease the length of the start-up period. Hence such a catalyst may cause a small but nevertheless significant reduction in the time required for a batch run; consequently the overall capacity of the hydrogenation unit would be increased somewhat.

Decreased start-up periods also result if increased rates of heating the oil are provided. The heat transfer rate depends on the amount of surface area provided, the temperature difference between the steam (or other heat transfer agent) and the oil and on the overall heat transfer coefficient. This coefficient is a function of several factors including the flow patterns of the oil around the heat transfer surfaces. When internal coils or tubing are used for heat transfer inside the reactor, higher levels of agitation in the oil result in higher coefficients.

The reaction rate constant  $k_1$ , if known in a given reaction system for a given temperature  $T_1$  (expressed in C) and pressure  $P_1$ , can be used to estimate the new rate constant  $k_2$  for a run at another temperature  $T_2$  and

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pressure  $P_2$  as follows (19):

$$k_2 = k_1 \left( \frac{T_2 - 103}{T_1 - 103} \right) \left( \frac{P_2}{P_1} \right)^n \quad [2]$$

where  $n$  varies from ca. 0.6 to 1.0. It is probably almost 1.0 at pressures up to 50 psig and decreases to 0.6 at ca. 300 psig.

Increased amounts of catalyst and agitation also increase the value of  $k$ . At low levels of agitation  $k$  increases, but eventually at high degrees of agitation  $k$  values change to only a small extent with changes in agitation. It would appear that a rather theoretical approach could be used to predict how agitation affects  $k$  values and even better to develop a more theoretical kinetic model. A complicating feature is that agitation should ideally perform at least three roles: (a) provide high shear stresses in the liquid phase; (b) provide high shear stresses at the liquid and catalyst interface; and (c) provide larger interfacial areas between the gas and liquid phases.

To provide high interfacial areas between the gas and liquid phases modern agitators often cause the gas to recirculate internally and to bubble continuously upward through the liquid.

The optimum height of the agitator impeller in reactors involving gas-liquid contact varies in a complex manner with other operating variables (11,39,40). This optimum height is not generally the same height as that to provide maximum levels of agitation in the liquid phase.

The  $k$  values are generally almost linearly proportional to catalyst loading if high rates of agitation are provided.

Although equations 1 and 2 are quite satisfactory for estimating the overall rates of hydrogenation of many batch runs, improved rate models are possible. Additional information, as will be discussed later, should be obtained relative to the actual concentration of reactants at the catalyst surface.

### Importance of Physical Transfer and Adsorption Steps

During hydrogenation, the reactants must first be transferred to the catalyst surface and are then adsorbed on the surface (5). Triglycerides that are triesters of glycerine and various long chain fatty acids contain fatty acid residues or chains that are either saturated, i.e., contain no unsaturated groups, or unsaturated, often containing either one, two or three unsaturated groups,  $-\text{CH}=\text{CH}-$ . In nature, the double bonds are predominantly in the *cis* geometrical configuration and are nonconjugated when more than one double bond occurs in a given chain. Chains containing zero, one, two and three unsaturated groups are represented here as *S*, *U*, *UU* and *UUU*, respectively. Unsaturated groups in these chains are competing for the "active sites" on the catalyst surfaces where reactions occur with adsorbed hydrogen to saturate (or hydrogenate) the double bond or to cause either geometrical or positional isomerization of the double bond. Eventually the products, both hydrogenated and isomerized, must be transferred from the catalyst surface back to the oil phase.

The transfer steps are often if not always the most controlling steps of the complicated sequence of events occurring during hydrogenation. The single most controlling step in batch hydrogenators is generally the transfer step of the hydrogen from the gas phase to the liquid phase where it is dissolved (19,38). This particular step is especially controlling at high rates of hydrogenation when large amounts of hydrogen must be transferred. Transfer steps in the pores of the catalyst are also controlling to at least some extent. Presumably in the pores, the unsaturated chains that are relatively large transfer rather slowly as compared to hydrogen that is much smaller (16,18,22). Variations in the resistances to the latter transfer steps explain in part at least why different catalysts often give

different rates of hydrogenation, selectivity and levels of isomerization. Various factors that affect transfer of reactants and of products in the pores of a catalyst have been considered (23). Information of that type probably is required in order to understand certain aspects of partial hydrogenation.

High rates of hydrogenation occur for a given temperature when high concentrations of reactants ( $-\text{CH}=\text{CH}-$  groups and hydrogen) are present at the catalyst surface. Higher hydrogen pressure, higher levels of unsaturation, i.e., more  $-\text{CH}=\text{CH}-$  groups, and increased agitation all promote higher concentrations of reactants. Higher temperatures and higher amounts of catalyst also promote faster rates. However, in order to obtain the desired selectivity ratio (2) and isomerization index (5), operating conditions must generally be adjusted so that somewhat reduced rates of hydrogenation occur, as will be discussed later in more detail.

A hydrogenation reactor is complicated in that three phases are normally present: a gas phase (hydrogen), a liquid phase (triglycerides containing small concentrations of dissolved hydrogen) and a solid catalyst phase dispersed throughout the liquid phase. The transfer steps in such a system are complex functions of several operating variables. Using the transfer of hydrogen from the gas to the liquid phase as an example:

$$\left[ \begin{array}{l} \text{Net rate} \\ \text{of hydrogen} \\ \text{transfer} \\ \text{from gas} \\ \text{to liquid} \\ \text{phase} \end{array} \right] = \left[ \begin{array}{l} \text{Rate at} \\ \text{which} \\ \text{hydrogen} \\ \text{reacts} \end{array} \right] + \left[ \begin{array}{l} \text{Rate of} \\ \text{accumulation} \\ \text{of hydrogen} \\ \text{in the} \\ \text{liquid} \\ \text{phase} \end{array} \right] + \left[ \begin{array}{l} \text{Net rate} \\ \text{at which} \\ \text{dissolved} \\ \text{hydrogen in} \\ \text{liquid flows} \\ \text{from reactor} \end{array} \right] \quad [3]$$

Since hydrogen solubility in the liquid phase is very low (38), the last two terms of the above equation are generally negligible and can be ignored. The first two terms can be expressed as follows for a differential volume ( $dV$ ) of the reactor (3):

$$k_g A (C_H^* - C_H) dV = k(f[C_H, C_U, \text{etc.}]) dV \quad [4]$$

This equation is most useful for analyzing how each operating variable affects the concentrations of reactants at the catalyst surface. Temperature, for example, has a most pronounced effect in both the transfer and reaction steps.

Temperature has probably only a relatively small effect on the mass transfer coefficient  $k_g$ . The interfacial area  $A$  between the gas and liquid phases is, however, temperature-dependent, since temperature changes the viscosity and interfacial tensions of the three phase mixture that is being vigorously agitated. Temperature has a small effect on the equilibrium concentration  $C_H^*$  of the hydrogen in the triglyceride oil.  $C_H^*$  actually increases with increased temperatures in the range of commercial interest (38). Since transfer of hydrogen from the gas to the liquid phase is often controlling, temperature indirectly affects the actual dissolved hydrogen concentration  $C_H$  partly because of mass transfer considerations. In general,  $C_H^*$  is significantly larger than  $C_H$  in commercial reactors.

Temperature also affects the chemical kinetics. The reaction rate constant is temperature-dependent as indicated by the Arrhenius equation. The kinetics of the reaction are also some complex function of the surface concentrations of the reactants and product expressed as  $C_H$ ,  $C_U$ , etc.

Similar analyses can be made using equation 2 of the effects of agitation, pressure and amounts of granular catalyst used (3). As mentioned earlier, the height of impeller (or impellers) in the liquid oil phase has a complex effect on the overall rate of hydrogenation; presumably the height often has an important effect on the rate of hydrogen transfer from the gas to the liquid phase.

The unsaturated groups (-CH=CH-) in a chain are adsorbed at the catalyst surface. The double bond located on a chain containing two or more double bonds, i.e., either *UU* or *UUU*, is more strongly adsorbed than is the double bond located on a chain containing only one double bond, i.e., *U*. This preferred adsorption is generally assumed to be responsible for obtaining high selectivity ratios (1,19,38). Adsorption of an isolated double bond seems rather reversible, whereas that for polyunsaturated chains is much less so. The time required to obtain equilibrium amounts of adsorbed monounsaturated and polyunsaturated groups at the catalyst surface is often relatively slow as compared to the rates of hydrogenation. The actual ratios of polyunsaturates to monounsaturates at the catalyst surface are often significantly less than the equilibrium ratio. In such cases the selectivity ratio is less than the maximum theoretical ratio obtainable with a given catalyst.

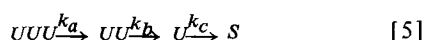
Considerably more information is needed concerning the adsorption phenomena occurring at the catalyst surface. Relatively little is known about the rate of approach to equilibrium except in a qualitative sense. The type (or types) of adsorption that occurs is also not thoroughly understood. Currently there are differences of opinion as to whether the adsorption of the unsaturated C=C bond is of a chemical or physical nature (19,20,38).

Hydrogen is also adsorbed at the surface, but this is certainly a chemical adsorption (chemisorption) step. The hydrogen molecule is broken into hydrogen atoms which then attack the double bond to either hydrogenate or isomerize it (7,8,20,36).

### Modeling of Partial Hydrogenation

Models to simulate the consecutive and simultaneous reaction steps for both hydrogenation and isomerization have been presented by several investigators (2,6,10,19,21,32,36,38). The more complex models require either analog or digital computers. Assumptions that are invariably made are as follows: (a) first order kinetics with respect to the concentration of the particular unsaturated group in the liquid phase, and (b) grouping of various isomers into families.

The following model has proved very successful for the calculation of the degree of selectivity often defined as the selectivity ratio (SR) (2,10):



In this model, each member of the *U*, *UU*, and *UUU* families is assumed to have the same reactivity as the other members of its particular family. Furthermore the so-called short circuiting of *UUU* directly to *U* or of *UU* directly to *S* is ignored; yet such phenomena apparently occur to some extent as explained earlier (1). The selectivity ratio is often defined as follows:

$$SR = k_b/k_a \quad [6]$$

SR values are as high as 50, or perhaps even 100, for highly selective hydrogenations. Values of 1.5-2 occur for very nonselective runs. Some companies now routinely calculate SR for each batch run as a part of their quality control program.

An attempt has recently been made to develop models to measure the extent of geometrical isomerization that occurs during hydrogenation. A model proposed indicates that the isomerization index can be made to vary from at least 0.3 to 40 (6). This index is defined as the ratio of the rate of geometrical isomerization to the rate of hydrogenation based on *cis*-monounsaturated groups. Two major faults hinder the use of this model. First, a large computer is required, and second, the model does not include terms for triunsaturated fatty acid chains (*UUU*) and hence

cannot be used for soybean oil. Hopefully, a more general and easily used method can be developed in the near future. It would be helpful for quality control purposes.

Although models used for measuring the selectivity ratio and the isomerization index are useful, they are very empirical in nature (5). The major fault of these models is that the actual concentrations of reactant groups at the catalyst surface are not known. The rate constants determined for the various reaction steps are really measures of the resistances to the transfer, adsorption and reaction steps. These rate constants must then be considered as only pseudo rate constants.

At least two groups of investigators have recently concerned themselves with the actual hydrogen concentrations in the oil and at the catalyst surface. Hashimoto et al. (21) developed a model in which terms were included for hydrogen concentration. This model did an excellent job of representing the diunsaturated, *cis*-monosaturated, *trans*-monounsaturated and saturated fatty acid groups. The model was tested using the data obtained for cottonseed oil hydrogenations by Eldib and Albright (19) and Wisniak and Albright (38). Since high rates of agitation were provided, the actual concentration of hydrogen in the oil was assumed for these specific runs to be equal to equilibrium concentration. For hydrogenations with lower levels of agitation, such as those usually present in commercial hydrogenators, sufficient information is generally not available for approximating the hydrogen solubility in the oil, especially since transfer of the hydrogen to the oil phase is normally the most controlling step of the entire process.

More recently Schön and coworkers (9,30) have suggested methods for estimating the rates of hydrogen transfer. Although considerably more effort apparently is needed, their approach is definitely promising relative to the long term objective of developing a model that will simulate the overall rates of hydrogenation and all major consecutive and simultaneous reactions occurring during partial hydrogenation. As better models are developed, it will be possible to optimize plant operations to an increased extent (27).

### BATCH REACTOR CONSIDERATIONS

Most hydrogenations of triglyceride oils are performed both in the U.S. and in the rest of the world in batch hydrogenators (4,10). In view of the fact that billions of pounds of triglycerides are hydrogenated each year, the question can be raised why continuous-flow reactors are not used more widely. However modern batch hydrogenators do have the following features (4): (a) The hydrogenators have low operating costs. Excluding the price of feed oil and hydrogen, these costs often range from ca. 0.25 to 0.35 cents per pound. (b) The hydrogenators are well automated, providing good control of the hydrogenation cycle so that quality products are consistently produced. Claims have been made that a single operator per shift is sufficient in a modern plant that hydrogenates ca. 720,000 lb per day. (c) Batch reactors are particularly suited for production of a wide variety of partially hydrogenated products. (d) Batch reactors are very effective in producing products with high selectivity ratios and high isomerization indexes. As will be discussed later, problems are often experienced in flow systems.

Operating costs for batch reactors have been maintained at low levels during the last 10-15 years by using larger units. Reactors that hydrogenate up to 60,000 lb per batch are currently in operation. Such a size is convenient, since some railroad tank cars hold that amount of oil.

### CONTINUOUS FLOW REACTOR SYSTEMS

Calculations indicate that small but perhaps significant savings could be realized in at least some cases if a

continuous flow reactor were used. Several developments in the last few years tend to make flow reactors more attractive: (a) Better and more uniform type oils are now available for hydrogenation. Techniques for refining and bleaching the raw triglyceride oils have been significantly improved so that most catalyst poisons are removed from the oils to be hydrogenated. In addition, to a considerable extent soybean oils have replaced other oils that were previously used. As a result, the quality of products obtained in flow reactors is easier to control. (b) The market for several types of hydrogenated products has grown to such a size that flow reactors appear to be practical. (c) More information and techniques are now available for designing flow reactors. (d) Catalysts can be obtained that are effective in obtaining quality products in flow reactors.

Economic analyses of the operating costs of batch and flow reactors indicate that a plant to produce 100 million pounds of products per year might save \$40,000 to \$60,000 per year, i.e., ca. 0.04-0.06 cents per pound of hydrogenated oil (4). Such savings are based on the assumption that the product qualities of the two processes are identical, and that no off-grade products are obtained when the flow reactor is switched from one product to another one.

For a flow reactor system, the following two factors are of importance: (a) Prevention or at least minimizing of back-mixing (or forward-mixing) of the oil as the oil flows through the reactor. Such back-mixing results in variations in the residence time of the oil in the reactor. Some polyunsaturated groups tend to pass through unreacted, resulting in lower selectivity ratios (and also lower isomerization indexes). (b) Effective and relatively uniform mixing (or contacting) between the oil and hydrogen throughout the entire reactor.

Pipe reactors in which the oil, catalyst and hydrogen flow concurrently through basically a horizontal pipe have been suggested. Although back-mixing of the oil would be minimal at rather low flow rates, adequate mixing or contacting of the oil and hydrogen would not be occurring. At higher flow rates, alternate slugs of liquid and gas would form; mixing would be good but very long pipes or coils would be required. Pressure drops would be high, and pumping costs for the oil and especially the hydrogen would also be high.

Pipe reactors arranged so that several U-bends are connected in series have also been considered. Hydrogen could be bubbled upward through the oil in the second half of each U-bend. The oil would flow slowly from one U-bend to the next. Sparging devices could be provided so that good agitation could be obtained as the hydrogen is bubbled upward through the oil. Pressure drops of the hydrogen in the reactor would be quite high and back-mixing of the oil in each U-bend could be expected.

Column or tower reactors provided with multiple plates or trays are related to the pipe reactor with U-bends. Such reactors are basically very similar to a distillation column with trays. In one design, the oil-catalyst mixture flows downward in the column from one plate to the next, and the hydrogen bubbles upward through the liquid oil on each plate causing good contact between the oil and hydrogen. If conventional bubble-cap or sieve plates are provided, the liquid on each plate is thoroughly mixed, i.e., a type of back-mixing. At least 10-20 plates are required to obtain reasonably high selectivity ratios.

A recent patent (26) describes a procedure for bubbling hydrogen through an oil as it flows from one compartment to another. Obviously some back-mixing of the oil occurs in this system, and a fairly large number of compartments (or stages) would be required to obtain high selectivity ratios.

Continuous flow stirred-tank reactors (CSTR) joined in series and operated with a concurrent flow of oil, catalyst

and hydrogen have also been considered. If a large number of CSTR units are provided, selectivity ratios and isomerization indices as high as those in a batch reactor can be obtained. Perhaps 10-20 units would in general be adequate for fairly high levels of selectivity and isomerization. Mathematical models based on experimental data obtained using a radioactive tracer have been presented for CSTR units arranged in various series and parallel flow arrangements (14).

Several continuous flow hydrogenation processes are now used commercially, and at least two are employed in the U.S. Procter and Gamble Co. built a continuous flow unit 15 or more years ago in their main plant and have presumably used it only for the large scale production of their general purpose shortening. There is no evidence that they have built comparable flow units in any of their several other plants. One might speculate that this reactor is only at best marginally better than batch reactors that they also use in large numbers. Relatively recently a flow unit based on the technology of Blaw-Knox Chemicals Plants, Inc., has been built and operated for partial hydrogenation of soybean oil (17). Details on this latter process have not yet been publicized.

A key advantage of the commercial units discussed next is that at least part of the heat needed for preheating the oil to reaction temperatures is provided by the exothermic heat of hydrogenation. The exit hot oil from the reactor is used in a heat exchanger to preheat the entering feed oil.

#### Procter and Gamble Process

The Procter and Gamble reactor is essentially a series of stirred autoclaves stacked one on top of another (28). The oil, hydrogen and catalyst flow concurrently through the reactor, from one stage to the next. Analysis of the reactor and probable flows in the reactor (4) indicate that the controlling steps are probably quite different than those in the conventional batch reactors. It is doubtful, for example, that the transfer of hydrogen from the gas to the liquid phase is as controlling a step as in batch reactors. Transfer steps of the unsaturates may, however, be more controlling. In this respect, the Procter and Gamble patent (28) indicates that special and highly active catalysts are needed in their reactor to obtain the desired product.

#### Lurgi Process

Some details of the Lurgi continuous flow process have recently been publicized (29,33). A vertical column containing 16 reactor chambers is provided. The oil, hydrogen and catalyst enter the bottom of the column and flow concurrently upward. "Trays with apertures" are provided between the chambers, and the hydrogen is caused to bubble upward through the liquid on each tray. Such an arrangement provides the necessary agitation. Details on the trays are not reported, but the claim is made that little or no back-mixing occurs between chambers or stages.

The unreacted hydrogen at the top of the column is recycled to the bottom inlet. The desired degree of hydrogenation is obtained by carefully controlling the feed rates of oil and hydrogen to the system. The pressure in the reactor automatically adjusts to provide the desired overall rate of hydrogenation.

Some pilot plant information is reported on the type of hydrogenated products that can be obtained (33). It would appear that only moderately high selectivity ratios were obtained.

Factors of importance in designing such a reactor obviously include the degree of back-mixing, the method of contacting the gas and liquid phases and the average residence time of the oil in the reactor. It would seem that a reasonably long residence time is used in the Lurgi reactor, and that considerable time might be required to switch from one product to another. The Lurgi reactor

appears quite suitable for essentially continuous production of a single product with average to moderately high selectivities.

### Pintsch-Bamag Reactor

The Pintsch-Bamag system also uses a column reactor with trays (31). The oil and catalyst enter the top of the reactor, but the hydrogen is fed at the bottom. Special sieve-type trays are provided to give several reaction chambers, and the liquid flows "across" one tray and then downward through a downcomer to the next tray. The hydrogen bubbles upward through the liquid on each tray.

Each tray (or plate) is provided with vertical baffles so that the liquid must follow a long, tortuous path on the tray, which minimizes back-mixing of the liquid. A column reactor with five to seven trays can be built so that the degree of back-mixing is quite small, being equivalent to that obtained in 30-50 well-mixed stages arranged in series (24,25). Design of the baffles on each tray is of course important relative to the degree of back-mixing. Since part of the hydrogen reacts, the amount of hydrogen available for "agitating" the liquid on each plate is less on the higher plates. It is not known whether the liquid level or the total cross-sectional area for the holes on a tray is identical for all trays.

Several years ago Bollens (12) patented a reactor similar to the Pintsch-Bamag reactor, except it was not provided with baffles on the trays. The use of baffles would appear necessary for obtaining highly selective hydrogenations. A discussion of the design considerations for a reactor with baffles has been presented (24,25,34).

### Buss Reactors

Relatively few details are available for the continuous flow reactor used in the Buss Ltd. process, but it is reported to be a multistate horizontal autoclave (15,29). Four stages were used in a pilot plant autoclave. The liquid flows over weirs from one stage to the next. In each stage liquid, and probably catalyst, is continuously removed at the bottom of the autoclave; the slurry is passed through heat exchangers to remove the heat of hydrogenation; it is then recirculated and mixed with hydrogen in an undescribed mixer, and apparently sprayed back into the stage from which it was removed.

The unit has been pilot-planted, and commercial units for 104,000-550,000 lb of oil per day are available. A commercial unit is operated in Colombia.

It is not clear how or if high selectivity or high isomerization could be obtained in this reactor. With only a limited number of stages, back-mixing would appear to be a problem.

## REACTOR IMPROVEMENTS

The key steps in the hydrogenation process have apparently been identified, and there is now a need to obtain additional information so that improved reactors can be designed: (a) Contacting of the gas, liquid, and solids is apparently the key step in most cases. Various investigations on the above have been reported recently (11,13,37), but considerably more is required. (b) The mechanism and kinetics of the adsorption phenomena for unsaturated groups on the catalyst surface need further clarification. (c) More information is required concerning the transfer of reactants in the pores of the catalyst. (d) A better understanding of the reaction steps on the catalyst surface is also desired.

When sufficient information is obtained for predicting

the concentrations of the reactants at the catalyst surface, better and probably more economical reactors can be built.

Flow reactors built to date have apparently been designed to duplicate the products obtained from batch reactors. However flow reactors can more easily provide unique sets of operating conditions as the oil is hydrogenated. Hence unique products should be obtainable. By proper choice of operating conditions and catalysts in various portions of the flow reactor, considerably different selectivity ratios and isomerization indexes could probably be realized. It is recommended that future investigators consider this potential advantage of flow reactors.

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