Reprinted From . . .

CEP
CHEMICAL ENGINEERING PROGRESS

MIXING IN HYDROGENATION PROCESSES

J.Y. Oldshue

Mixing Equipment Co.,
Rochester, N.Y.

JUNE 1980

Pages 60-64

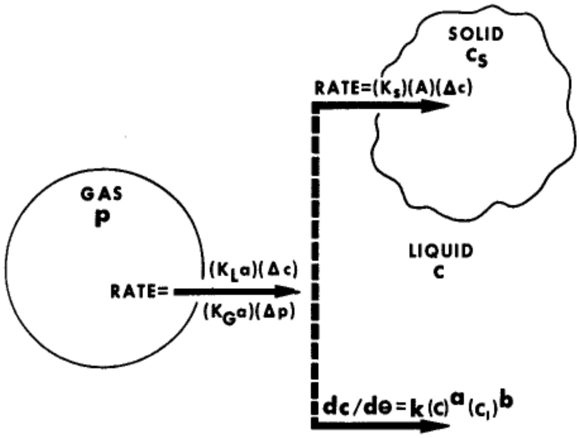

Figure 1. Schematic of three possible controlling process steps: gas-liquid mass transfer, liquid-solid mass transfer, and chemical reaction.

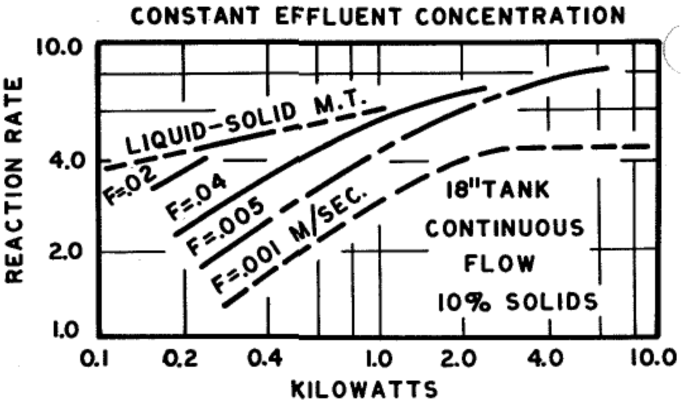

Figure 2.
Single stage hydrogenation process.

Mixing in Hydrogenation Processes

Proper selection of mixing equipment and location of impellers can improve operations in a hydrogenation unit.

J. Y. Oldshue, Mixing Equipment Co., Rochester, N.Y.

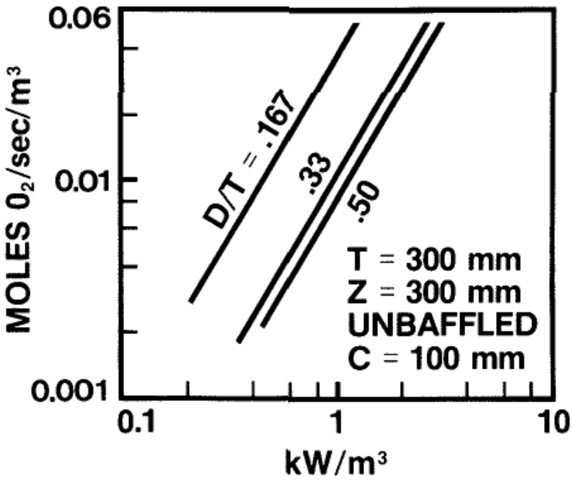

Figure 5. Experiments in an unbaffled tank showing the effect of different *D/T* ratios in incorporation from the head space.

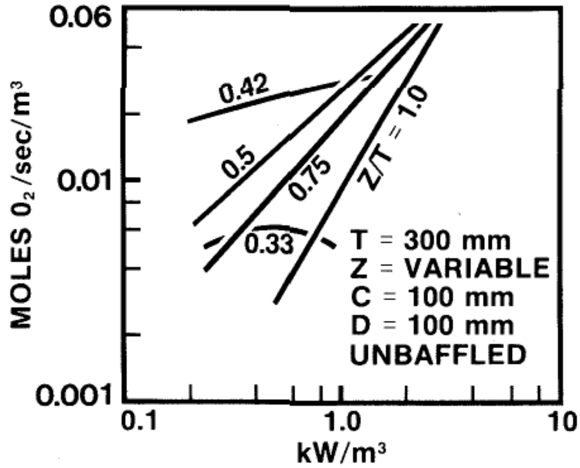

Figure 6. Data from an unbaffled tank showing the mass transfer rate as a function of power level at different liquid levels in the system.

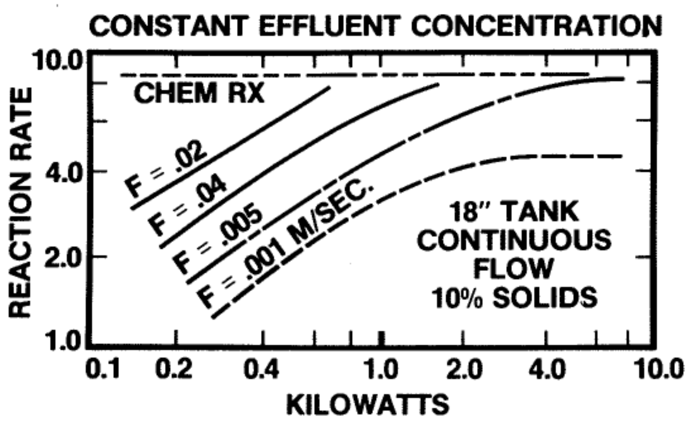

Figure 3. Data similar to that in Figure 2, but for a process in which there is an ultimate limiting chemical reaction.

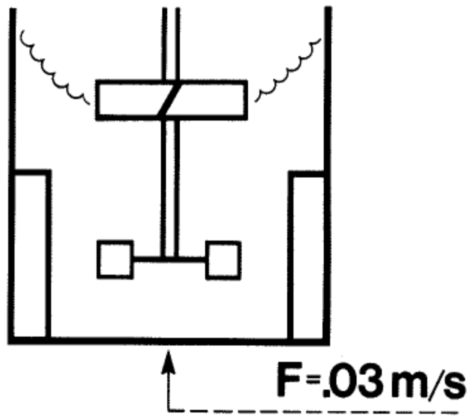

Figure 4. Schematic of axial flow upper and radial flow lower impeller for submerged gas reintroduction and head space reincorporation, half baffles in a typical hydrogenation process.

Hydrogenation is the classic case of a combination gas-liquid-solid system. Most typically there is a catalyst involved, usually finely divided solids. This system involves mass transfer from gas to liquid, liquid to solid, and a chemical reaction.

The classical steps are illustrated by Figure 1, which shows a breakdown of the rates into a mass transfer coefficient and a concentration driving force. In general, the mixer's only effect is on the mass transfer coefficient. The tank geometry, head pressure, and the gas composition affect the driving force. The value of using the mass transfer coefficient as a correlating technique is so we can use selected values for the pressure, tank geometry, and gas composition to try a wide variety of economic considerations in overall process design.

Normally we need some data which gives us the effect of mixer speed and gas velocity on the process result. An example, in Figure 2, is a continuous catalytic hydrogenation pilot plant study. The final effluent chemical concen-

---

0360–7275/80/3007–0060 $01.00 © 1980 AIChE

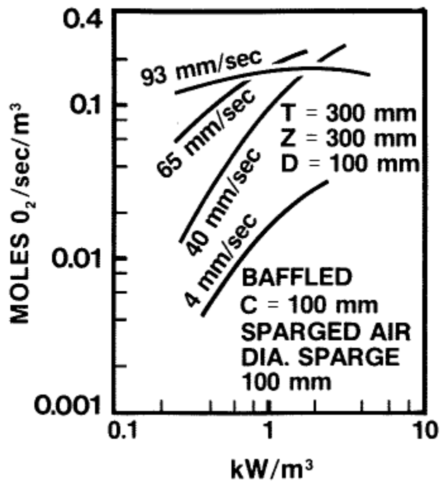

Figure 7. Data from a 300-mm diameter, baffled tank showing mass transfer as a function of power level and gas rate.

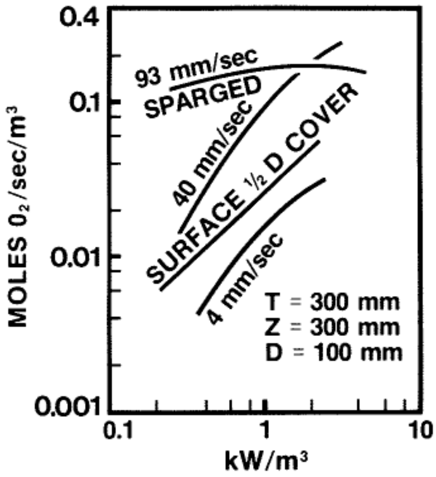

Figure 8. Data from 300-mm diameter tank showing the optimum mass transfer rate for surface reincorporation as compared to sparging gas through the system.

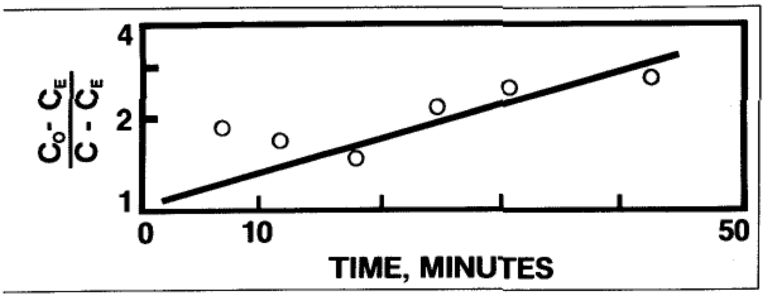

Figure 9. Typical plot for the desorption of carbon dioxide from the surface of the mixing tank. c_o is the starting concentration, c_E is the equilibrium concentration, and c is the concentration anytime.

tration is kept constant by changing the throughput through the single stage reactor as mixing conditions are varied.

Suppose, for example, that Figure 2 provides a typical set of data, in which we varied the power level over three or four steps by varying the speed at a given gas rate. The slope of the curve shows a typical relationship where the first part is gas-liquid mass transfer controlled, while the second part is probably controlled by a liquid-solid mass transfer process.

To further confirm this, we run other gas velocities, which indicate there is a bounding envelope based on the liquid-solid mass transfer at any power level, with gas-liquid mass transfer being important until this limiting solid-liquid mass transfer value is reached. These types of data can then be used for scale-up to many different types of geometries because the mass transfer rate is transformed into a mass transfer coefficient, and is used in typical correlations which are then scaled up to a larger system. Then selected values of the tank geometry, head pressure, and gas composition can be used as variables to predict different kinds of final process results.

If the same data which gave Figure 2 were obtained in a process controlled ultimately by a chemical reaction rather than liquid-solid mass transfer, we would have curves as shown in Figure 3. They indicate the ranges of reaction in which different process mechanisms are important.

Data from mass transfer studies

In order to calculate K_LA, we must have an estimate of the concentration driving force. This means we would have to estimate the dissolved hydrogen concentration in the liquid phase as well as Henry's Law constant for the particular system. This is very difficult to obtain and usually not available.

Another approach is as follows: We know the partial pressures of the gas exiting at various times. We can then estimate the relationship of the equilibrium partial pressure in the liquid to the P^* corresponding to the exit stream leaving the reactor.

At the high reaction rate condition, the dissolved hydrogen level and corresponding P^* value is probably close to zero. We calculate the K_GA at that condition. By knowing, the other mixer power levels and gas rates, and knowing the effect of power level and gas rate on the mass transfer coefficient K_GA, we can calculate from the actual K_GA for any other run, and what the partial pressure would have had to be to satisfy the mass transfer rate measurements. This then allows us to prepare a curve of P^* vs percentage reacted, which can be used to calculate mass transfer rates in a full-scale tank from the scaled-up values of K_GA.

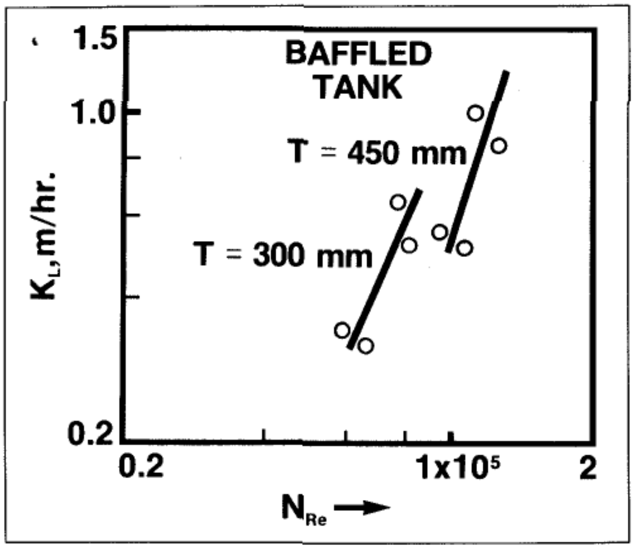

Figure 10. The effect of Reynolds number in two different tank sizes on the mass transfer coefficient K_L.

For continuous hydrogenation, usually a mixture of gas and liquid is withdrawn from the reactor. The unused hydrogen and off-gas can be recirculated through the system or combined with other feed-gas if desired.

However, in some continuous processes and in most batch processes, it may be desired to recirculate the gas from the head space. This leads to what is commonly referred to as a "dead-end hydrogenation system" in which the gas is fed either to the head space or beneath the liquid surface at the rate in which the reaction is using hydrogen, and no recirculation or recompression is needed.

If there is no major by-product off-gas, and if the hydrogen gas used is essentially 100%, then there is little build-up of inerts in the head space as the reaction proceeds. On the other hand, even a small percentage of inerts, or a small percentage of byproduct off-gas, means that the head space can change markedly from values of hydrogen partial pressure to 50% on down to 10% or less, depending on the length of time the reaction is carried out. All these factors must be considered in calculating the mass transfer driving force.

In any event, what is needed is some evaluation of the effectiveness of the surface reincorporation of hydrogen to improve the mass transfer throughout the batch.

Visual studies, as well as mass transfer studies, have indicated qualitatively that putting baffles half-way up in the tank allows the upper impeller to operate in a swirling, vortexing mode while the lower part of the tank operates in a baffled mode. This gives a more effective condition than either an unbaffled tank or a fully baffled tank.

The same observation was found with both dual axial flow impellers and dual radial flow impellers.

However, the highest improvement in process result was found when we used a surface axial flow impeller, partial baffles in the tank, and a submerged radial flow impeller, Figure 4. The fresh hydrogen gas introduced beneath the lower impeller has a chance to pass through the tank through both the lower and upper impellers, and the upper impeller is used for reintroducing hydrogen gas into the liquid. Normally, the diameter of the axial flow turbine is made larger than the diameter of the lower radial flow turbine so the distribution of power between the two impellers is approximately 40% in the upper and 60% in the lower. Other combinations, of course, are used when particular circumstances dictate.

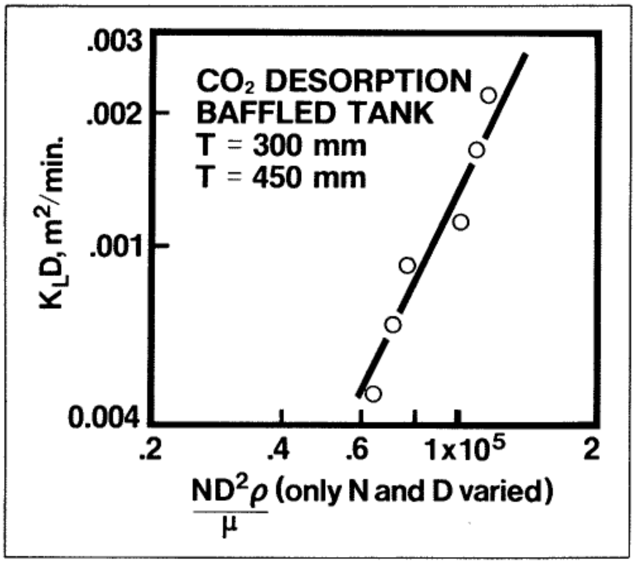

Figure 11. Correlation showing the use of the group K_LD as a function of Reynolds number for two different tank sizes.

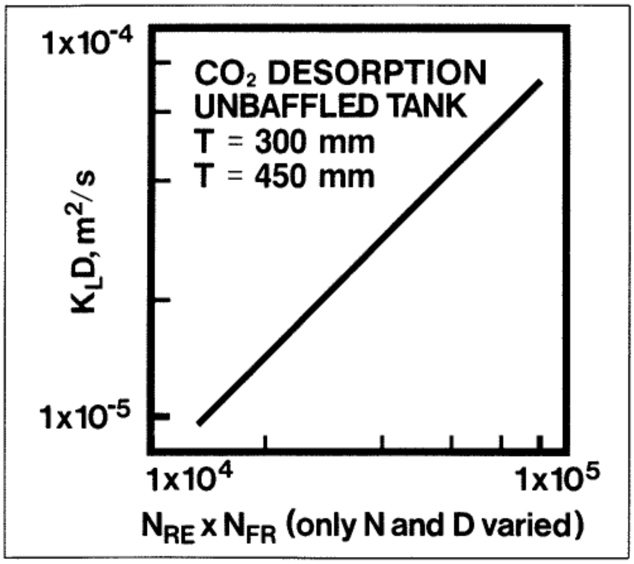

Figure 12. Correlation showing the use of the group K_LD as a function of N_{RE} and N_{FR}.

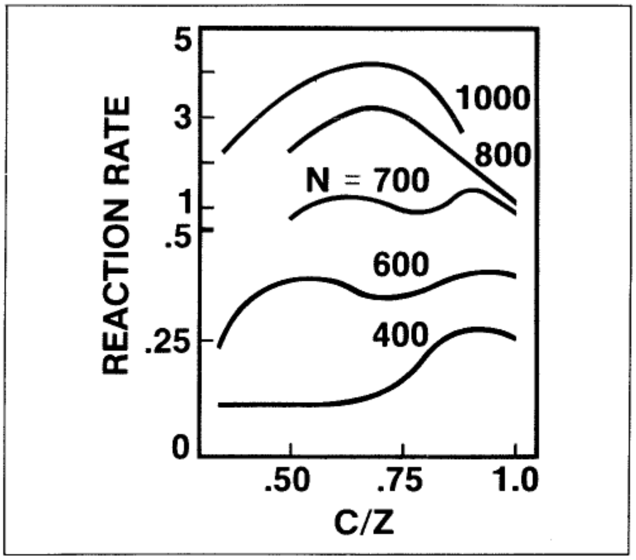

Figure 13. Data for various impeller speeds for constant liquid level and various impeller positions off bottom.

Another consideration on scale-up is that the surface area per unit volume of the process is decreased as tank size increases, so the proportion of hydrogen mass transfer available from surface reincorporation tends to decrease as a percent of the total hydrogenation rate on scale-up.

In addition, the Z/T ratio should normally be between 0.8 and 1.2 so that the surface area is maximized per unit volume on any scale for more effective reincorporation from the head space.

Surface reincorporation

Figure 5 shows mass transfer rates from surface reincorporation only in a fully baffled tank with three different impeller diameter ratios at a constant liquid level. It can be seen that the smaller D/T ratio is more effective than larger D/T ratios, indicating that surface reincorporation and mass transfer is enhanced by low flow, high fluid shear rate relationships. These were obtained by sulfite oxidation techniques.

Figure 6 shows data obtained when the liquid level is changed at a constant impeller position all the way from a Z/T of 1 down to a Z/T of 0.33, which is at the impeller level. These data show that there are a variety of relationships between geometric variables depending upon the power level and the liquid level. Coverage of about one-half impeller diameter seems to be optimum for mass transfer from the surface.

Figure 7 shows data from various superficial gas velocities with a submerged impeller. This shows that gas-liquid mass transfer rates several times higher than the surface reincorporation rate can be obtained by sparging gas at various velocities through an impeller in a fully baffled tank.

This means that it is normally desirable to put the gas first through a lower radial flow impeller in a baffled part of the tank, and take advantage of that mass transfer ability and then use the top recirculation impeller to take advantage of its ability in drawing down gases passed through the system not absorbed. Figure 8 shows Figure 7 with a line from Figure 6 added.

By saturating the liquid in the tank with carbon dioxide and then turning on the mixer, it is possible to desorb at the surface. The interface can be kept free of CO_2 build-up by a fan blowing across the surface. Typical data are given in Figure 9, which shows data taken of various concentrations of CO_2 against time. Data taken similar to that shown in Figure 9 were calculated in terms of the mass transfer coefficient, K_L, since the total surface area for desorption was used as the surface of the tank. Some of the change in K_L incorporates changes in the actual surface due to mixing flow patterns.

Figure 10 shows data in a baffled tank where two different tank sizes were used. Using dimensionless numbers, the curve shown in Figure 11 was obtained, which shows the correlation of K_LD vs Reynolds number for the two different tank sizes used. These data are suggested for use in analyzing the change of absorption rate or reincorporation rate for baffled tanks. Unbaffled tanks show a different relationship, $K_LD \propto N_{Re}, N_{Fr}$, as shown in Figure 12.

Some data on actual hydrogenation were presented by Wisniak and Stefanovic. Figure 13 is adapted from their

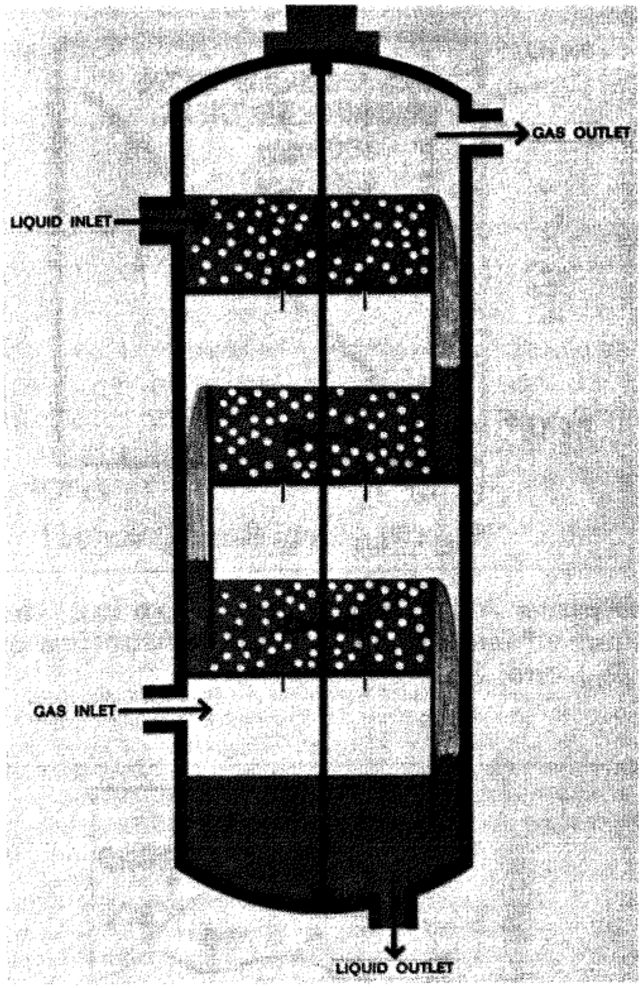

Figure 14. Schematic of a multistage countercurrent gas-liquid process which prevents interstage mixing of the liquid phase at high power levels normally needed for gas-liquid contacting.

data. A single impeller was located at one half of the liquid depth, and four different diameters used. This plot shows the effect at constant speed. At constant horsepower the results would be inverted. Figure 13 shows the reaction rate with a single impeller incorporating hydrogen from the head space at different speeds, showing that, in general, an impeller position about two-thirds of the liquid depth is the most effective.

In general, the impeller head can be used to suck gas down against the prevailing liquid height. This is extremely successful in small size equipment but becomes extremely difficult in larger scales. In fact, once the liquid level gets more than 6 or 8 ft above the impeller, it becomes usually impractical to try to use a self-inducing impeller. Data published by Zlokarnik give information on those kinds of processes.

If the gas energy is equal to or greater than the mixer power level, then usually a gas-controlled flow pattern will result. On the other hand, if the mixer is providing three or four times more power than the gas flow going through the system, then, normally, a mixer-controlled flow pattern will result. This must be considered on scale-up, since the mass transfer correlations are different in these two modes of operation.

Sometimes we need to consider multistage continuous hydrogenation. Figure 14 shows a typical example of a unit which can be used to eliminate the interstage mixing between the liquid phases which would occur if a continuous liquid-filled column were used.

This design allows high gas rates and power levels to be used as the material passes up through the column and also provides for the removal of self-poisoning off-gases from each stage if that is necessary. By means of a proper hydraulic pressure gradient, gas can be introduced or removed from several stages depending upon our process requirements.

In conclusion

In general, pilot plant data should be taken on a hydrogenation process with dual impellers, a lower radial-flow impeller in the baffled portion, and upper axial flow impeller in the upper section unbaffled. Based on knowledge of the mass transfer rates of both impellers, an estimate should be made of the percent of the reaction mass transfer supplied by the lower and upper impellers in the pilot scale. Scale-up of the mass transfer ability of the lower impeller and the upper impeller are made independently and then combined to give the overall process result.

To examine present full-scale performance, the data on the existing full-scale hydrogenator can be examined in the light of expected performance of the upper and lower impellers and estimates of the change in performance from introducing different impeller combinations can be made. This, then, allows the proper information to be obtained for prediction of improved process results.

Another consideration is that the superficial velocity of the gas based on equal volumes of gas per volume of liquid per minute normally increases, so that pilot plant data must be run at both the superficial velocity to go along with the pilot process as well as superficial velocity to be expected on full scale. #

Nomenclature

C—Impeller distance off bottom
c—Liquid concentration
c_o—Starting concentration
c_E—Equilibrium concentration corresponding to partial pressure in gas phase
D—Impeller diameter
K_LA—Mass transfer coefficient per unit volume
K_L—Mass transfer coefficient per unit transfer area
N—Impeller speed
N_{FR}—$(N^2D)/g$ = Froude number
N_{RE}—$(ND^2\rho)/\mu$ = Reynolds number
T—Tank diameter
P^*—Equilibrium partial gas pressure corresponding to c
ρ—Fluid density
μ—Fluid viscosity

Literature cited

1. Wisniak, J., and S. Stefanovic *et al., J. Amer. Oil Chemists Soc.*, **48**, 379 (1971).
2. Zlokarnik, M., *Chem.-Ing.-Tech.*, **42** (21) 1,310 (1979).

J. Y. Oldshue is vice president, Mixing Technology, Mixing Equipment Co., a unit of General Signal. The holder of B.S., M.S. and Ph.D. degrees in chemical engineering from Illinois Institute of Technology, he is a registered professional engineer in New York State. He has also served as a visitor for accreditation of chemical engineering curricula for ECPS and has taught several continuing education courses through AIChE and other organizations. He is an AIChE Past President.