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FLUID MIXING VARIABLES IN SUSPENSION AND EMULSION POLYMERIZATION

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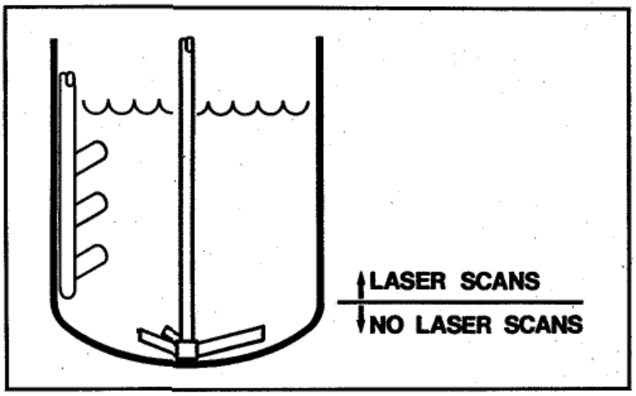

Figure 1. Retreat blade impeller.

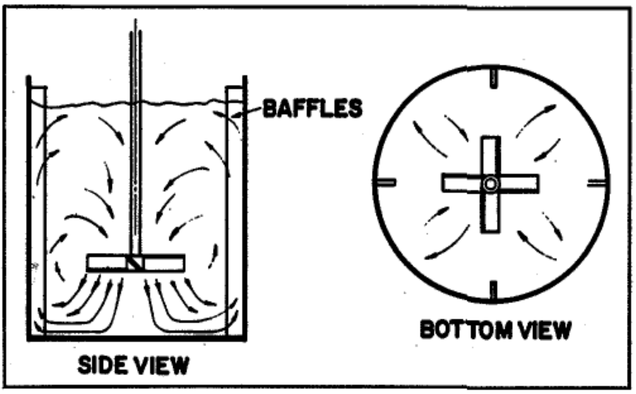

Figure 2. Typical flow pattern obtained with standard baffles.

Fluid Mixing Variables In Suspension and Emulsion Polymerization

The performance of a large-scale suspension or emulsion polymerizer may be directly related to the knowledge of the correct flow and shear variables of that mixer.

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These processes involve the production of a liquid-liquid dispersion. The drop size produced in this dispersion has an effect on the reaction rate and the ultimate size of the particles produced in the process.

Mixer power levels and fluid shear rates can have a large effect on distribution of polymer solid sizes in the process. We will explore the ways in which mixers provide liquid-liquid dispersion, and some of the differences between small and large tank sizes.

Examine *D/T* ratio

Many polymerizations progress from laboratory to pilot-plant to full-scale polymerizers, where suspension polymerizers are normally 10,000 gal (38 m^3), and emulsion polymerizers are usually smaller vessels. The polymerization may be done with axial flow turbines or the glassed type of impeller commonly known as a retreat blade turbine. In any case, impeller speeds, D/T (D = Impeller Diameter; T = Tank Diameter) ratios, and other variables are usually not critically examined in the laboratory. Such laboratory impellers may be similar or completely different from full scale; they may have large D/T ratios or small D/T ratios depending upon what is available at the time of the running of the laboratory tests.

Pilot-plant vessels in common use are steel or stainless, either glassed or unglassed. The main difference in glassed and metal equipment is that it is normally difficult to put sufficient baffling in glassed equipment to prevent major amounts of swirl and vortexing from being present.

The retreat blade configuration was developed, because it is one shape that can be glassed and not developed for its mixing characteristics. This impeller is used in corrosion services, but also has become widely used in the polymerization market. It was first used in this market during the early days of PVC manufacture. During this initial process, the PVC tended to be sticky in nature and adhered to most metallic tanks. Its adhesion characteristics to glass were less than stainless tanks; therefore, glass tanks and impellers were used. As is evident, the retreat blade impeller was installed not because of its mixing characteristics, but because it was glassed.

The formulation of PVC manufacture changed in the 1950s, producing PVC that had greatly reduced adhesion characteristics. Because of this, stainless steel tanks and mixers slowly replaced the glassed equipment. The standard configuration of vessel and retreat blade turbine is schematically illustrated in Figure 1. As stated above, swirling and vortexing are common. The metal alloy tank can be equipped, if necessary, with four wall baffles and normally would use the axial flow turbine, Figure 2. The D/T ratio normally falls between .5 and .7 for retreat blade turbines and between .3 and .45 for axial flow turbines.

Figure 3 illustrates that with most impeller types, includ-

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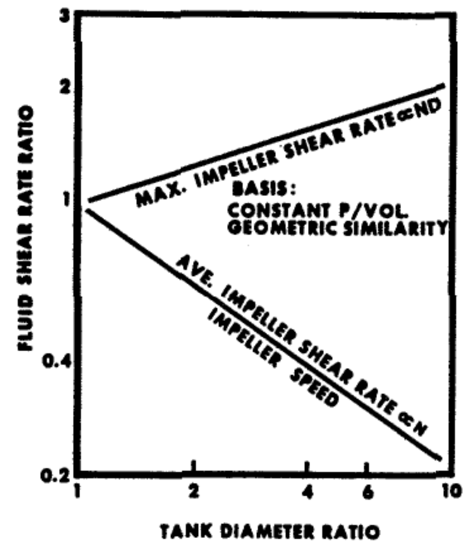


Figure 3. Maximum vs. average shear rate.

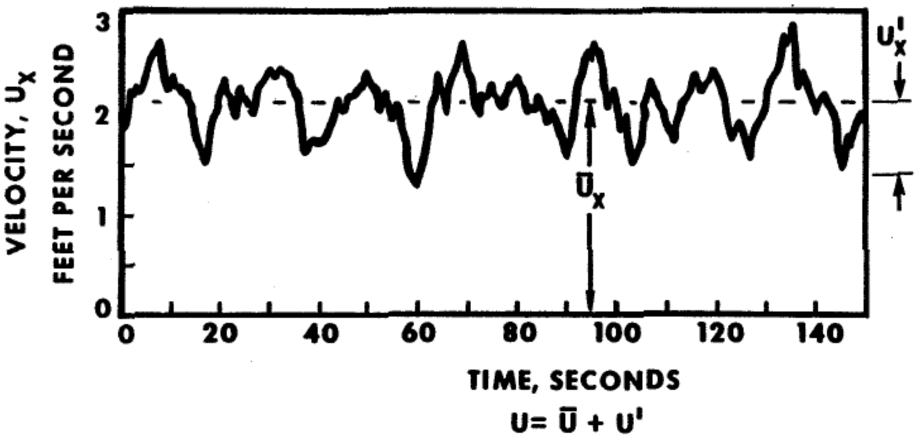
Table 1. Properties of a fluid mixer on scale-up.

Property	Pilot Scale 76 L	Plant Scale 4,320 L			
P	1.0	216	7776	36	0.16
P/Vol	1.0	1.0	36	0.16	0.0007
N	1.0	0.3	1.0	0.16	0.03
D	1.0	6.0	6.0	6.0	6.0
Q	1.0	65	216	36	6.0
Q/Vol	1.0	0.3	1.0	0.16	.03
ND	1.0	1.8	6.0	1.0	0.16
$\frac{ND^2\rho}{\mu}$	1.0	10.8	36	5.8	1.0

SI Conversion: L = gal × 3.79

ing retreat blade turbines and axial flow turbines, the ratio of maximum shear rate around the impeller to average shear rate around the impeller tends to increase when dealing with the maximum shear rate. These shear rates operate as a function of the average velocity at a point and typically are

Figure 4. Velocity measurements obtained with high-frequency recorder.



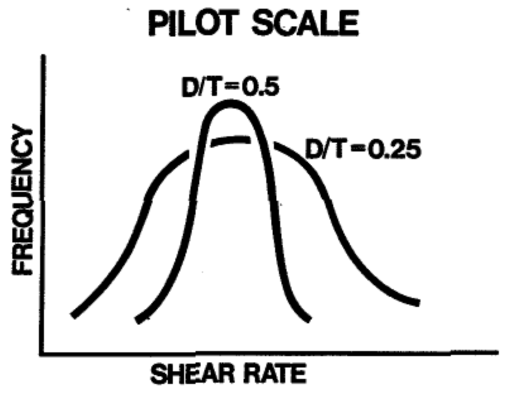


Figure 5. Frequency of shear rate in pilot-scale system.

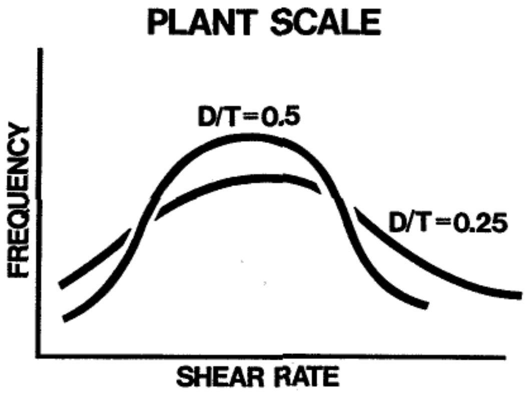


Figure 6. Frequency of shear rate in a plant unit.

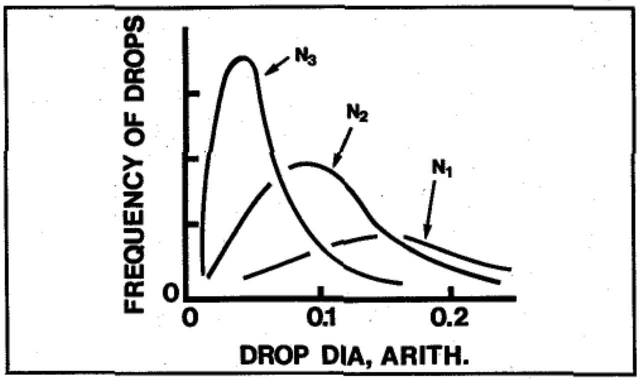


Figure 7. Frequency of drop distribution.

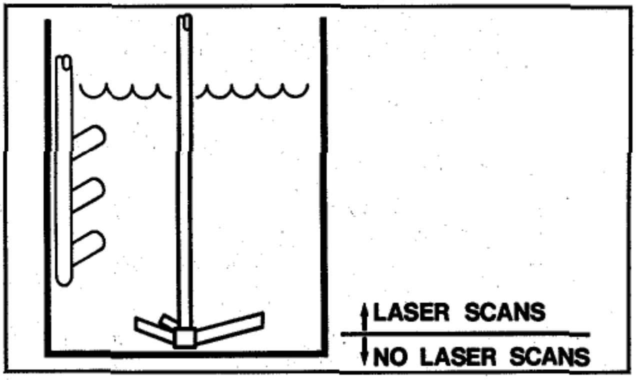


Figure 8. Retreat blade turbine in flat-bottom tank.

involved when particle sizes are 300 to 500 micron or larger.

Figure 4 shows a typical velocity trace at a point from *which average and fluctuating velocities were obtained (4).* Micro-scale shear rates, however, which typically operate at 100 to 300 micron or smaller may even affect the molecular level of the polymerization and are a function more of the energy dissipation at a point and of the *RMS* (Root Mean Square) of the velocity fluctuations, Figure 4. While they have markedly different values in various areas extending from an impeller through the rest of the tank, they do not change their relative relationship on scale-up to the same degree that macro-scale shear rates do.

In addition to a given tank diameter, changing the D/T ratio, which essentially means changing the diameter of the impeller, changes the ratio of the pumping capacity to fluid shear rates with a relationship shown below in which x is a positive number:

$$Q/\,(\text{shear rate}) \propto D^X$$

Depending upon the mathematical relationship used to express shear rate, the exponent X is usually between 1 and 1.5.

Fluid motion and scale-up

Another difference in small and large tanks is that swirl and vortexing tend to increase in magnitude on scale-up. Therefore, the process, that can be operated successfully in *the laboratory without baffles or with minimum baffles,* tends to have more swirling and vortexing in the plant size. Another feature of scale-up is that the pumping capacity per unit volume of the tank usually goes down markedly, especially if constant power per unit volume, constant tip speed, or some relationship in-between is used for scale-up.

Table 1 illustrates some of the variables involved when different mixing parameters are used as constants. According to Table 1, a series of parameters—power, power per unit volume, impeller diameter, speed, tip speed, pumping capacity, pumping capacity per unit volume, and Reynolds number—are shown and all are given a value of 1. Using a tank size scale-up ratio of 6:1, we see the changes in these variables with four different parameters held constant.

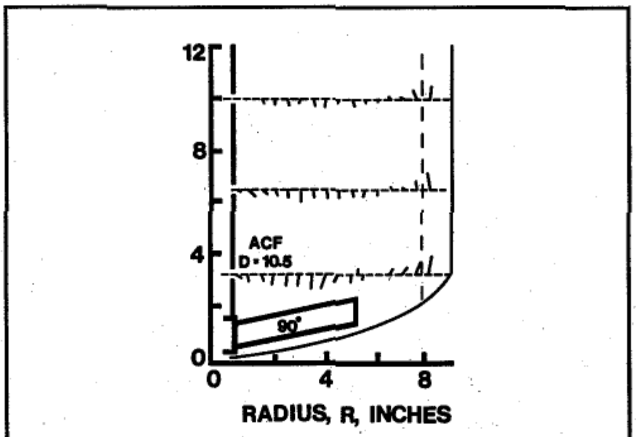
In Column 3, Table 1, P/V is held constant and we observe that the operating speed decreases and the pumping capacity per unit volume decreases, while the tip speed of the impeller goes up. In Column 4, in order to maintain constant pumping capacity per unit volume in a classical sense, the operating speed must remain constant, and the power per unit volume increases with the square of the tank size, in this case 36 times. This could provide equal blend time and circulation time between these scales, but it turns out that recent data indicate that blend times and circulation still decrease on scale-up even with the condition shown in Column 4 (*2*).

In Column 5, Table 1, we have listed the results of constant tip speed. This shows that the power per unit volume decreases directly with tank size by a factor of six, and the flow per unit volume is reduced considerably over the pilot unit. Column 6 shows constant Reynolds number. This is not practical, and Reynolds numbers should always increase on scale-up.

We don't want to imply that any of these particular parameters should be a constant on any given mixing application; *in fact it is more practical to use these parameters* as correlating parameters which change on scale-up, rather than trying to search, perhaps in vain, for a constant parameter to handle every suspension or emulsion polymerization.

Another phenomenon is the fact that the distribution of micro-scale shear rates changes on scale-up giving a wider distribution at a given D/T ratio, Figures 5 and 6. However, increasing the D/T ratio narrows the distribution in any given tank size. This shows, for example, that if it were desired to duplicate the shear rate distribution in the plant scale, we would have to run a much smaller D/T ratio in the pilot scale than we would expect to run in the plant to more closely relate the shear rate distribution on those two scales.

It turns out that by making the impeller blades narrower,



SI Conversion: m = ft × 0.3048; mm = in. × 25.4

Figure 10. Laser velocity in dish-bottom tank.

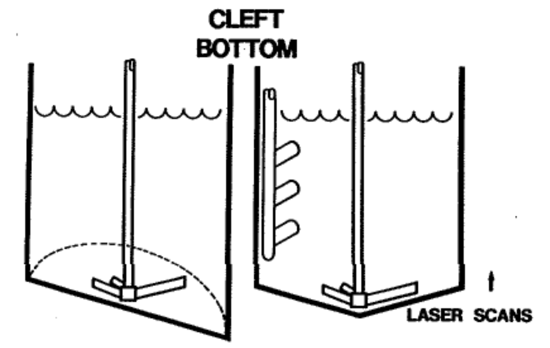


Figure 9. Retreat blade turbine in sloping-side tank bottom.

we can also cut down the pumping capacity in the pilot scale to be more reasonable to the plant value and arrive at a much more mixing-oriented model in the pilot plant. Emulsion polymerizations require enough shear to form the emulsion, but too much shear and not enough flow may coagulate out the colloids. Thus, it is important to realize these shear rate differences.

Suspension polymerizations are not quite as shear-sensitive to maximum shear rates as emulsion polymerizations. However, gross changes in scale-up of the Q/H ratio will affect the peaking performance.

Full-Size Installations. When designing a medium-size reactor, let's say at this point 5,000 gal (19 m^3), the glassed tank and impeller system runs into severe problems of swirling and vortexing, which cause operating and mechanical design problems as well as raising many questions about the required mixing fluid regime. A certain amount of vortexing to draw down light liquids or solids can be helpful. The swirling flow pattern in and of itself is not a good or a bad thing. It depends upon what the process requires. However, swirling or vortexing conditions do tend to limit the amount of power that can be applied so they can limit the possibility of obtaining various types of mixing conditions that might be desirable for a particular process.

Considering large size-polymerizers, 10,000 to 30,000 gal (38 to 114 m^3), normally metal construction is the only practical means and some form of axial flow turbine or metal turbine is usually indicated. If this means shifting impellers and other variables from the glassed type of impeller and baffles, there is a further set of variables introduced in the translation of flow regimes and impeller shear rate relationships.

Alloy tanks can usually be baffled appropriately either with so-called standard baffles, which are four baffles each $1/12$ the tank diameter (T) in width, or if some further additional vortexing and swirling is needed the baffles can be reduced to approximately ½ that width, or $1/24$ T.

It is quite easy to put in a second or third impeller or vary the geometric shapes of impellers and baffles. Baffles can be cut off close to the surface to allow impellers to vortex or swirl at that point to provide for the addition of other ingredients or to prevent light materials from separating at the surface.

Emulsion polymerizations involving larger-size particles and most polystyrene suspension applications require tank baffling of some degree so that suspension of the particles is maintained.

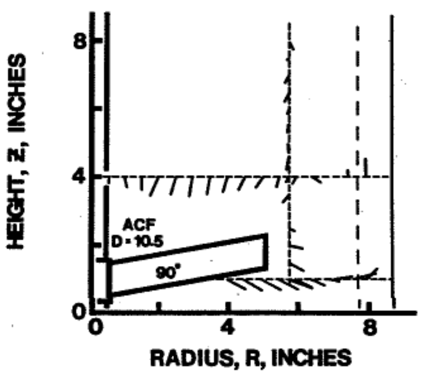
The major item of cost in a mixer is the drive mechanism, whose cost is normally related to the torque output required. Torque is the power divided by the impeller speed, so that with small impellers at higher speeds a lower initial cost mixer often results from the given amount of power to be applied. Thus, on competitive bids for mixing equipment, manufacturers are often striving to decrease D/T, or blade width or blade angle at increased speeds to reduce mixer costs.

By using a more efficient pumping capacity impeller, this higher speed can be obtained with the desired pumping capacity throughout the system. With the normal axial flow turbine, mixer sizes such as this usually tend to decrease the flow and increase the shear, making the shear rate difference between large tanks and small tanks even more pronounced than shown in Figures 5 and 6.

Drop-size distribution

In a mixing tank, there are shear rates which, when multiplied by viscosity, give shear stress. It is shear stress that basically determines the particle size produced in a given area of the mixing tank. If the fluid exhibits some non-Newtonian nature the variety of shear rates shown in Figures 5 and 6 are further increased in variety of shear stresses by the fact that different viscosities exist for different shear rates.

Both suspension and emulsion polymerizations involve liquid-liquid dispersion at least initially. Leaving the basic



SI Conversion: m = ft × 0.3048; mm = in. × 25.4

Figure 11. Laser velocity in flat-bottom tank.

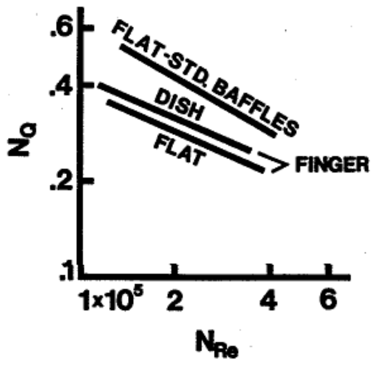
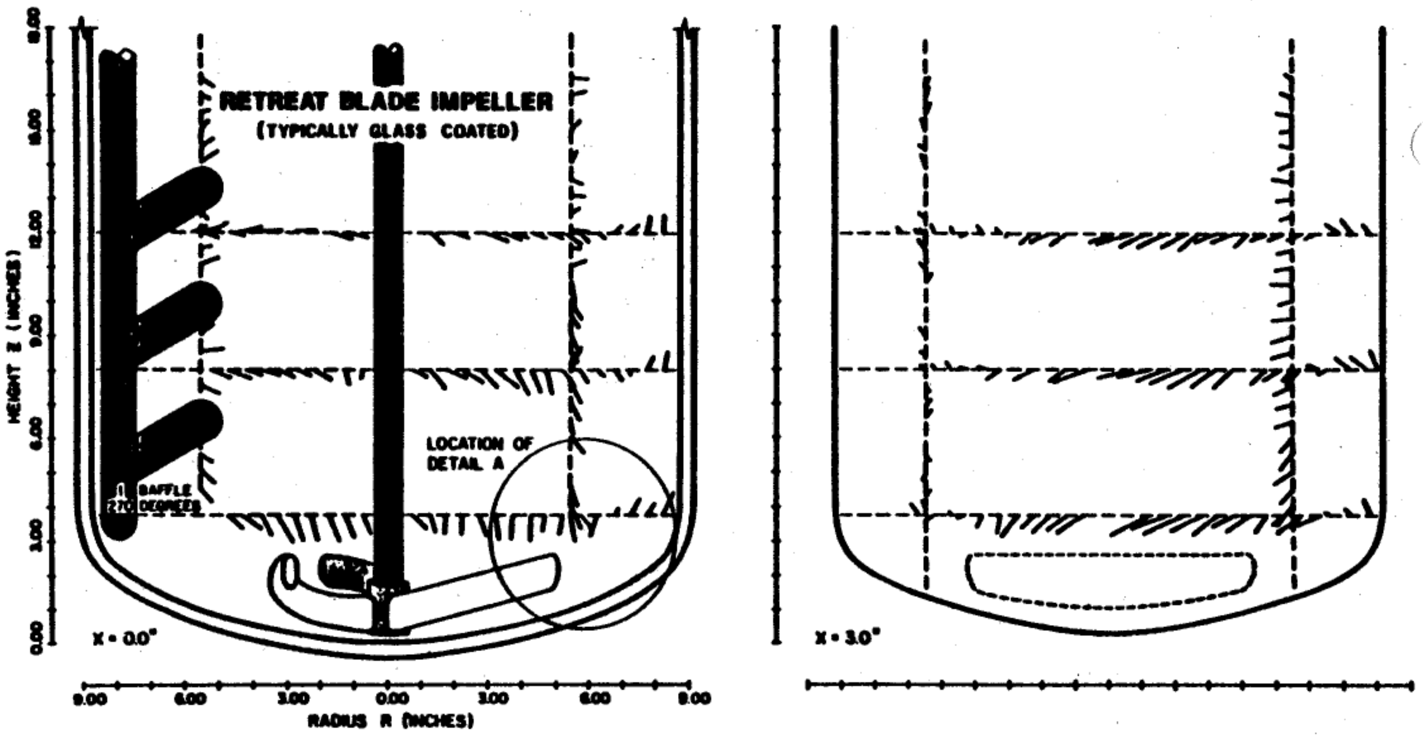


Figure 12. Flow numbers for flat-bottom tank.



SI Conversion: m = ft × 0.3048; mm = in. × 25.4

Figure 13. Velocity of retreat blade turbine.

fluid mechanics aside, drops of two liquids respond to shear stress depending upon the ratio of viscosity and surface tension. Figure 7 shows that at a low mixer speed, N_1, it turns out to be fairly normal distribution of drop sizes since in all cases surface tension forces are not large enough to inhibit the smaller size droplets (*3*) from forming. This normal drop-size distribution also depends upon the relationship between coalescence and dispersion in a mixing tank, since particles must respond to these different shear rates as they pass in and around the impeller zone.

At a higher speed, Curve N_2, it is seen that the distribution becomes skewed because as surface tension becomes more important, there is some inhibiting action on how small a drop can become. It becomes almost a rigid sphere which cannot be decreased further. At a still higher speed, Curve N_3, distribution becomes even more skewed because of the particular physical properties of the liquid.

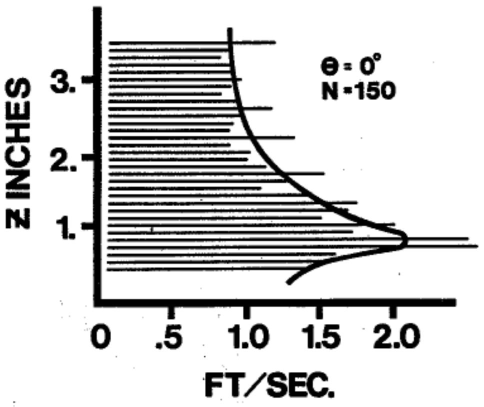
The drop size is not a function of speed or surface tension alone, but the interaction. The high mixer speed with the high surface tension can produce a normal drop-size distribution, while a low speed coupled with a low surface tension can provide a skewed drop-size distribution. Certainly, in these types of polymerizations, the more uniform the particle size distribution, the more saleable the product. In fact, it would be nice to have all the particles the exact same size.

This emphasizes the point that we cannot separate fluid mechanics from the physical properties of the system. Understanding fluid mechanics is basic to the understanding of the mixing tank, but the quantitative and qualitative relationships of those fluid mechanics to the process is why every one of the several thousand mixing processes handled every year are just a little bit, or a great deal, different.

Experimental measurements

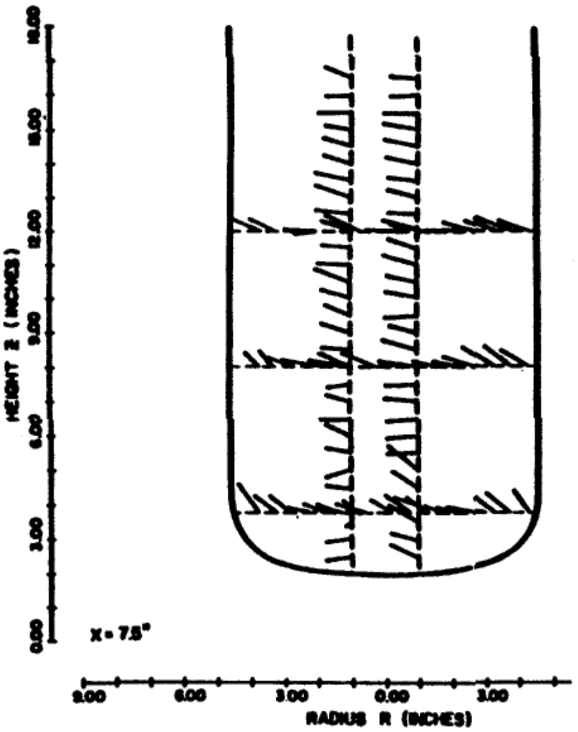
Other articles have described techniques of measuring pumping capacity and fluid shear rates in mixing tanks (*1*). Hot-wire techniques have been used, and presently Laser Dopler Velocitmeter (LDV) techniques are being used. Reported here are some results using the impellers and baffles typical of glassed equipment. Figure 1 indicates the problem of making velocity measurements in the dish bottom.

A modified dish (cleft), bottom, was used in an attempt to get some relative numbers which are quantitatively signifi-



SI Conversion: m = ft × 0.3048; mm = in. × 25.4

Figure 14. Flow pattern.



cant. These modifications include running in a flat bottom as well as in an angle bottom tank, Figures 1, 8 and 9. This is a progress report on studies still under way. Figure 10 shows the velocities in the upper part of the dish bottom tank. Figure 10 illustrates the velocities in the plane perpendicular to the LDV. Figure 11 shows impeller zone flow in a flat bottom tank. Flow numbers based on inlet flow for the retreat blade turbine are shown in Figure 12.

The flow numbers are based on the actual top-to-bottom flow in the system. The swirling flow pattern associated with the single-finger baffle results in a decreased flow number at a given speed and diameter. The effect of the swirling flow (horizontal flow component) is illustrated in the outermost scans ($x = 6.0$ and $x = 7.5$) of Figure 13. The Power number/Reynolds number curve must be available to make an evaluation of the total energy and flow required.

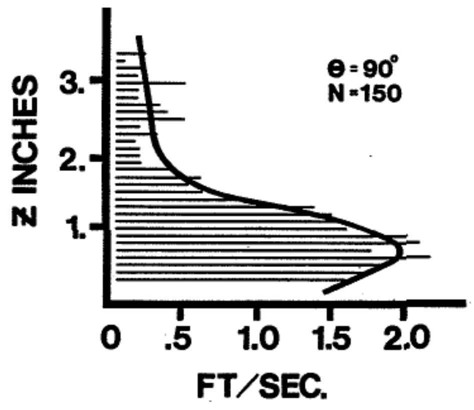
In order to obtain the average macro-scale shear rate around the impeller, velocities must be available in the impeller zone. Figures 14 to 16 show impeller zone velocity vectors using the cleft-bottom tank, Figure 9. Figure 14 shows the discharge velocity profile looking straight on center at the impeller ($\Theta = 0°$). Figure 15 shows the discharge on the right hand ($\Theta = 90°$) of the impeller, and Figure 16 the left-hand side ($\Theta = 270°$). Note the flow reversal around the baffle position. These curves can also be used to calculate the average and maximum shear rate around the impeller.

Circulation time in large tanks

In order to complete the description of a polymerization vessel, we must have some idea of the circulation in large systems compared to small. This section contains data excerpted from the paper of Middleton (*2*). He placed a radio transmitter in a small pill, about 8 mm in diameter and placed a radio antenna around the rotating impeller. These were radial-flow, flat-blade turbines.

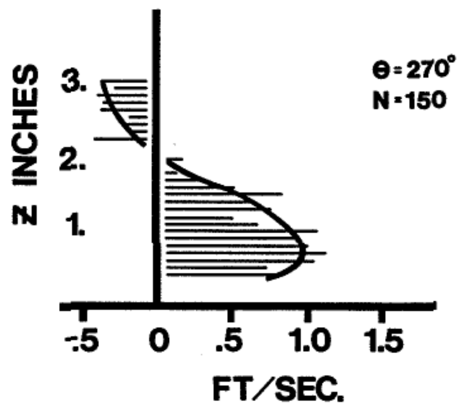
One of the first characteristics noted was the fact that the distribution of circulation times in the mixing tank could be the result of anywhere from one to ten tanks in series. Middleton (*2*) shows the experimental results of a typical run in which the curve corresponds to 1.76 tanks in series.

For the small 0.18-m^3 tank, the calculation of the pumping capacity per unit volume gave a good approximation to the circulation time of the particle. As tank size was progressively increased, the calculated circulation time would be much less than the calculated pumping capacity per unit volume indicating that large tanks are much less uniformly blended and mixed than thought from a pure-fluid mechanics calculation. In addition, in large tanks there is a greater standard deviation from the circulation time as tank size is increased. If we perceive the tank being involved with a series of mixing loops, it is seen that larger tanks have a



SI Conversion: m = ft × 0.3048; mm = in. × 25.4

Figure 15. Velocity probe at impeller zone, plane perpendicular to velocity meter.



SI Conversion: m = ft × 0.3048; mm = in. × 25.4

Figure 16. Velocity flow, plane perpendicular to velocity probe on the side with a single-finger baffle present.

much larger number of loops than the small tanks as a rule.

Apparently the concept of drawing arrows around mixing tank flow patterns is a very simplistic one and does not always, or perhaps not even often, represent the true situation. At a given pumping capacity, a mixing impeller flow pattern has a certain persistence. If it is in a tank much larger than its natural flow influence, the flow pattern will start to recirculate and set up a variety of other flow patterns in the tank. The particles caught in these velocities will circulate over wider and wider varieties of times depending on how big the system is. As pumping capacities increase and speed is increased, these numbers of auxiliary circulations will decrease until there is presumably a high enough impeller speed that even large tanks could have one complete circulation.

This indicates that reactant concentrations, particle distributions, time in and around various shear rate zones, time in and around mass transfer sources, or heat transfer surfaces can be quite varied on scale-up, and will give a much different picture of how a tank will operate compared to what might be predicted on small scale.

This leads into the next question of blend time and circulation time which is a complicated phenomenon. Only in laminar flow does circulation time have an experimentally verified relationship to blend time.

Blend time in the lower viscosity areas of transition and turbulent flow has a much less defined mechanism. In the case of chemical reactions, if we know something about the micro-scale shear rate within these circulation times, the selectivity of the reaction is affected (*1*).

If gas is present, as gas rate is increased, the circulation time increases as well as the standard deviation of these circulation times so that gas-liquid-liquid systems have a further complexity in polymerization processes.

In summary

In the mixing tank, there is a Pandora's box of many sizes and shapes of shear stresses. We have to choose appropriate mixing phenomena in order to make meaningful extrapolations on mixing scale-up. In the political arena, it has often been said that simple solutions to complex social phenomona are the essence of anarchy. In a mixing tank, simple solutions to the analysis of complex problems can be the essence of confusion and disaster.

Having an appreciation for the complexity of the mixing system always helps in a qualitative way to arrive at the limits within which prediction can be made with accuracy, but with caution. It also allows one to predict the possibility of success in pursuing mixing studies in the laboratory or pilot scale.

In looking at a mixing tank, there is a concept of superficial liquid velocity in the system which is obtained by dividing impeller pumping capacity by the cross-section area of the tank, and leads to a very simplistic view of process results.

In the laboratory, a very high excess pumping capacity per unit volume and short circulation time can mask many chemical and physical factors that show up in the plant. It is necessary (5) to sensitize the pilot plant by using nongeometric techniques to get blend time, circulation time, and other phenomena to approximate what is happening in the plant-size unit. Making the small-scale mixing tank as poor a mixing device as the plant tank may be in order to make studies of chemical variables meaningful.

In our experience, unless this is done and we watch out, the effect of chemical reaction and polymerization variables will be missed completely in the laboratory and pilot plant, and "funny things" will happen on the way to the large-size reactor.

The performance of a large-scale suspension or emulsion polymerizer may bear a direct relationship to the knowledge of the correct flow and shear variables of that mixer. #11

Notation

ACF = retreat blade turbine
D = *impeller diameter*
^tA = mean circulation time in mixing vessel
F = superficial gas velocity
N = impeller rotational speed
ND = peripheral speed
N_{Re} = Reynolds no., ratio of inertia force to viscosity force, $ND^2\rho/\mu$
N_Q = flow number, Q/ND^3
P = power
P/Vol = power per unit volume
Q = impeller pumping capacity
Q/Vol = impeller pumping capacity per unit volume
u = liquid velocity
$\overline{u}$ = mean velocity
$\overline{u}'$ = mean fluctuation velocity
z = liquid depth
RMS = root mean square
σA = standard deviation of circulation time in mixing vessel
ρ = density
μ = viscosity
T = tank diameter
X = *exponent*
V = volume
LDV = laser doppler velocity meter
i = number of tanks in loop

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