MIXING OF VISCOUS NEWTONIAN AND NON-NEWTONIAN FLUIDS

V. V. Chavan
Unilever Research
Vlaardingen, The Netherlands

and

R. A. Mashelkar
Chemical Engineering Division
National Chemical Laboratory
Pune 411 008, India

1. Concepts and Criteria

By 'mixing' we understand spatial intermingling of different constituents. This can be brought about by several mechanisms: (i) by mechanically breaking and separating the constituents in smaller elements and then recombining them, (ii) by deforming the constituents using shear or tensile stresses, (iii) by transferring the element of one constituent to the other by forced or natural convection, and (iv) by molecular diffusion.

In any industrial mixing operation one or more of these mechanisms may prevail at the same time, depending upon the physical properties of the materials involved and the operating conditions. It is of practical interest to propagate 'mixing' by manipulating the conditions so that these mechanisms can be used to our advantage. The purpose is to acquire a 'homogeneous' mixture. For any quantitative investigation the word 'homogeneous' or 'homogeneity' should be properly defined.

The dictionary meaning of homogeneous is 'of the same kind'. If this were a requirement, no mixture can be homogeneous. In the technical world by 'homogeneous' we generally imply "composed of 'parts', which are all of the same kind". If the scale of these 'parts' is well defined, there will be no ambiguity in the term homogeneity. This scale was termed by Danckwerts (1953) as 'scale of scrutiny'. In other words, the scale of scrutiny is the minimum size considered for any analysis. The analysis of segregated regions on this scale should lead one to conclude that the mixture is heterogeneous (not of the same kind). The scale of scrutiny very much depends upon the purpose for which the 'mixture' is to be used. For example, in the case of toilet soap (which is, amongst many things, a mixture of a pigment and soap) the scale of scrutiny depends upon the resolving power of the eye. It may correspond to the product used. For the drugs in tablet form it is the weight of one tablet. For a detergent mix it is the weight put into the washing machine. In the case of compounded rubber, it is the volume over which the individual grain of additive can be active.

Thus, the scale of scrutiny considers the scale at which the homogeneity should be scrutinized. However, it does not give any quantitative criterion for 'homogeneity'. Statistical measures, such as experimentally estimated standard deviation S or variance S^2 are defined as

$$S^2 = \frac{1}{N_s - 1} \sum_{i=1}^{N_s - 1} (C_i - C_m)^2 \tag{1.1}$$

Here the mean C_m can be estimated. The coefficient of variance C_v defined as

$$C_v = \frac{S \times 100}{C_m} \tag{1.2}$$

can be used as a measure of mixability. However, these measures suffer from the disadvantage of not being referred to any general standard reference. The more elaborate approaches used to describe the 'degree' or 'goodness' of mixing are divided into three parts for the sake of convenience: (a) small-scale segregation, (b) large-scale segregation (random), and (c) large-scale segregation (systematic).

1.1 Small-Scale Segregation

In this case, Danckwerts (1953) proposed two quantities to describe a mixture. These are (i) scale of segregation, and (ii) intensity of segregation.

1.1.1 SCALE OF SEGREGATION

Scale of segregation simply means the dimension that characterizes the size of the clumps of an unmixed component in the mixture. For a mixture of two components with the mean concentration (volume or weight fractions) C_m and $(1 - C_m)$, the 'point' values of the concentration will be C_i and $1 - C_i$; the 'point' here is the scale of scrutiny. If the concentrations measured at two points which are at a distance r apart are C_0 and C_r, a coefficient of correlation can be defined as

$$R(r) = \frac{(C_0 - C_m)(C_r - C_m)}{(C_i - C_m)^2} \tag{1.3}$$

At $r = 0$, $R(r) = 1$. Within a segregated clump, $R(r)$ will reduce from 1 to 0. When one of the points is outside the clump, where the mean concentration is C_m, $R(r)$ will be zero. This, of course, is the ideal case. For small-scale segregation it is assumed that beyond the segregated zone concentrations do not fluctuate very much around the mean. In other words, after a finite value of r, there are minor fluctuations (in comparison to the span 0 to 1) in $R(r)$ around zero and as $r \to \infty$, $R(r) \to 0$. For large-scale segregation, however, $R(r)$ will fluctuate between $+1$ and -1. A typical correlogram for small-scale segregation is shown in Fig. 1.

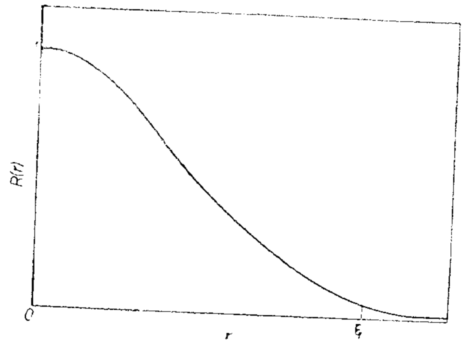


Fig. 1 A correlogram for small-scale segregation

Danckwerts defined a scale of segregation on a linear scale (S') and on a volume scale (V') as follows:

$$S' = \int_0^\infty R(r)\,dr \tag{1.4}$$

$$V' = 2\pi \int_0^\infty r^2 R(r)\,dr \tag{1.5}$$

Contribution to the area under the curve decreases rapidly for $r > \xi$

and consequently the limit of integral can be taken at a finite ξ. The magnitude of S' and V' will vary in the same sense as the size of the clump, which by itself is not always possible to define in a random process. For this reason it is convenient to use them as unambiguous measures of scale of segregation, even though their significance is not easily visualized. Danckwerts has also discussed the methods to measure S' and V', which mainly constitute measurements of the .point-values, or the contents in the line sample or in a volume sample (volume being more than a point and much smaller than the total bulk volume).

1.1.2 INTENSITY OF SEGREGATION

The intensity of segregation can be defined as,

$$I = \frac{\sigma^2}{C_m(1 - C_m)} \tag{1.6}$$

where σ^2 is the expected population variance. Consider a system of two miscible liquids. Initially, when they are separated into two zones with point concentrations either 1 or 0, I is equal to 1. Finally, when the concentration becomes uniform throughout at a value of C_m, I becomes zero. Thus I gradually reduces from 1 to 0. The fractional decay of I for miscible liquids is given by:

$$-\frac{1}{I}\left(\frac{dI}{dt}\right) = -6\mathscr{D}\left[\frac{d^2R(r)}{dr^2}\right]_{r=0} \tag{1.7}$$

It can be further argued that for rapid reduction in I, either the molecular diffusibility should be very high or there must be constant flattening, elongation or subdivision of the clumps so that high concentration gradients are always present at the boundaries. The methods used to obtain the scale of segregation enable one to calculate I, as long as σ^2 can be estimated with sufficient confidence. Alternatively, as suggested by Danckwerts, an infinitely rapid reaction can be used for such measurements.

Zwietering (1959) extended the concepts proposed by Danckwerts for continuous mixing. These are discussed in Sec. 4.

1.2 Large-Scale Segregation (Random)

When mixing two immiscible liquids or dispersing pigments in viscous materials or mixing powders or pastes, the segregation is on a large scale. This is quite common when molecular diffusion becomes a very slow process. The point-values of concentration are either 1 or 0. Function $R(r)$ now fluctuates within ± 1. The measures of mixing in this case are provided mainly by the work done in the area of powder mixing.

Since all these approaches assume complete randomness, we assume a binomial distribution when a two-component system is considered.

The probability distribution in this case is given by:

$$P_b(C) = \binom{x}{x_c} C_m{}^{x_c}(1 - C_m)^{x-x_c} \tag{1.8}$$

where x is the number of particles in a sample and x_c is the number of particles of the component whose concentration or volume-fraction $\frac{x_c}{x}$ we denote as c. C_m is the population average of c, which is known in many cases. $P_b(C)$ denotes the probability that x_c particles (of the kind whose concentration is c) are in a sample of x particles and

$$\binom{x}{x_c} = \frac{x!}{x!(x - x_c)!} \tag{1.9}$$

The population mean is C_m and the population variance σ^2 is $(C_m(1-C_m)/x)$. When factors such as size distribution of the particles and the density differences are considered the variance assumes different form (Lacey, 1957; Vallentin, 1967). Before the constituents are randomly distributed, i.e., when there are two separate zones of the two constituents the population variance can be obtained as $C_m(1 - C_m)$. Various methods have been described in literature where the experimentally obtained variance S^2 is compared with σ_r^2 and σ_0^2 to give an empirical mixing index. A typical form can be seen in the index proposed by Lacey (1957).

$$M' = 1 - \frac{S^2 - \sigma_0^2}{\sigma_0^2 - \sigma_r^2} \tag{1.10}$$

To ease the process of evaluation, the binomial distribution may be approximated by normal distribution under some conditions (Hald, 1952). The mixture under evaluation is postulated to be random; whether the sample size and the number of samples are appropriate with the hypothesis of randomness can be verified by comparing the estimated mean and variance with C_m and r^2 using t-test or χ^2-test (see Mohr (1959) for more details). The coefficient of variance for the population is

$$C_v = \frac{\sqrt{\sigma^2}}{C_m} = \sqrt{\frac{1 - C_m}{xC_m}} \tag{1.11}$$

This is the parameter which characterizes the intensity of segregation.

For a fixed sample size (from the scale of scrutiny) and reasonably large number of samples (to cover the bulk), the test of randomness or the population coefficient of variance determines the degree of mixing. Conversely, for a fixed variance, Buslik (1973) suggests the sample size as the mixing index. If the weight of the particles is constant then the weight of the sample is directly proportional to the number of particles. On the basis of the weight of the sample Buslik (1973) suggests a homogeneity index. This index seems to be useful especially for immiscible liquids, where there are no disintegrated particles. However, determination of Buslik's index in a practical case is likely to be a laborious procedure. For the mixing of liquid or paste, a suitable approach is to carry out experiments for different sample sizes within a range predetermined by the scale of scrutiny and then perform the tests for randomness. While using this method for liquids and pastes some ambiguity is created by the fact that one does not really have particles. The best way will be to assume a fictitious value for x, bearing in mind that the higher the value of x, more closely is one looking within the sample and that the expected coefficient will have a lower value.

Although the methods described above provide a measure for intensity of segregation, they do not give any idea about the scale of segregation. In this respect the method described by Kristensen (1973) which considers the variance within the sample, along with the variance between the sample, will be useful.

The above ideas have been quantitatively utilized in the mixing of pastes by Michaels and Puzinankas (1954), Earle (1959) and Hall and Godfrey (1965), among others. For instance, Hall and Godfrey take x as the square of the grid dimension for an area sample. One frequently finds confusion in literature while using statistical concepts for the interpretation of mixing data and the foregoing discussion should be helpful in avoiding such confusion.

1.3 Large-scale Segregation (Systematic)

In this case, the scale of segregation can be visually observed and measured. In very viscous liquids mixing occurs either due to shear or tensile deformations (laminar mixing); or because of the streamline division and redistribution (distributive mixing).

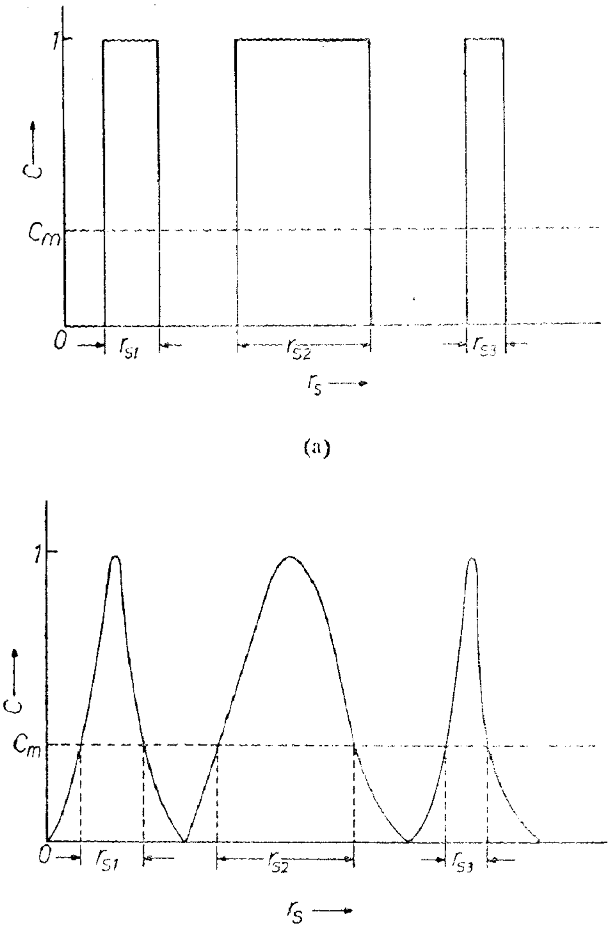
If the concentration at any point in the mixture (or mixer) is measured, a plot similar to the one shown in Fig. 2(a) or 2(b) will appear. The taper in Fig. 2(b) is due to molecular diffusion, which although present, is negligibly small. The scale of segregation can easily be defined in this case, as it will be the size of the clusters r_{s_1}, r_{s_2}, etc. Since it will not always be constant, a representative value can be defined and used as an index.

The intensity of segregation is now defined as (Mohr, 1959)

$$I = \frac{\sqrt{S^2}}{C_m} \tag{1.12}$$

Although the polpulation mean C_m is known, the population variance is not known, and thus there is no equivalent of expected intensity of segregation (as in a random mixture). The intensity will be dependent on sample size, which should be determined by the scale of scrutiny. It is obvious that the sample volume should be more than $(r_{s,\,avg})^3$ for a correct representation of the intensity of segregation of the mixture.

For a better understanding of mixing in this category the 'laminar mixing' and the 'distributive mixing' should be examined in some detail.



(a)

(b)

Fig. 2 Large scale segregation (systematic) in the absence of (Fig. 2a) and in the presence of (Fig. 2b) molecular diffusion

1.4 Laminar Mixing

The average striation thickness (scale of segregation) can be computed from the ratio of the interfacial surface area between the components and the total volume of the system (Mohr, 1959).

$$r_s = \frac{2V}{A_i} \tag{1.13}$$

This expression is a result of picturing the material as being deformed by mixing process into roughly plane parallel sheets. The analysis of Spencer and Wiley (1951) for undirectional shear (simple shear flow between two infinite parallel plates) leads to the following equation for the changes in the interfacial areas.

$$\left(\frac{A_i}{A_{i_0}}\right)^2 = 1 - 2\left(\frac{du_1}{dx_2} \times t\right) \cos \alpha_1 \cos \alpha_2 + \left(\frac{du_1}{dx_2} \times t\right)^2 \cos^2 \alpha_1 \quad (1.14)$$

where A_i and A_{i_0} are the final and initial interfacial areas. u_1 is the velocity; the gradient of which is in the direction x_2, cos α_1 and cos α_2 are the direction cosines of the normal to the original surface with respect to x_1 and x_2, respectively. The above equation points clearly towards important factors in the laminar mixing problem, for instance, the importance of the orientation of the original surface between the two species. It is obvious that cos α_1 should be finite for the deformations to change the interfacial area or to reduce the striation thickness (see Fig. 3).

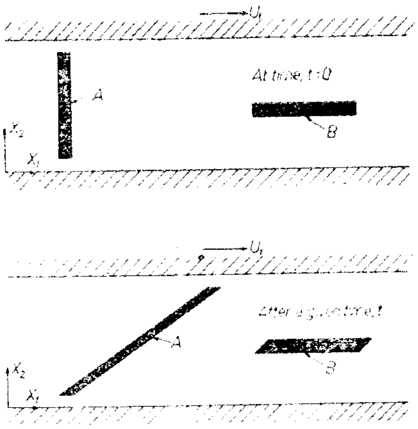


Fig. 3 Influence of orientation in laminar shear mixing

Bergen (1959) describes a two-dimensional picture of the changes in striation thickness for a couette flow between two concentric cylinders (see Fig. 4). If one describes the flow in cylindrical coordinates then the

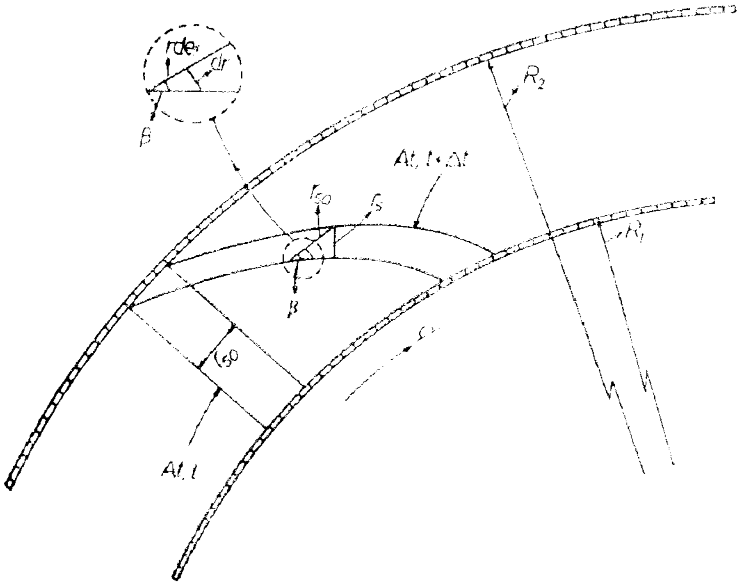


Fig. 4 Laminar shear mixing in concentric cylinder systems

shear rate can be written as

$$\dot{\gamma} = -r\frac{d(V_\theta/r)}{dr} = \frac{d}{dt}\left(r\frac{d\theta}{dr}\right)$$

and if the inner cylinder is rotating with an angular velocity Ω, then

$$\dot{\gamma} = \frac{2\Omega}{r^2}\left(\frac{R_2^2R_1^2}{R_2^2 - R_1^2}\right) \tag{1.15}$$

At any radial position, we have

$$\left(\frac{r_{s0}}{r_s}\right)^2 = \operatorname{cosec}^2\beta = 1 + \cot^2\beta = 1 + \left(r\frac{d\theta}{dr}\right)^2 \tag{1.16}$$

Furthermore, when $r\dfrac{d\theta}{dr} \gg 1$, $\dfrac{r_{s0}}{r_s} = r\dfrac{d\theta}{dr}$.

For a steady flow (since $\dot{\gamma}$ does not change with θ or t) in an interval of time Δt, one obtains

$$\frac{r_s}{r_{s0}} = \frac{(r/R_1)^2}{2\Omega\Delta t}(1 - (R_1/R_2)^2) \tag{1.17}$$

or considering that $\Omega(\Delta t) = 2\pi N_r$, we obtain in terms of the number of revolutions

$$\frac{r_s}{r_{s0}} = \frac{(r/R_1)^2}{4\pi N_r}(1 - (R_1/R_2)^2) \tag{1.18}$$

Thus the minimum changes occur at $r = R_1$ and maximum at $r = R_2$. Simple calculation can be done to show that the time required to obtain the maximum striation thickness to be much less than the scale of scrutiny.

The above relations hold for a Newtonian fluid, and it is easy to show that for a non-Newtonian power law fluid,

$$\frac{r_s}{r_{s0}} = \frac{n(r/R_1)^{2/n}}{4\pi N_r}(1 - (R_1/R_2)^2) \tag{1.19}$$

It is seen that with increased pseudo-plasticity shear mixing becomes more difficult.

Some calculations of the changes in the striation thickness have been made by Shrenk, et al. (1963, 1969). They have discussed specifically the flow through an annular channel with rotating walls under the conditions of an axial pressure flow. In another work, flow in the rotating tube is considered. On the basis of simple calculations for the flow of viscous Newtonian liquids they obtained the distribution of striations at a particular axial length in r-θ' plane. Their analysis considers the blending of two viscous Newtonian liquids at low Reynolds numbers and shows a good agreement for the mixing of black (carbon black) and white (TiO_2) pigmented polystyrene. Mohr, et al. (1957) have extended the basic concepts of laminar shear mixing to obtain the distribution of striations for an extruder. They explain the effect of geometrical variables on the maximum striation thickness. The total amount of shear received by an element was obtained as the sum of the product of the shear rate and residence time for each part in the flow path. The hydrodynamics used was approximate and was valid only for Newtonian liquids. Recent studies in hydrodynamics of extrusion for Newtonian (McKelvey, 1959) and non-Newtonian liquids (Bigg and Middleman, 1974) are more close to reality. However, the laminar shear mixing concepts have not yet been used to study and interpret the mixing phenomena. Furthermore, only non-directional flows have been considered. The direct extension for more complicated hydrodynamic situations is likely to be tedious. Chavan, et al. (1975a) have used these concepts to explain the mixing time (defined later) results for a helical screw mixer in a draught tube. Mohr, et al. have proposed an equation for laminar shear mixing of two liquids with different viscosity. The changes in the striation thickness are described by an equation

$$\frac{r_s}{r_{s0}} = \frac{3}{M_1}\frac{\mu_2}{\mu_1} \tag{1.20}$$

where M_1 is the net amount of shearing strain in the major component, μ_1 is the viscosity of the major component and μ_2 is the viscosity of the minor component. Note that the changes in the striation thickness within the minor component (same viscosity μ_2 throughout) in terms of the shearing strain in the major component are predicted. Furthermore, non-directional stratified flow of two immiscible liquids is considered. There is apparently a need for the solution of fluid dynamic problems involving the flow of two or more immiscible phases.

Murakami et al. (1972) showed experimentally (on a cone and plate viscometer) that one can discard completely Mohr's equation for blending. They observed that the striation thickness of the minor component (viscosity μ_2) does not change much with the viscosity ratio ($0.6 < \mu_2/\mu_1 < 3$). This is valid only when the minor component is placed perpendicular to the direction of flow and when it is sheared for a limited time. In principle, once the initial position of the minor component is changed it will try to orient itself and deform so that equality of stresses and velocities is satisfied at the interfaces.

So far changes in striations only due to stress deformation have been discussed. In flowing media, tensile deformations also prevail. These are brought about by changes in the velocities in the direction of flow due to gradients such as $\frac{\partial u_1}{\partial x_1}$, $\frac{\partial u_2}{\partial x_2}$ and $\frac{\partial u_3}{\partial x_3}$. Mohr (1959) performed an analysis for the calculation of changes in interfacial area under such circumstances:

$$\left(\frac{A_i}{A_{i_0}}\right)^2 = \frac{\cos\alpha_1}{X_1} + \frac{\cos\alpha_2}{X_2} + \frac{\cos\alpha_3}{X_3} \tag{1.21}$$

where X_1, X_2 and X_3 are relative changes in direction x_1, x_2 and x_3. No detailed calculations on an actual flow problem have been done so far and they are clearly desirable.

1.5 Distributive Mixing

When shear and tensile deformations are small, mixing occurs due to the division of stream lines and redistribution. Shearer (1973) analysed the changes in the striation thickness in the plane perpendicular to the flow for (a) an assembly of rotating blades, (b) a stacked array of helically flighted ducts, (c) an assembly of planetary rollers. Here, the author is probably justified in assuming a plug flow, since the changes in the striation thickness in the plane perpendicular to the flow (r-θ' plane) are under consideration, whereas the main shear gradient exists in other plane (r-z plane). The tensile deformations can be neglected, if the rate of change of velocities in the direction of flow is negligible. Thus the approach of 'distributive mixing' can be used. The method used is as follows: knowing the initial striation thickness and following the flow (while keeping proper count of the number of subdivisions and the resulting redistribution) one is able to obtain a simple relation for the final striation thickness and the number of times the material has been subdivided and redistributed. The hydrodynamics assumes importance in an indirect way, i.e., in obtaining the average residence time.

Spencer and Wiley (1956) have proposed a method where compression and distribution can be considered together. This is useful especially in studying the blending on a roller mixer.

The recent work of Bigg (1975) on mixing in polymer flow systems is of considerable interest. His study shows that residence time distribution curves (see sec. 4.1.3) give information on the distribution of material along the primary flow direction. However, they do not provide information on mixing in the transverse flow direction for laminar flow systems. For most polymer processing applications, mixing in transverse direction is very important. Bigg considers a number of cases, such as mixing in screw extruders, mixing in rotating cylinders and static mixers, and shows that the striation thickness and strain are closely related. From the shapes of the curves relating striation thickness with strain it is clear that mixer design is an important factor in efficiently utilizing strain to optimize mixing.

2. Means of Mixing

For efficient mixing, proper conditions will have to be created and maintained so that mechanisms described in sec. 1 could prevail. The selection of a mixer is obviously dependent upon the specific case under consideration. A frequently used selection guide is given by Ho and Kwong (1973). It is evident from this that the choice of agitator is largely governed by the liquid viscosity and to a lesser extent by the mixing tank size. The guide is somewhat limited in application since some variation in the design and operating variables can shift the selection procedure considerably. In addition, of course, problems of construction, endurance of equipment, etc., come in; a useful discussion of these aspects is given by Uhl and Gray (1966). It is also conceivable that a multitude of modifications to the impeller design are possible, addition of each of which would mean that we may have to study an infinite number of individual problems. Fortunately, this is not the case and all the mixers can be broadly subdivided on the basis of their shape and action; a useful information can be found in Uhl and Gray (1966). The static mixers which are used in pipes have been described by Chen (1973).

Different mixers act by producing different flow patterns. A detailed knowledge of the hydrodynamics in a mixing vessel will be most useful in not only analysing the mixer performance but also in scaling up. An *a priori* knowledge of hydrodynamics appears to be almost impossible in view of the presence of a complex time-dependent three-dimensional laminar or turbulent flow. Detailed experimental measurements of velocity distribution in the stirred vessel is an obvious answer; but in view of the number of variables involved, this becomes too expensive and time-consuming. Fortunately, an alternative can be found in which some gross integral quantities can be more easily measured. These give useful information concerning the hydrodynamics in the mixing vessel. In what follows we shall discuss in some detail the definitions, measurement techniques and utility of these quantities. Their relation to actual hydrodynamics will be discussed in a subsequent section. We shall consider the process of batch mixing and continuous mixing separately.

3. Batch Mixing

In batch mixing experiments usually the measurements of the following are made:

1. Flow patterns and velocity distribution
2. Overall discharge rates, circulation capacities and circulation times
3. Power consumption
4. Mixing times

In what follows, we shall describe the measurement techniques used for each purpose rather briefly and then elaborate on the available information obtained with viscous Newtonian and non-Newtonian fluids. It should be emphasized here that a great deal of information dealing with the above aspects exists in literature particularly in relation to the turbulent region flow of low-viscosity Newtonian fluids, but due to lack of space this will not be reviewed here; only pertinent references will be pointed out.

3.1 Flow Patterns and Velocity Distribution

The knowledge of flow patterns and velocity distribution is helpful in understanding the mixer performance and in building up realistic physical models. Furthermore, it helps in linking it up with the other integral quantities such as circulation capacities, circulation times, power consumption, mixing time, etc. A gross observation on flow patterns (obtained, for example, by injecting a dye tracer) gives an idea about the overall motion in the vessel, points out the dead zones, etc. The detailed observations on velocity distribution, however, are the more important ones, since they help in the estimation of velocities, velocity gradients, total strains, etc., in different parts of the vessel.

3.1.1 MEASUREMENT TECHNIQUES

There are several measurement techniques which can be used. In the following, we shall review very briefly some of them; in each case pointing out their limitations in relation to the high viscosity Newtonian and non-Newtonian liquids with which we are concerned here.

(i) *Particle technique*: In this case a neutrally buoyant particle of, say, polyethylene or polystyrene is suspended in the liquid in the vessel and movement of the fluid is tracked by a camera. By using appropriate measurement procedure (see, e.g., Kelkar, *et al.*, 1973; Peters and Smith, 1967) a three-dimensional velocity distribution can be obtained. The particle migration effects (which are particularly complex in viscoelastic non-Newtonian fluids) should be taken care of; absence of such effects could be, for instance, ensured by looking for closed circulation loops. A streak photography method (e.g. Seyer and Metzner, 1969) is essentially similar and a suspension of microbubbles of air is what is used in this technique. Sometimes a cloud of fine particles of aluminium or naphthalene (or other material capable of reflecting light) is used. A thin flat beam of bright collimated light is passed into the transparent liquid and a two-dimensional velocity distribution is obtained.

(ii) *Pitot tube*: This classical technique should be used with great care with viscoelastic non-Newtonian fluids. Any stagnation point velocity or pressure measurement can give spurious results (see e.g. Metzner and Astarita, 1967) due to the abnormal kinematic conditions which the viscoelastic fluids develop under conditions of rapidly changing deformations.

(iii) *Hot-wire anemometer*: The principle of this technique is again well-established, but when used with viscoelastic non-Newtonian fluids this can give some problems. Indeed, the studies of James and Acosta (1970) showed that the heat transfer rate from a cylinder immersed in a viscoelastic fluid becomes independent of the free stream velocity after a certain critical velocity is reached. Ultman and Denn (1970) have analysed this problem and shown this to be consistent with the presence of a shear wave velocity, with which the information is transported in elastic fluids.

(iv) *Laser-Dopler method*: This method, which involves the measurement of Dopler shift of a thin laser beam is perhaps the best to use since the flow field is left undisturbed thus avoiding any anomalous effects. In recent years, there has been an increasing trend to use this method in the study of velocity distribution in non-Newtonian fluids (e.g., Rudd, 1971).

3.2 Flow Patterns and Velocity Distribution in Viscous Newtonian Fluids

The study of flow patterns for various types of impellers has been extensively reported (Gray, 1966). At low Reynolds numbers, a turbine agitated vessel essentially produces a tangential motion. At high Reynolds numbers, the secondary circulation begins due to the centrifugal forces. The fluid is thrown away radially and by reasons of continuity, it is brought in axially.

In the case of propellers and pitched blade turbines, there is primarily an axial motion along with the tangential circulation. At higher Reynolds numbers, however, radial motion begins and stagnant pockets are formed in the bottom corner of the vessel (for downward pumping of the impeller). Often baffles are used with these impellers to suppress the vortices (to reduce the tangential motion) and to promote the axial and radial motion.

In the case of paddles and anchors the primary motion is tangential. The radial and axial motion develops at higher rotational speeds. The Reynolds numbers at which appreciable radial and axial motion develops are much higher for anchors than those for paddles and turbines; the close clearance between the impeller and the vessel is apparently responsible for this. The secondary motion in the case of anchors (in the vertical plane, i.e., in the plane perpendicular to the impeller plane) is shown in Fig. 5 (Beckner and Smith, 1966). As the Reynolds number is increased $\left(\frac{d^2N\rho}{\mu} > 10\right)$ a vortex is developed behind the blade. At higher Reynolds numbers a twin vortex is formed $\left(\frac{d^2N\rho}{\mu} > 100\right)$. The decrease in the clearance causes these vortices to be formed at lower Reynolds numbers. A detailed investigation of these vortices and also of the vertical secondary motion has been performed by Peters and Smith (1969).

In the case of helical impellers (ribbon, screws, or combined ribbon-screw) the axial flow is the primary flow. The situation is thus similar to that in the case of propeller or pitched blade turbine mixers; although the flow patterns are somewhat more complex. Nagata et al. (1957) first described the primary circulation in a ribbon agitated vessel. Fig. 6 shows a typical pattern for a ribbon pumping upward. The liquid near the impeller flows upwards (whilst simultaneously rotating), inwards along the free surface, and downwards near the shaft and radially outwards near the

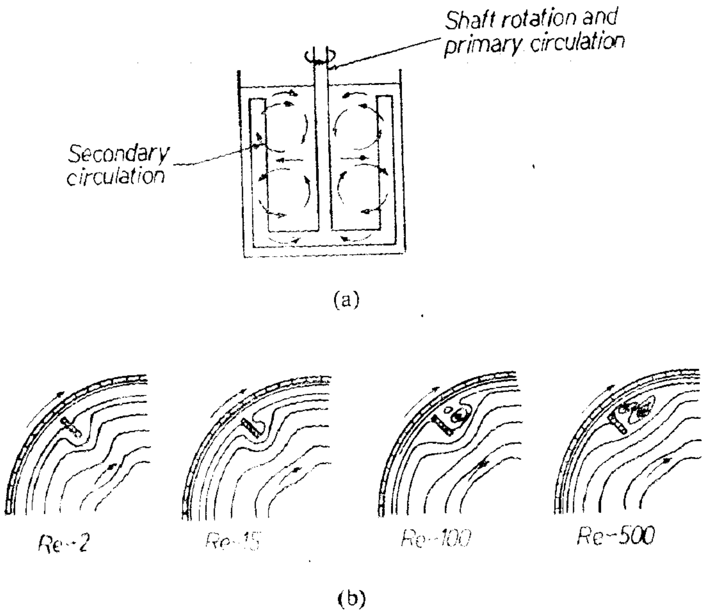


Fig 5. Secondary circulation in an anchor agitated tank: (a) overall circulation, (b) flow near the blade (after Beckner and Smith, 1966)

base. Os'hima and Yuge (1970) mention that the diameter of the core of the liquid coming downwards was about 1.5 times greater than the shaft diameter; this factor must obviously be depending on geometry. At higher Reynolds numbers (Re > 20) secondary flows were noted by these authors. For ribbons pumping upwards it was observed (Bourne and Butler, 1969) that the liquid from the bottom travels back to the bottom through a short path without going to the surface. For ribbon pumping downwards the primary flow is exactly opposite and a secondary flow exists at the surface. When the screw impellers are used along with a draught tube a primary circulation occurs inside the draught tube (like the one near the ribbon impeller). The fluid flows downwards in the draught tube with a simultaneous tangential motion (for a screw pumping downwards) and travels upwards in the annular space more or less parallel to

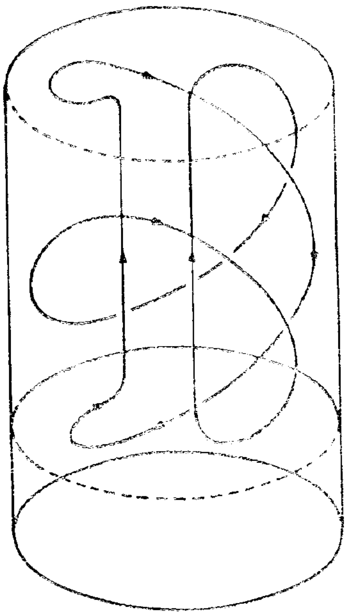


Fig. 6 Primary circulation in a ribbon agitated vessel (Nagata et al., 1957)

the vessel wall with very small angular velocities and goes back to the draught tube. No observations on secondary flows have been made as yet. The primary flow was found to exist for a considerable range of Reynolds numbers (up to Re $\sim$ 200). The flows will somewhat depend upon the gap between the impeller and the draught tube. The screw without the draught tube behaves similar to the propellers. As in the case of propellers, screws are used in an eccentric fashion. This helps in damping the secondary motion and in increasing the primary flow.

At high speeds (or at higher Froude numbers) a vortex is formed on the liquid surface. Its occurrence depends very much upon the geometry. For turbines it occurs at Re $\sim$ 300 (Uhl and Gray, 1966). For a ribbon pumping upwards or a screw pumping downwards it occurs much earlier than that for an anchor impeller (Fr $\sim$ 0.01). Baffles are generally used to damp these vortices. In the case of turbine and propeller this will obviously depend upon the distance between the impeller and the liquid surface.

3.3 Flow Patterns and Velocity Distribution in Non-Newtonian Fluids

The rheological complexities associated with the liquid being agitated can very significantly influence the flow patterns and velocity distribution. The nature of the rheological complexity will, of course, govern the net influence on the hydrodynamics. The limitation of space does not enable us to give an account of the science of rheology; however, such information may be readily found in many standard textbooks (Middleman, 1968; Skelland, 1967; Astarita and Marrucci, 1974).

The influence of shear dependent viscosity is most easy to understand and analyse. For instance, one would expect that for pseudoplastic (shear thinning) fluids, the apparent viscosity of the fluid in the near impeller region should be rather low and increase progressively as one moves away from the impeller. This will consequently result in high velocities and velocity gradients in the near impeller region, which will die away rapidly from the impeller. The early photographic studies (e.g., Metzner and Taylor, 1960) did confirm this. The singularly important result which Metzner and Taylor (1960) were able to obtain on the basis of their velocity distribution measurement was that the average shear rate in the vessel was linearly proportional to RPM. We shall see later (sec. 3.5) that this result plays an extremely important role in the prediction of power requirements in non-Newtonian fluids. It should be emphasized that Metzner and Taylor observed near solidification of a dilatant fluid in the region of the impeller. The size of this core increased rapidly with rotational speed; the effect became particularly important as the ratio of the tank diameter to the agitator diameter was increased. The angular velocity distribution measurements of Peters and Smith (1969) made on anchor agitators are also in agreement with the trends observed by Metzner and Taylor in that they observed considerably flatter velocity profiles for a shear thinning fluid in comparison to a Newtonian fluid.

Fluid elasticity can very significantly influence the flow patterns around agitators. In fact, a fundamental approach to the understanding of velocity distribution around agitators may be to study the rotational flows around simple bodies such as spheres and discs (Kelkar et al., 1972). The advantage here is that at least the shape complexities of the agitators (which preclude the possibility of any theoretical study) are avoided and the velocity distribution can be viewed from a theoretical angle.

If one considers a third order viscoelastic fluid which portrays the characteristics of a finite shear thinning viscosity and elasticity (manifesting itself in the form of finite normal stress difference in viscometric flows) then for a sphere of radius R rotating at an angular velocity Ω, one obtains the stream function ψ as (Walters and Savins, 1965)

$$\psi(r, \theta') = \tfrac{1}{4}\left(\frac{\bar{\alpha}_2}{\bar{\alpha}_1}\right)R^3\Omega^2\left\{\frac{\rho R^2}{\alpha_2} - [1 + 2(R/r)]\right\}\left(1 - \frac{R}{r}\right)^2 \sin^2\theta' \cos\theta' \quad (3.1)$$

The projections of streamlines on a plane containing the axis of rotation have been shown in Fig. 7.

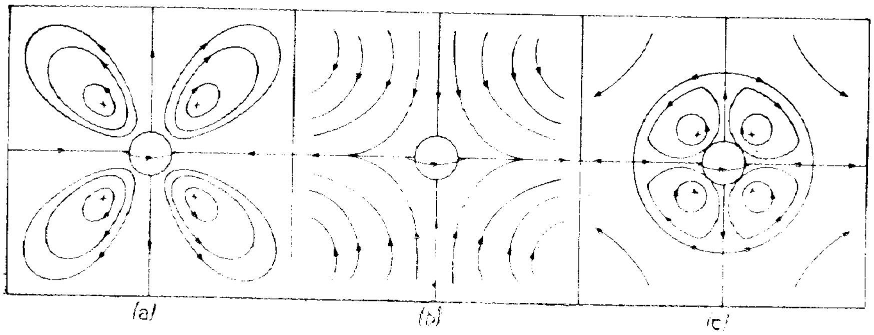


Fig. 7 Secondary flow around a sphere rotating in a viscoelastic liquid: (a) Normal forces dominating, (b) Centrifugal forces dominating, (c) Normal and centrifugal forces comparable

It is evident that different flow situations will arise for different values of the parameter $\rho R^2/\bar{\alpha}_2$ (which is a ratio of inertial stresses to normal stresses for a third-order fluid). This number plays an important part in determining the flow field around spheres, and is likely to play an equally important part in describing the flow field around agitators, and consequently in determining the circulation and mixing times.

While analysing the flow field around a sphere in detail, three cases arise depending on the value of the parameter $\rho R^2/\bar{\alpha}_2$. When $\rho R^2/\bar{\alpha}_2 < 1$, the normal stresses determine the direction of the secondary flows in the entire space around the sphere. In such a case, the fluid moves in highly segregated fashion and in fact, at points $r = 6\bar{\alpha}_2/R$ and $\theta' = \sin^{-1}\sqrt{(2/3)}$, the fluid will move in closed circles around the axis of rotation without getting mixed with the bulk of the fluid (Fig. 7a). When $\rho R^2/\bar{\alpha}_2 > 3$, the centrifugal forces dominate the entire flow field (Fig. 7b), and elasticity will have no significant effect in modifying the flow pattern. For a fluid with $1 < \rho R^2/\bar{\alpha}_2 < 3$, there will be a sphere of radius R inside which closed loops and consequently, highly segregated zones, will be observed. Outside the sphere of radius R there will be a centrifugal zone (Fig. 7c).

In fact, such a flow reversal has also been observed by Waters and King (1971) in the case of a disc rotating in viscoelastic fluids. Giesekus (1963) studied the changes in flow patterns due to the interaction of elasticity and inertia in the case of commercial agitators and found qualitatively similar flow patterns. Feldkamp (1962) gives an account of extensive photographic work to illustrate these phenomena. Kelkar (1972) obtained detailed three-dimensional velocity distributions in viscoelastic fluids by using the particle technique and confirmed the results of the earlier workers.

Ide and White (1974) undertook an extensive investigation of the influence of rheological properties on flow patterns, especially with a view to investigate its implications in bulk polymerising styrene to polystyrene. They used spheres, discs and turbines as agitators. The observed flow patterns were in good agreement with the earlier workers. They also used a screw-propeller agitator. In Newtonian fluids, the action of the screw propeller is to push the fluid vertically in the tank. In the case of viscoelastic fluids, they found that normal stress effects reinforced the screw propulsion mechanism. These results should be contrasted with the different behaviour of the screw in the draft tube system discussed later.

The study of Ide and White (1974) is particularly interesting since they observed flow patterns during bulk polymerization of styrene. They found that at low conversions, the flow patterns around the sphere and other agitators involved a primary axisymmetric flow and secondary flow consisting of a fluid being drawn in at the poles axially and expelled at the equator. As the conversion increased, the secondary flow field around a sphere divided into two regions, one adjacent to the sphere consisting of closed circulating motions and second at larger distances from the sphere. Similar flow patterns were observed with other agitators.

The implications of such changes in the secondary flow patterns on the performance of a mixing vessel should be clearly appreciated. The photographic study of Kelkar et al. (1972) is particularly important in this connection. Their velocity distribution measurements in viscoelastic fluids showed quite clearly that although the secondary flow patterns can be changed quite significantly, the primary flow remains practically unaffected. Since the major contribution to the shear stresses in the vicinity of the rotating body comes from the variation of the primary flow velocity component with radial distance, the power consumption appears to be relatively unaffected by the modifications brought in due to elasticity. However, the secondary flow patterns will have a significant effect on residence-time distribution, molecular-weight distribution (in the case of polymerization reactors), mixing times, circulation times and related kinematically controlled processes; some of these will be discussed in the appropriate sections later on.

Very little experimental work has been published on the influence of elasticity on flow patterns with other agitators. Peters and Smith (1969) have provided some experimental data on the influence of elasticity on flow patterns around anchor agitators. The most significant differences were found in front of the agitator blade. The viscoelastic fluids appeared to experience a greater degree of disturbance around the stagnation point, and there was same evidence of building up of a rather indeterminate boundary layer in front of the blade. Furthermore, viscoelastic liquids produced a considerably enhanced vertical circulation.

The influence of fluid elasticity on the velocity distribution in vessels stirred with helical agitators has not been extensively studied. Chavan, et al. (1975a), however, provided some qualitative observations wherein they showed that for highly elastic liquids and at least for some geometrical configurations, the angular flow increased whereas the axial flow was damped considerably. The detailed velocity distribution studies of Carreau et al. (1976) support this. Fig. 8 shows some typical data obtained by these workers. For a 2% CMC solution (which showed negligible elasticity), the strong axial upflow and downflow can be clearly seen,

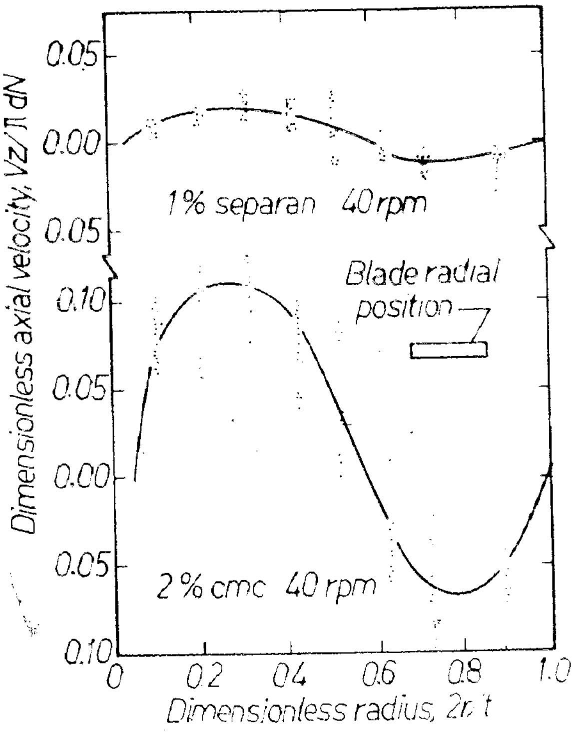


Fig. 8 Axial velocity distribution in a ribbon agitated vessel (Carreau P. J. et al., 1976)

whereas for a 1% PAA solution (which was strongly elastic), the axial flow can be seen to be significantly damped. The mechanisms responsible for such a phenomenon are not quite clear, however, it is suspected that the peculiar behavior of elastic liquids in kinematic fields of rapidly changing deformation is responsible. More detailed studies are obviously needed in this area.

3.4 Discharge Rates, Circulation Capacities and Circulation Times

From the velocity measurements, an important integral hydrodynamic quantity can be easily obtained. It is the overall discharge rate or the average time elapsed between the successive passes of a fluid element through the impeller. Gray (1966) gives a comprehensive summary of the investigations of turbines and propellers, where the calculations for the overall radial and axial flow are done from the velocity measurement.

3.4.1 MEASUREMENT TECHNIQUES

A direct measurement on discharge flow is possible in the case of screws and propellers with draft tube where the flow is predominantly axial. In this method, instead of allowing the liquid to circulate back to the draught tube it was made to overflow into a measuring cylinder by extending the tube above the liquid level. The liquid is fed into the tube by some external means. A correct estimate of the axial throughput can only be obtained if the liquid inside the draught tube is levelled with the rim of the vessel, i.e., no extra gravitational head is imposed. Sometimes this method has been used without proper care. Chavan (1972) has discussed the probable errors. Often the discharge rates thus measured are considered to be due to the impeller alone. This obviously is incorrect since the presence of the draught tube and its positioning in the vessel very much influence the values of the discharge rate.

The average time taken by the fluid element to complete one loop can be measured by following a particle or by ejecting a small pulse of an electrolyte and measuring the conductivity of the liquid leaving the periphery of the impeller. The circulation time, θ_c, can be used to calculate the liquid pumping rate, q, as

$$q = \frac{V}{\theta_c} \tag{3.2}$$

where V is the volume of the liquid in the tank. The dimensionless number which is normally used is called a circulation number and defined in terms of the impeller diameter as

$$\bar{C}_i = \frac{q}{Nd^3} \tag{3.3}$$

A few comments need to be made about the relevance of discharge-flow measurement.

The discharge-flow measurements from velocity profiles are quite accurate, but those using the experimental average-circulation time can be questionable. It is obvious that a small particle follows a route depending upon its initial position. Under steady-state conditions one loop should correspond to one circulation. Thus the circulation-time measurements should very much depend upon the initial position of the particle or the tracer. In an agitated vessel, however, there may be some random motion (Chavan, 1972). Thus, because of the random nature of the initial position of the particle before each circulation, the discharge rate given by equation 3.1 is a statistical estimation of the overall discharge rate. In this procedure of measurement of circulation time one can also obtain a statistical distribution of the circulation times, which again is an estimation of the velocity distribution in the plane perpendicular to the flow. O'shima and Yuge (1970) and Ivonue and Sato (1967) have obtained such information on various impellers.

3.4.2 EXPERIMENTAL OBSERVATIONS

Gray (1966) has summarized the information on circulation times and discharge rates for turbine and propeller agitators. This information, however, pertains to Re $> 10^5$, i.e., for turbulent conditions where C_i is independent of Re. Gray has compared the circulation numbers on the basis of equal power consumption. As an example, one can note that a rotating disc required about 300 times more energy to give the same discharge rate as an eight-bladed turbine. The circulation numbers for propellers were typically in the region of 0.4 to 0.6, whereas for turbines they were in the region of 0.6 to 2. Since we are mainly concerned with the mixing of high viscosity liquids, such information is probably not totally relevant to us.

The literature on circulation capacities (and times) for high viscosity liquid agitation with helical impellers has been well summarized by Chavan (1972). The circulation number varies between 0.4 to 1 for ribbons and between 0.01 to 0.5 for screws in a draft tube. These are independent of Reynolds number (for Re < 10 or Re < 50) but are strongly influenced by the geometrical configuration. Studies with a large number of purely viscous liquids revealed that circulation numbers were not at all influenced by shear-thinning characteristics. The observations with strongly elastic liquids, however, showed that the circulation was damped as a result of elasticity and the circulation numbers were lowered quite significantly. Chavan and Ulbrecht (1974) have provided a correlation which adequately described the data for purely viscous fluids; whereas Chavan et al. (1975a) have described a method to correlate the data on elastic liquids for a given geometrical configuration. The paper by Chavan et al. (1975b) is also of interest. Circulation times for other agitators operating under laminar conditions in viscoelastic liquids have not been measured as yet. The peculiar flow reversals and the two-zone velocity distribution regions arising out of the presence of elasticity should strongly influence the circulation times. The enhanced vertical circulation in elastic liquids reported by Peters and Smith (1969) for anchor agitated vessels and by Feldkamp (1962) for propellers would imply that the circulation numbers may increase on account of elasticity rather than decrease as in the case of helical agitators. Detailed studies exploring these aspects would be highly desirable.

Specific comments need to be made concerning the influence of circulation times and circulation time distribution in polymerization reactors. An interesting study in this context is mentioned by Olson and Stout (1967) with specific reference to condensation polymerization of bifunctional polymers. The study is with a specific reference to a turbine impeller which produces circulation loops of the polymer; the viscosities of the polymer mass are so high that material in the circulation loops remains segregated. The water of condensation is removed by diffusive transport to the surface of the polymerizing mass. The contribution of the diffusive process to the rate of reaction is approximated by assuming that the water concentration is proportional to the circulation time of the segregated fluid elements. The effect of mixing upon the product molecular-weight distribution has been found and it has been shown that the assumed mixing pattern significantly alters it. Indeed, if the circulation time is low at the end of polymerization, the polymer may be expected to have poor uniformity. This example clearly illustrates the role of circulation loops in batch polymerization systems.

3.5 Power Consumption

The space available here is too limited to cover the enormous power consumption data which have been published over the years; nor is it the purpose of this review. The published reviews (Uhl and Gray, 1966; Wohl, 1968; Penny and Bell, 1967) give a good appraisal of such information. At present, one can make a reliable estimate of the power consumption for various impeller designs and for a number of geometrical arrangements for Newtonian liquids. A great deal of information is also available on non-Newtonian liquids and multiphase systems. We will present here a viewpoint of the analysis of the data, rather than giving a ready-made design method.

3.5.1 MEASUREMENT TECHNIQUES

The methods of measuring power input to a stirred vessel have been discussed by Holland and Chapman (1966). These methods fall into four groups.

1. Measuring the power supplied to an electric motor by measuring current, voltage and power factor and correcting the copper and iron losses and gear box friction losses.
2. The reaction torque on a motor stator is measured by suspending

the entire motor on a torsionless suspension and the force required to hold it stationary is measured.

3. The mixing vessel is mounted on a frictionless turntable and the force required to hold the table stationary is measured.

4. The torque in the mixer shaft is obtained by measuring the twist over an intentionally weak part of the shaft.

Method (1) is not preferred for research work as it is difficult to get precise values of the power unless the losses are correctly estimated. It seems that methods (3) and (4) are generally used for simplicity and accuracy.

3.5.2 DATA ANALYSIS

Since power consumption was first measured for rotating impellers in the late 19th century, the data have often been correlated using dimesional analysis. It may be expected to be a function of the following variables:

(i) *Geometrical variables*: Impeller diameter (d), tank diameter (t), liquid depth (h)
(ii) *Material properties*: Density (ρ), viscosity (μ)
(iii) *Process variables*: Rotational speed of the impeller (N), gravitational acceleration (g)

The relationship can simply be written as,

$$P = f(d,\ D,\ h,\ \rho,\ \mu,\ N,\ g) \tag{3.4}$$

Dimensional analysis gives

$$\frac{P}{d^5N^3\rho} = \bar{K}\left(\frac{d^2N\rho}{\mu}\right)^{e_1}\left(\frac{dN^2}{g}\right)^{e_2} \tag{3.5}$$

where $\bar{K}$ is a constant for particular set of geometrical variables and could be obtained as

$$\bar{K} = \bar{K}_1\left(\frac{D}{d}\right)^{a_1}\left(\frac{h}{d}\right)^{a_2} \tag{3.6}$$

The dimensionless groups $(P/d^5N^3\rho)$, $(d^2N\rho/\mu)$ and (dN^2/g) are known as power number (Po), Reynolds number (Re) and Froude number (Fr), respectively.

The above analysis is valid only under the following conditions: (a) either a single liquid or two miscible liquids having similar properties are present in the vessel, (b) the temperature changes due to energy dissipation are so small that variation in fluid properties because of the temperature changes is negligible, (c) the flow behavior of the liquid can be characterized by a single parameter, i.e., viscosity. Thus the liquid is Newtonian.

The values of $\bar{K}$, e_1 and e_2 have been determined by a number of workers for several different geometrical variables. e_1 assumes different values in the range of -1 to 0 depending upon the operating range of Reynolds numbers. It has been found to have a value of -1 below a certain critical value of Reynolds number. This critical Reynolds number varies between 10 to 100 and it seems to be influenced by the geometry of the system. At very high Reynolds numbers ($\mathrm{Re} > 10^4$) power number becomes independent of Reynolds number. The region where e_1 is -1 is commonly understood as laminar region. It may be proper to designate it as creeping flow region as the majority of the non-viscometric flow situations give rise to such relationships only when the inertia terms in the Navier-Stokes equations are dropped. The effect of Froude number on the power consumption would be apparent only when some power is consumed in producing significant waves on the surface of the liquid or in sustaining a vortex in liquid around the impeller shaft. It is found that for unbaffled vessels these effects are negligible below Reynolds number of 300. This limit is exceeded for $\mathrm{Re} > 10^3$ when the baffle system is adequate or when the impeller is suitably off-centred. Nagata and Yokoyama (1955) state that the effect of Froude number is so negligible as to be indeterminate except by a very accurate dynamometer. When such effects are present, a practical method of analysis is available (Uhl and Gray, 1966 and Skelland, 1967).

For standard designs $\bar{K}$ and e_1 in equation 3.5 can be easily obtained. However, to obtain a generalized correlation, a series of experiments with wide variation in geometrical variables will be required. Often, the geometrical correlations are obtained with one or two variables and even when these variables are not independently varied, their dependence on other variables is neglected. This is incorrect mathematically as well as physically. The most important variables, however, can be obtained with proper physical reasoning or by conducting special experiments.

For inelastic non-Newtonian fluids, dimensional analysis can be performed on lines similar to those for Newtonian fluids. The results will depend upon the specific model chosen. Thus, for instance, we obtain for a power-law model

$$P_0 = P_0\left(\frac{d^2 N^{2-n}\rho}{K}, n\right) \tag{3.7}$$

and for an Ellis model

$$P_0 = P_0\left(\frac{d^2 N\rho}{\mu_0}, \frac{N\mu_0}{\tau_0}, \alpha\right) \tag{3.8}$$

Here $(d^2N^{2-n}\rho/K)$ and $(d^2N\rho/\mu_0)$ are the corresponding Reynolds numbers. The dimensionless number $(N\mu_0/\tau_0)$ was introduced by Kelkar et al. (1972) and called a viscosity number. Obviously, with the aid of dimensional analysis alone one cannot get quantitative information about the involvement of the dimensionless parameters of the rheological model.

The first attempt to incorporate the parameters which describe the deviation of any inelastic fluid from the Newtonian characteristics involve the use of results obtained in a pipe flow. This analogy was first suggested by Metzner and Otto (1957). It has been shown by Skelland (1967) that such a Reynolds number does not give a unique power curve for a wide range of flow behaviour index. Mitsuishi and Hirai (1969) state that this is not a failure of the analogy but of the power-law approximation. They suggest an alternative method involving the use of Ellis and Sutterby models. Chavan (1972) has conclusively shown that even with such models, pipe-flow analogy does not offer a unique curve, even in the laminar region.

In order to obtain a power correlation in terms of the rheological parameters, the knowledge of shear rates (at least in the immediate vicinity of the impeller) is necessary. In an extremely significant contribution, Metzner and Otto (1957) showed that the average shear rate in the vessel can be assumed to be directly proportional to the rotational speed at least in the laminar region (see Magnusson (1952) for related work). This shear rate can be obtained as follows. First, it is necessary to obtain the plot of Po-Re for Newtonian fluids for the system under consideration. Then the power number is calculated from the power data for the non-Newtonian liquids. For this power number the corresponding Reynolds number could be obtained from the Newtonian plot. The average viscosity given by the Reynolds number would give the corresponding shear rate ($\dot{\gamma}_{\mathrm{av}}$) from the viscometric data. A relationship such as

$$\dot{\gamma}_{\mathrm{av}} = k_s N \tag{3.9}$$

has been obtained by various workers for various impellers and the values of k_s have been reported. For the agitation of pseudoplastic liquids by turbines, propellers and paddles k_s assumes a value between 10 and 13. For dilatant liquids Metzner et al. (1961) obtained a linear relation (up to $n = 1.5$). The validity of the linear relationship in equation 3.1 was subsequently established by Metzner and Taylor (1960) (see sec. 3.1). From the available information it appears that one can accept a linear relationship under creeping flow conditions. However, there is some uncertainty about the extension of this method for higher Reynolds number and also about whether k_s can have a universal value even in the low Reynolds number range. The results on turbine (Metzner, et al., 1961) show that the generalized Reynolds number $\mathrm{Re} = \dfrac{d^2 N \rho}{\mu_a}$, (where $\mu_a = \mu_a(\dot{\gamma}_{\mathrm{av}})$ obtained from viscometric data) can give a unique curve up to Re = 160 (laminar region ends at Re = 10) within ±20 per cent. However, this is not observed in every case and Skelland (1967) comments that such extension is not justified on account of insufficient evidence. The constant of proportionality, k_s, can otherwise be a constant for a particular pseudoplastic liquid and geometrically similar system. In other words, k_s should be generally a function of geometry and rheology. The problems can best be overcome by considering a power-law relationship. In creeping-flow (or laminar) region one can obtain a relationship

$$P_0 = \bar{K}(k_s)^{1-n}\left(\frac{d^2 N^{2-n} \rho}{K}\right)^{-1} \tag{3.10}$$

From experimental data on power consumption on Newtonian and inelastic liquids and from the flow curve, k_s can be measured (as described earlier). Also, the range of shear-rates ($\dot{\gamma}_{\mathrm{av}}$) will be known to give K and

n. Calderbank and Moo-Young (1959) and Beckner and Smith (1966) have obtained k_s in this way and related it to the geometry and rheology.

After knowing the operating rotational speeds and the values of k_s from literature an approximate estimate of the shear rates can be obtained. When k_s is dependent on n, a trial and error procedure may be needed to estimate k_s. However, a rough estimation could be possible from the previous information in similar situations. Thus, for example, for helical impellers k_s varies from 10 to 100; then if rotational speeds range from 0.1 to 10 sec^{-1} then a range of shear rates of 1 to 1000 sec^{-1} may be appropriate.

Note that equation 3.9 does not give an average shear-rate in the entire vessel in all the regimes. The shear-rates thus obtained can only characterize the flow near the impeller and that too only in the laminar region. Even in the laminar region, the shear-rates at the tip of the impeller are as much as seven times higher than those given by equation 3.9. At higher Reynolds numbers, the maximum shear-rates in the vortices behind the blade have been found to be of an order of magnitude higher (Van't Riet and Smith, 1973).

The power consumption data for Bingham plastic fluids can be correlated by using simple dimensional analysis considerations (see Nagata et al., 1970).

The influence of fluid elasticity on power consumption is negligible under creeping flow conditions (Kelkar et al., 1972; Chavan, 1972 and Rieger and Novak, 1974). At higher Reynolds numbers, however, it appears that elasticity suppresses the secondary flows and one obtains a reduction in power consumption in comparison to a purely viscous liquid (Kale et al., 1973).

3.6 Mixing Times

Mixing time is a purely experimental criterion, basically designed to compare the performance of agitators. It essentially gives an idea about the time required to carry out a required degree of homogenization. A properly measured mixing time can form a good basis for comparing the contribution of the hydrodynamics towards the completion of mixing.

3.6.1 MEASUREMENT TECHNIQUES

Primarily, a small quantity of liquid differing from the bulk in either concentration of a tracer or temperature and otherwise having the same physical properties is mixed with the bulk liquid in the vessel. The changes in the tracer concentration (or temperature in the thermal methods) can be measured as a function of time. Techniques involving conductivity, atomic absorption spectrometry, refractive indices (Schlieren method) or light intensity (dye addition or decolorization using fast reactions such as acid-base or iodine-sodium thiosulphate) are frequently used. The colorization or decolorization can be visually observed (Coyle et al., 1970). In visual methods, there can be subjective errors and hence these should be avoided. The instrumental methods provide point values of different quantities. The selection of a point in the vessel for measurements and spotting the end-point are two major difficulties. Complete mixing on molecular level in the entire vessel is difficult to achieve and difficult to measure. The merits and demerits of various techniques of measurement have been discussed by Ford et al. (1972).

3.6.2 DATA ANALYSIS

The change in the selected intensive property (concentration, temperature, radioactivity) as a function of time is measured during mixing time experimentation. If mixing time is so defined that the value of the measured quantity is, say, within 10 to 25 per cent of the finally expected average value, then a rational interpretation of the data can be obtained (Hoogendoorn and Den Hartog 1967, Chavan 1972). The phenomena such as molecular diffusion or conduction will obviously influence the mixing time. However, it seems that the first 75 to 90 per cent change is mainly controlled by hydrodynamics (such as convection or shear or tensile deformation or turbulence). The overall changes due to diffusion will be relatively slow in this period. It will assume an important role as the tracer is dispersed more and more in the bulk. In the final stages of the process it will be the major contributing factor.

Extensive information on mixing times has been reported by Gray (1966), and Ho and Kwong (1973); the latter authors have given a particularly useful summary of the published work on mixing times for both Newtonian and viscoinelastic non-Newtonian fluids. Chavan (1972) has described the effect of non-Newtonian behavior on mixing times in vessels agitated with helical impellers. His findings could briefly be summarized as follows. The mixing times are inversely proportional to the rotational speed for very low and very high Reynolds numbers. In between, they vary with a negative power of Reynolds number; the exponents in general being between -0.3 and -2. The limiting Reynolds number, for which $N\theta_m$ is constant, is much higher for the axial flow impellers than for the other impellers. In this region, the shear thinning properties do not influence the dimensionless mixing time (note the similar conclusions on circulation times described in sec. 3.4).

Only recently certain papers have appeared which examine the influence of fluid elasticity on mixing times in agitated vessels. Chavan et al. (1975a, 1975b) found experimentally that mixing times increased significantly as a result of fluid elasticity when helical agitators were used. Ulbrecht (1974) has nicely summarized this work. Indeed, the observations made in the foregoing concerning the damping of axial circulation as a result of fluid elasticity do suggest an increase in mixing times, and the experimental findings of Carreau (1976) also bear this out. On the other hand, an enhanced vertical circulation as a result of fluid elasticity in the case of anchor agitated vessels (Smith, 1970) gives considerably shorter mixing times; sometimes reductions by a factor of four have been reported. No general conclusions regarding the effect of fluid elasticity can thus be drawn and the detailed hydrodynamic changes have to be carefully examined in each case.

The recent study by Yap et al. (1978) is particularly illuminating so far as problems of scale-up for viscoelastic fluids are concerned. With special reference to ribbon agitators they showed that for geometrically similar mixers the criterion to be observed is that the power per unit volume in the mixers be equal for equal degrees of homogeneity of the mix. This observation is based on the inverse relation between the power number and the Reynolds number and the fact that the number of impeller revolutions for a given degree of homogeneity is constant. These conditions are satisfied for Newtonian as well as purely viscous (pseudoplastic) non-Newtonian fluids, but there are significant differences for highly viscoelastic liquids. As a matter of fact it is found that the mixing efficiency in viscoelastic liquids is almost 2 to 5 times less than that in the case of equivalent Newtonian fluids. Furthermore, in highly viscoelastic liquids

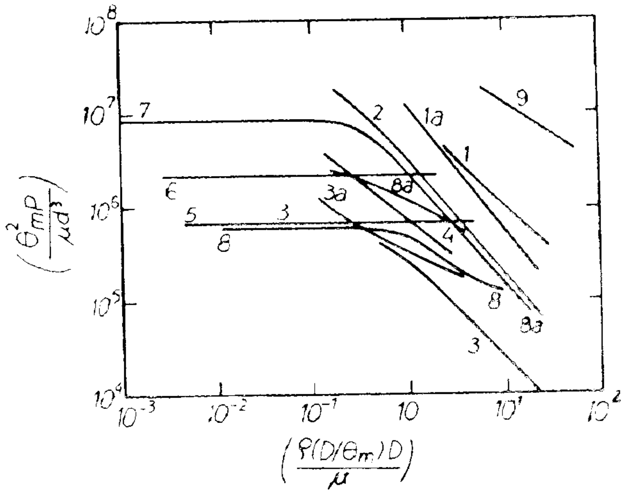


Fig. 9 Comparison of mixer performance (Hoogendoorn and Den Hartog, 1967)

1 Turbine + Baffles
1a Turbine
2 3 Inclined Blade Paddles
3 3 Inclined Blade Paddles + Draught Tube
3a 1 Inclined Blade Paddle + Draught Tube
4 Screw
5 Screw + Draught Tube
6 Ribbon
7 Propeller A + Draught Tube
8 Propeller B + Draught Tube
8c Propeller B
9 Anchor

mixing efficiency does not appear to be very sensitive to the geometry. Further work is decidedly warranted in this area, since most polymer melts handled in practice show significant viscoelastic phenomena.

The information on mixing and power consumption can be suitably combined to provide a rational basis for comparison of performance of different agitators. A typical comparison has been shown in Fig. 9 where, at a particular mixing time, the power required to achieve the desired degree of mixing increases with $(\theta_m^2 P/\mu D^3)$. No such comparison has been compiled for mixing of non-Newtonian fluids, and it will be clearly desirable to do this.

It should be emphasized that we have considered the mixing of only a single fluid. When blending of two fluids with widely different rheological properties is considered, the situation becomes much more complex. Only a start on studying this important problem has been now made (see, e.g., Ford and Ulbrecht, 1975).

4. Continuous Mixing

In the foregoing, we have described some aspects of mixing related to a description of gross parameters such as the power consumption, mixing time, circulation time, etc. Such information is useful from the point of view of estimating the suitability of a given mixer configuration for a given purpose. Indeed, this information may be entirely adequate when non-reactive processes are to be carried out (such as blending of two miscible non-reacting fluids). However, when one considers the use of a mixing device for the purpose of contacting two or more chemically reacting compounds, the situation becomes much more complex. Indeed, the mixing device now has the job of providing optimum time-composition, time-temperature and time-shear environment. Such an environment then depends upon the fluid mechanics in the device, and we have emphasized in sec. 3.3 as to how complicated this problem of understanding the detailed fluid mechanics is. However, over the years, various methods have been devised to account for the modification of reactor behaviour caused by the mixing and contacting patterns. We shall briefly review these now. It should be emphasized that the basic aspects related to the field of non-ideal flow have been well summarized in some excellent reviews such as Levenspiel and Bischoff (1963), Bischoff (1966), Neuman (1974) and in the recently revised textbook of Levenspiel (1972). Consequently, the fundamental definitions will not be reviewed in depth. What will be considered, however, are the special problem areas concerned with the highly viscous liquids.

4.1 Residence Time Distribution

The development of the concept of residence time distribution at least in the modern chemical engineering era dates back to Danckwerts' classic paper (Danckwerts, 1953); although earlier papers could be found out. The concept of residence time distribution avoids the need to know the exact flow pattern in the vessel, but seeks to know only the information regarding how long the molecules stayed in the vessel, or in other words the residence time distribution (RTD) of the fluid. A stimulus-response technique can be obviously used to obtain information on RTD.

The two ideal cases of plug flow and perfect mixing are obvious but for intermediate cases, several age distribution functions have to be defined in order to describe quantitatively the age distribution of the fluid. The definitions of the well-known *E*, *F* and *C* curves follow simply and a standard textbook (such as Levenspiel, 1972) should be referred to understand the physical meaning of these. In the following we shall discuss briefly the methods by which such information can be obtained, the methods of interpretation and the manner in which this information should be used.

4.1.1 MEASUREMENT METHODS

It is understandable that in plug flow conditions RTD will consist of a delta function, since all the molecules pass through with the same residence time. If mixing takes place, then there is a spread in RTD. In case some material stays for long (dead space) or passes through very quickly (by passing), we have a greater spread. Thus, if we inject at the inlet of the mixing device and observe the tracer behaviour at the outlet, we get information on macromixing which relates to the duration of the stay of various fractions in the vessel, but not to what they did in the vessel. The latter part of the information is called micromixing and will be dealt with in the next section.

Basically, a step change in concentration at the inlet is what is used but other signals such as a sine wave (Kramers and Alberda, 1953) and even random noise (Angus and Lapidus, 1963) may be used. It is also possible to use unsteady behaviour reacting systems (Lelli, 1965) or steady state measurements at different flow rates or temperatures (Hoare, 1961). However, an inert tracer has obvious advantages over a reacting tracer. A novel method is the one developed by Goldish et al. (1965) who used a special tracer (completely soluble in the test fluid), which is colourless until activated by a flash photolysis. This means that a flash of light produces a pulse of colored material without actually having to physically inject a tracer into the system.

We have discussed the problems of choosing a suitable tracer for the mixing time measurements in sec. 3.6. The problems of the choice of tracer in the study of RTD when handling non-Newtonian fluids are quite similar. In a certain range, at least, the rheological properties can be very sensitive to electrolyte concentration, pH, temperature, etc. Consequently, a great care usually needs to be exercised in the choice of appropriate tracer.

The points concerning the rapid injection of the tracer (without disturbing the normal flow pattern) and a correct measurement at the outlet are important. Some problems concerning this are described by Bischoff (1963) and White (1962).

The technique of injecting and measuring the tracer can significantly influence the interpretation of the residence-time experiments. The papers by Levenspiel and Turner (1970) and Turner (1971) are particularly illuminating in this regard. They considered two methods of injection, the first in which the tracer is added in proportion to the flow through each point in the injection plane and second in which the tracer is added uniformly across the injection plane. They also considered two methods of measurement, one in which the mixing-cup reading is taken and second in which the average concentration over the cross-sectional plane of the measurement is measured. The data interpretation will depend upon the combination of injection-measurement that has been used.

4.1.2 INTERPRETATION OF RESPONSE

Once the RTD curve is obtained, a gross deviation from the idealized plug flow or completely mixed models is easy to detect. However, considerable information can be extracted from the RTD curve. The details of analysing the RTD curves have been given by Levenspiel (1972), Himmelblau and Bischoff (1968) and others. Naor and Shinnar (1963) have provided fairly sensitive means of determining dead space and bypassing from the RTD curve. Bischoff and McCracken (1966) have considered the utility of these different methods in relation to actual problems.

This information should ideally be helpful in predicting the performance of a chemical reactor. Whether this is possible or not, very much depends upon whether the system being considered is linear or non-linear. By additivity property of linear processes it follows that mere stimulus response information should be adequate to depict the behaviour of a vessel as a reactor, as long as the reaction rate is linear in concentration. However, for non-linear systems, we really need point-to-point information because a knowledge of the exact history of each molecule is necessary (micromixing information). This aspect will be dealt with in a later section.

A further point in the interpretation of the tracer data involves the development of flow models. This usually involves the definition of a flow model containing certain parameters and then correlating these parameters in terms of the system variables. Hopefully, these correlations can then be used to predict the behavior of new situations (without actually having the tracer data on the new situation). This is helpful in design practice. It is important to note here that the parameters should have some physical meaning. As pointed out by Bischoff (1966), a volume parameter in a flow model may have a value larger than that of the actual physical volume of the reactor, and although this may not cause a serious problem in mere curve fitting, it lacks the desirable feature of being able to decipher the actual operation of the reactor being studied.

A number of models (some of the important ones are reviewed in the ensuing discussion) may be formulated on the basis of the tracer information. Basically, this consists of breaking up a large model into smaller regions (which may or may not be on the basis of the feel for the fluid mechanics in the system), each of which may be represented by a dispersion model, by-passing, dead space, etc. The parameters introduced represent flows to, sizes of and extent of mixing in, various regions and do a good job in terms of curve fitting. However, the same tracer information can, at times, give rise to several different flow models or parameters. It thus appears that, whenever possible, it is important to base the model on physical reasoning, so that the parameters are physically meaningful.

We shall now consider in some detail the experimental and theoretical work which has appeared in the past on the aspects of RTD in very viscous systems, especially, the non-Newtonian systems.

4.1.3 RTD IN CLOSED CONDUITS

The simplest case to consider is a straight circular tube in which a fluid flows under laminar conditions. With increasing use of tubular polymerization reactors, the study of RTD under such conditions assumes importance.

The parabolic profile for a Newtonian fluid causes a wide spread in the residence times and the E curve is easily obtained as

$$E = \frac{1}{2\theta^3}, \quad \tfrac{1}{2} \leqslant \theta < \infty \tag{4.1}$$

$$= 0, \quad \text{elsewhere} \tag{4.2}$$

The same problem can be treated for a non-Newtonian fluid as well. If an Ostwaald-de-Waele power-law fluid description is used, then the corresponding age distribution functions may be easily evaluated. Szabo and Nauman (1969) and Cintron-Cordero et al. (1968) have examined this problem. Novosad and Ulbrecht (1966) made use of these age distributions to predict the conversion in elementary reactions carried out in tubular reactors.

In a recent paper, Osborne (1975) has developed purely convective models for tubular reactors. He points out that polymerization reactors are often fairly short with fairly rapid reaction but have a pronounced velocity profile. He developed mathematical expressions so that any of the four commonly used tracer techniques can be used to obtain an empirical profile index. He has also given a method to calculate the distribution of products resulting from a sequence of first order reactions. Edwards and Saletan (1967) in a similar way calculated the effect of non-uniform velocity distribution on RTD by using a quartic profile equation with an unknown parameter which represented the ratio of the centreline to the mean velocity.

It should be emphasized that polymerization flow reactors combine laminar flow with low diffusivities. The higher viscosity of the more completely polymerized material near the wall serves to sharpen the velocity profile predicted for a Newtonian fluid. Centre-line velocities as much as eight times the average velocities have been observed (Edwards and Saletan, 1967). Indeed, Brasie (1968) finds that the experimental RTD measurements appear to correspond more to the elongated velocity profiles (corresponding to dilatancy) than to the flattened profiles (corresponding to pseudoplasticity inherent to the polymeric solution). The strong coupling of the heat effects with reaction in such reactors makes it rather unlikely that the simplified analysis mentioned above will be applicable to polymerization reactors. However, there are other situations where the analysis may be applicable. This concerns the thermal pasteurization of liquid foods, which is usually carried out in tubular conduits. The death rate of micro-organisms is directly proportional to their population density hence the system resembles a first-order reaction. The large literature in the area of food technology (see, e.g., Charm, 1971) should be referred to to understand the implications of this.

Certain modifications of the straight tube configuration can dramatically alter the hydrodynamics and consequently the residence time distribution. As an example, consider the coiling of a straight tube. A centrifugally driven secondary flow is set up which is superimposed on the primary axial flow. This has the effect of narrowing down the RTD considerably. Aspects of this have been studied theoretically by Ruthven (1971) and experimentally by Trivedi and Vasudeva (1975) for Newtonian fluids. The non-Newtonian fluid flow in coiled tubes is being extensively studied only recently (see the work of Mashelkar and Devarajan, 1975) and consequently no RTD studies have been performed as yet. Coiled tube as a reactor configuration, of course, has an additional advantage that the strong secondary motion produces higher heat transfer coefficients. Furthermore, it may prevent the build up of high viscosity material during polymerization at the walls and consequently narrow down the molecular weight distribution. Coiled tube as a reactor shows a great promise and hence the aspects of RTD should be certainly looked into.

Similar comments hold for non-circular tubes as well, although the strength of the secondary circulation is much smaller in this case. Non-Newtonian viscoelastic materials have the peculiarity that rectilinear motion (as in the case of Newtonian fluids) is not possible and a four-celled secondary circulation sets in (see Green and Rivlin, 1956). This will also narrow down RTD.

4.1.4 RTD IN AGITATED VESSELS

The multi-parameter models developed to describe RTD in continuous stirred tank reactors envision such non-idealities as by-passing, stagnant zones, piston flow, etc. The review by Olson and Stout (1967) shows that RTD in a well-stirred reactor corresponds to the exponential distribution of a completely mixed reactor when the circulation rate is much greater than about five times the throughput. Such a condition may be easily achieved in low viscosity systems, but in high viscosity systems (such as polymerization and fermentation reactor), they are far more difficult to achieve.

The high viscosity systems of our interest will invariably operate under laminar conditions. The information on circulation rate (see sec. 3.4) and mixing time (see sec. 3.6) should be helpful in designing to achieve good mixing. For example, in a continuous system, if we keep the mixing time rather small in comparison to the mean residence time, then RTD fairly close to perfect mixing may be achieved. The studies on RTD in continuous agitated vessels assume great importance. Although enough is known in the area of low-viscosity liquids, little information is available for high viscosity liquids.

Zaloudik (1969) provided RTD data for agitated vessels in which flat-bladed turbines were used to agitate corn-syrup solutions in the laminar and early transition region. Significant deviations from the completely mixed system were detected and a two-parameter model was developed to describe RTD. Stokes and Nauman (1971) analysed the data of Blanks and Stokes (1970), which were obtained with polystyrene solutions of viscosities in the range of 4 to 200 poise. Dual flat-bladed turbines and a combination of pitched-end flat-bladed turbines were used. Stokes and Nauman made use of a single parameter tanks-in-series model. Recently Moo-Young and Chan (1971) have provided RTD data on both Newtonian and non-Newtonian power-law fluids agitated by flat-bladed turbines. The model used by Moo-Young and Chan had a combination of completely mixed regions with a dead-space and a plug flow region. They correlated the model parameters in terms of the Reynolds number, a pseudo-plasticity index and the product of the agitator speed and the mean residence time. The range of the parameters considered by Moo-Young and Chan includes values typical of industrial polymerization reactors. However, anchor, helical screw and ribbon and pitched turbine agitators are more commonly used for polymerization and it would be important to obtain information on RTD in such systems. Furthermore, the model liquids tested by Moo-Young and Chan were purely viscous. When a viscoelastic liquid is agitated, the interaction of inertia and elasticity may produce very peculiar flow patterns (see sec. 3.3) and this may significantly influence the residence time distribution.

It is only in recent years that the importance of mixing considerations in polymerization reactors is being recognized. In sharp contrast to mixing studies in simulated fluids, there is an increasing trend towards examining the role of mixing in actual polymerization reactors. The work of Cole (1976) is particularly valuable in this regard. Cole studied the non-ideal mixing patterns in continuous stirred tank polymerization reactors and characterized these in terms of a mixing model. Anionic solution polymerization of butadiene was then undertaken to study the influence of mixing. Correlations were then developed between the operating parameters, mixing model parameters and molecular weight distribution parameters.

It is conceivable that similar efforts could be undertaken for the correlation of other polymer characteristics, such as copolymer sequence distribution, etc. It is clear that such studies would be of immense help to engineers due to the following reasons:

1. Changes in product characteristics due to scale-up effects as new products move from laboratory scale to production scale could be anticipated and corrected for. This speeds up the scale-up sequence by eliminating trial and error experimentation in large equipment. This will become particularly important as the need for products with more detailed specifications for more demanding applications will increase.
2. Operating conditions in laboratory and pilot plant equipment could be selected judiciously so that the plant scale mixing conditions could be duplicated.
3. The need for design changes in production equipment may be shown early so that the nature of the changes needed could be inferred.
4. More intelligent design of future equipment at any scale could be made, provided test results from the existing equipment are considered relative to the product properties desired.

4.2 Micromixing

As remarked earlier, for non-linear reactions the residence time distribution by itself does not define the state of mixing since it merely defines what is termed as macromixing and not micromixing. A completely segregated system represents one limit of micromixing, that is, where there is no mixing at all. There is, of course, an upper limit on micromixing, which corresponds to the maximum amount of molecular level mixing possible and Zwietering (1959) has termed this as the state of maximum mixedness. In the completely segregated reactor the mixing between fluid elements which have spent different times in the reactor occurs in the exit stream, whereas in the maximum mixedness case mixing occurs immediately, viz. at the entrance.

If considerations are restricted only to the conversion of the reactants (and not to the details of the product yield) then the maximum mixedness gives the lowest possible conversion of reactants for reaction orders greater than one and highest conversion for reaction orders less than one. Complete segregation gives the highest possible conversion for orders greater than one and the lowest conversion for orders less than one. The conversion for a first-order reaction is entirely determined by RTD and it is independent of the level of micromixing. Novad and Thyn (1966) have given useful charts to depict these effects.

It is clear that we have to be able to describe the intermediate state of segregation (or micromixing) by the use of certain models. Some efforts have been made in this direction. Curl (1963), for instance, has proposed a coalescence model wherein he considers a model of dispersed phase droplets flowing through an ideal stirred tank. If the reaction occurs in the droplets and they do not coalesce, then this phase will act as a macrofield. On the other hand, if they do coalesce and disperse then they approach the microfluid behaviour. Spielman and Levenspiel (1965) have shown how the conversion can be obtained from such a model by using a Monte-Carlo procedure.

Ng and Rippin (1965) have proposed the idea of a two environment model, wherein a reactor with arbitrary RTD is viewed as consisting of clumps of unmixed fluid (entering environment) and already mixed fluid (leaving environment). In the usual formulation of the two environment model, the division between the segregated and maximum mixedness is based on the age of the fluid element. Typically, a fluid enters the reactor in the segregated environment and leaves in the maximum mixedness environment. Chen and Fan (1971) have, however, proposed a reversed two environment model as being more representative of the polymer reactors. It is assumed that the reactants are initially well mixed, but become segregated as the viscosities increase during polymerization.

5. Concluding Remarks

The present review has been confined to the mixing of viscous fluids. A considerable research effort is currently under way all over the world and new avenues for research are certainly emerging. Although the present review encompasses most of the important areas, certain fields have not been adequately converted. Some of the important areas, for example, are as follows:

1. Demand of uniform polymer melt quality in terms of both composition and temperature has given rise to the application of motionless mixers. Information on these mixers is growing (see, e.g., Schott et al., 1975, Chen and MacDonald, 1973). Applications of these mixers in other areas, e.g., gas dispersion in viscous liquids (see, e.g., Smith, 1978) is also being considered. This is an evolving area of research and considerable basic and applied research inputs will be necessary to take these mixers to a commercially viable stage.
2. Curious anomalies result in polymer-additive systems. It has been shown (White and Lee, 1974) that during Poiseuille flow the lower viscosity fluid of the two fluids will migrate to the region of highest shear (e.g. mould release agents). Conversely, solid particles in a

polymer-particle system will migrate to the region of lowest shear during Poiseuille flow accounting for resin rich surfaces in filled systems (Kubat and Szalanczi, 1974). These problems of 'demixing' are quite important and are receiving wide attention of the researchers.

3. Peculiar mixing problems arise during the two phase contact of a gas and a non-Newtonian liquid and the subsequent heat and mass transport processes (see, e.g., Mashelkar, 1976, Astarita and Mashelkar, 1977). This area is also in a stage of infancy.

In the present review we have attempted to analyse some aspects of a topic which not too long ago was being treated entirely as an art and is now rapidly achieving a sound scientific basis. The introduction of well-defined statistical means for estimating the goodness of mixing, the linking with the laminar and distributive mixing, increased emphasis on attempts to analyse a substructure rather than observation of a gross phenomenon and furthermore the linkup of such substructure to the hydrodynamics have aided considerably in evolving such a scientific basis. The black box viewpoint is vanishing and this is a welcome sign.

In the areas just covered we have provided analysis as well as constructive suggestions for future research in each individual case. It should be emphasized that our attempt has been to be representative rather than encyclopaedic so that a rational analysis of the present day knowledge of the subject could be made. It is hoped that the review will be useful for researchers and designers alike.

LIST OF SYMBOLS

a_1, a_2	Exponents in equation 3.6
A_i	Interfacial area
A_{i0}	Initial interfacial area
C_i	Concentration at any point
C_m	Mean concentration
C_v	Expected coefficient of variance
C_0, C_r	Concentrations at two points distance r apart
$\bar{C}_i$	Circulation number
d	Impeller diameter
D	Tank diameter
$\mathcal{D}$	Diffusivity
E	Exit-age distribution function
e_1, e_2	Exponents in equation 3.5
Fr	Froude number
g	Gravitational acceleration
h	Height of the liquid
i	Number
I	Intensity of segregation
K	Consistency index
$\bar{K}$, $\bar{K}_1$	Constants in equations 3.5 and 3.6
k_s	Constant in equation 3.9
M_1	Net amount of shearing strain received
M'	Lacey's index
n	Pseudoplasticity index
N	Revolutions of the stirrer per second
N_1	No. of revolutions (see equation 1.17)
N_s	Number ~~in~~ of a sample size
P	Power consumed
P_0	Power number $\left(\frac{P}{d^5 N^3 \rho}\right)$
P_b	Probability distribution function
q	Impeller discharge rate
R	Radius of the sphere
$R(r)$	Coefficient of correlation
R_1, R_2	Radii of the inner and outer cylinder
Re	Reynolds number
r	Radial distance
r_s	Striation thickness
r_{s_0}	Initial striation thickness
$r_{s\,avg}$	Average striation thickness
S	Estimated standard deviation
S^2	Estimated variance
S'	Linear scale of segregation
t	Time
u_1	Velocity in x_1 direction
v	Velocity in θ direction
V'	Volume scale of segregation
V	Bulk volume
x_1, x_2, x_3	Co-ordinates
X_1, X_2, X_3	Relative changes in distance in x_1, x_2, x_3 direction
x	Number of particles in a sample
x_c	Number of particles of component under consideration

GREEK LETTERS

α	Parameter in the Ellis fluid model
$\cos\alpha_1$, $\cos\alpha_2$, $\cos\alpha_3$	Direction cosines
$\bar{\alpha}_1$, $\bar{\alpha}_2$	Material parameters for a third order fluid
β	Angle defined in equation 1.16
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_{av}$	Average shear rate
θ	Residence time (dimensionless)
θ'	Angular coordinate
θ_m	Mixing time
θ_c	Circulation time
μ	Viscosity
μ_a	Apparent viscosity
μ_0	Parameter in the Ellis fluid model
μ_1, μ_2	Viscosities of components (1) and (2)
ρ	Density
σ^2	Expected population variance
σ_0^2	Expected variance between two completely segregated components
σ_r^2	Expected variance of a binomial distribution
τ_0	Parameter in the Ellis fluid model
ψ	Stream function
Ω	Angular velocity

REFERENCES

Angus, R. M. and L. Lapidus, *AIChE J.*, **9**, (1963), 810.

Astarita, G. and G. Marrucci, Principles of Non-Newtonian Fluid Mechanics, McGraw Hill, Berkshire (1974).

Astarita, G. and R. A. Mashelkar, *Chem. Eng.* (Lond.), (1977), 100.

Beckner, J. L. and J. M. Smith, *Trans. Inst. Chem. Engrs.*, **44**, (1966), 224.

Bergen, J. T., in *Processing of Thermoplastics*, Bernhardt, E. C. (Ed.), Reinhold, N.Y. (1959).

Bigg, D., *Polym. Eng. Sci.*, **15**, (1975), 684.

Bigg, D. and S. Middleman, *Ind. Eng. Chem. Fundls.*, **13**, (1974), 66.

Bischoff, K. B. *Can. J. Chem. Eng.*, **41**, (1963), 129.

Bischoff, K. B., *Ind. Eng. Chem.*, **58**, (1966), 18.

Bischoff, K. B. and E. A. McCracken, *Ind. Eng. Chem.*, **58**, (1966), 18.

Blanks, R. F. and R. L. Stokes, paper presented at the 67th National AIChE Meeting, Atlanta, (1970).

Blaskinski, H., B. Kochanski, and E. Rzyski, *Int. Chem. Eng. Process Ind.*, **10**, (1970), 176.

Bourne, J. R., *Chem. Eng.*, **180**, (1966), 202.

Bourne, J. R. and H. Butler, *Trans. Inst. Chem. Engrs.*, **47**, (1969), 111.

Brasie, W. C., paper presented at the 63rd National AIChE Meeting, St. Louis, (1968).

Buslik, D., Powder Technology, 7, (1973), 111.

Calderbank, P. H. and M. B. Moo-Young, *Trans. Inst. Chem. Engrs.*, **37**, (1959), 26.

Carreau, P. J., I. Patterson and C. Y. Yap, *Can. J. Chem. Eng.*, **54**, (1976), 135.

Charm, S., *Fundamentals of Food Engineering*, The Avi Publishing, Connecticut (1971).

Chavan, V. V., Ph.D. Thesis, University of Salford (1972).

Chavan, V. V. and J. Ulbrecht, *Ind. Eng. Chem.* (Proc. Des. Develop.), **12**, (1973), 472.

Chavan, V. V., M. Arumugam and J. Ulbrecht, *AIChE J.*, **21**, (1975a), 613.

Chavan, V. V., D. E. Ford and M. Arumugam, *Can., J. Chem. Eng.*, **53**, (1975b), 628.

Chen, S. J., *J. Soc. Cosmet. Chem.*, **24**, (1973), 639.

Chen, S. J. and A. R. MacDonald, *Chem. Eng.*, **85**, (1973), 105.

Chen, M. S. K. and L. T. Fan, *Can. J. Chem. Eng.*, **49**, (1971), 704.

Cintron-Cordero, R., R. A. Mostello, and J. A. Biesenberger, *Can. J. Chem. Eng.*, **46**, (1968), 434.

Cole, W. M., *AIChE Symp. Ser.*, **72** (160), (1976), 51.

Coyle, C. K., H. E. Hischland, B. J. Michel and J. Y. Oldshue, *AIChE J.*, **16**, (1970), 903.

Curl, R. L., *AIChE J.*, 9, (1963), 175.

Danckwerts, P. V., *Research* (London), 6, (1953), 355.

Danckwerts, P. V., *Chem. Eng. Sci.*, **2**, (1953), 1.

Danckwerts, P. V., *Appl. Sci. Res.* 3 (A), (1952), 279.

Earle, R. L., *Trans. Inst. Chem. Engrs.*, **37**, (1959), 297.

Edwards, W. M. and D. J. Saletan, *Ind. Eng. Chem.*, **59**, (1967), 37.

Feldkamp, K., Thesis, Technische Hochschule Braunschweig, (1962).

Ford, D. E., R. A. Mashelkar and J. Ulbrecht, *Proc. Tech. Int.*, **17**, (1972), 803.

Ford, D. E. and J. Ulbrecht, *AIChE J.*, **21**, (1975), 1230.

Giesekus, H., *Rheol. Acta*, **3**, (1963), 59.

Goldish, L. H., J. A. Koutsky and R. J. Adler, *Chem. Eng. Sci.*, **20**, (1965), 1011.

Gray, J. B., in *Mixing: Theory and Practice*, Vol. 1, Acad., N.Y. (1966).

Green, A. E. and R. S. Rivlin, *Quart. Appl. Math.*, **14**, (1956), 299.

Hald, A., *Statistical Theory for Engineering Applications*, Wiley, N.Y. (1952).

Hall, K. R. and J. C. Godfrey, AIChE-IChE Symp. Ser. No. 10, (London: Instn. Chem. Engrs.) (1965).

Himmelblau, D. M. and K. B. Bischoff, *Process Analysis and Simulation: Deterministic Systems*, Wiley, N.Y. (1968).

Ho, F. C. and A. Kwong, *Chem. Eng.*, **80**, (1973), 95.

Hoare, M. R., *Ind. Eng. Chem.*, **53**, (1961), 197.

Holland, F. A. and F. S. Chapman, *Liquid Mixing and Processing in Stirred Tanks*, Reinhold, N.Y. (1966).

Hoogendoorn, C. J. and A. P. Den Hartog, *Chem. Eng. Sci.*, **22**, (1967), 1689.

Ide, Y. and J. L. White, *J. Appl. Polym. Sci.*, **18**, (1974), 2997.

Ivonue, I. and K. Sato, *Kogaku Kogaku*, **5**, (1967), 121.

James, D. F. and J. Acosta, *J. Fluid Mech.*, **42**, (1970), 269.

Kale, D. D., R. A. Mashelkar, and J. Ulbrecht, *Chem. Eng. Tech.*, **46**, (1974), 69.

Kelkar, J. V., Ph.D. Thesis, University of Salford, (1972).

Kelkar, J. V., R. A. Mashelkar and J. Ulbrecht, *Trans. Inst. Chem. Engrs.*, **50**, (1972), 343.

Kelkar, J. V., R. A. Mashelkar, and J. Ulbrecht, *J. Appl. Polym. Sci.*, **17**, (1973), 3069.

Kramers, H. and G. Alberda, *Chem. Eng. Sci.*, **2**, (1953), 173.

Kristensen, H. G., *Arch. Pharm. Chem. Sci.*, **1**, (1973), 102.

Kubat, J. and A. Szalanczi, *Polym. Eng. Sci.*, **14**, (1974), 873.

Lacey, P. M. C., *J. Appl. Chem.*, **7**, (1957), 257.

Lelli, U., *Ind. Eng. Chem. Fund.*, **4**, (1965), 360.

Levenspiel, O., *Chemical Reaction Engineering*, Wiley, N.Y. (1972).

Levenspiel, O. and K. B. Bischoff, *Adv. Chem. Eng.*, **4**, (1963), 95.

Levenspiel, O. and J. C. R. Turner, *Chem. Eng. Sci.*, **25**, (1970), 1605.

Magnusson, K., *Iva*, **23**, (1952), 86.

Mashelkar, R. A., *Chem. Ind. Develop.*, **10**, (1976), 17.

Mashelkar, R. A. and G. V. Devarajan, *Trans. Inst. Chem. Engrs.*, **54**, (1976), 100.

MaKelvey, J. M., *Polymer Processing*, Wiley, N.Y. (1962).

Metzner, A. B. and G. Astarita, *AIChE J.*, **13**, (1967), 550.

Metzner, A. B. and R. E. Otto, *AIChE J.*, **3**, (1957), 3.

Metzner, A. B. and J. S. Taylor, *AIChE J.*, **6**, (1960), 109.

Metzner, A. B., R. H. Feehs, H. L. Romos, R. E. Otto and J. P. Tuthill, *AIChE J.*, **7**, (1961), 3.

Michaels, A. S. and V. Puzinankas, *Chem. Eng. Prog.*, **50**, (1954), 604.

Middleman, S. *The Flow of High Polymers*, Wiley, N.Y. (1968).

Mitsuishi, N. and N. J. Hirai, *J. Chem. Engg. Jap.*, **2**, (1969), 117.

Mohr, W. D. in *Processing of Thermoplastics*, (Bernhardt, E. C., (Ed.), Reinhold, N.Y., (1959).

Mohr, W. D., R. L. Saxton and C. H. Jepson, *Ind. Eng. Chem.*, **49**, (1957), 1855.

Moo-Young, M. B. and K .W. Chan, *Can. J. Chem. Eng.*, **49**, (1971), 187.

Murakami, Y., K. Fujimoto and S. Votani, *J. Chem. Engg. Jap.*, **5**, (1972), 1.

Nagata, S., *Mixing: Principles and Applications*, Halsted Press, (1975).

Nagata, S., M. Nishikawa, H. Tada, H. Hirabayashi and Gotoh, *J. Chem. Eng. Jap.*, **3**, (1970), 237.

Nagata, S., T. Yanagimoto and T. Yokoyama, *Kagaku Kogaku*, **21**, (1957), 278.

Nagata, S. and T. Yokoyama, *Mem. Fac. Engg.*, Kyoto Univ., **14**, (1955), 253.

Naor, P. and R. Shinnar, *Ind. Eng. Chem. Fund.*, **2**, (1963), 278.

Newman, E. B., *J. Macromol. Sci.-Revs. Macromol. Chem.*, C **10**, (1974), 75.

Novad, Z. and J. Thyn, *Collect. Czech. Chem. Commun.*, **31**, (1966), 3710.

Novosad, Z. and J. Ulbrecht, *Chem. Eng. Sci.*, **21**, (1966), 405.

Ng, D. Y. C. and D. W. T. Rippin, Proc. 3rd European Symp. on Chem. Reaction Engg., Amsterdam (1964).

Olson, J. H. and L. E. Stout, in *Mixing: Theory and Practice*, Vol. 2, V. W. Uhl and J. B. Gray (Eds.), Academic Press, N.Y., (1967).

O'Shima, E. and K. Yuge, *Kagaku Kogaku*, **39**, (1970), 115.

Osborne, F. T., *Chem. Eng. Sci.*, **30**, (1975), 159.

Penney, W. R. and K. J. Bell, *Ind. Eng. Chem.*, **59**, (1967), 40.

Peters, D. C. and J. M. Smith, *Trans. Inst. Chem. Eng.*, **40**, (1967), T360.

Peters, D. C. and J. M. Smith, *Can. J. Chem. Eng.*, **47**, (1969), 268.

Rieger, F. and V. Novak, *Trans. Inst. Chem. Eng.*, **52**, (1974), 285.

Rudd, M. J., Chem. Eng. Progr. Symp. Ser. No. 111, **62**, (1971), 21.

Ruthven, D. M., *Chem. Eng. Sci.*, 26, (1971), 1113.

Schott, N. R., B. Weinstein, and D. La Bombard, *Chem. Eng. Prog.*, **71** (1), (1975), 54.

Seyer, F. A. and A. B. Metzner, *AIChE J.*, **15**, (1969), 426.

Shearer, C. J., *Chem. Eng. Sci*, 28, (1973), 1091.

Shrenk, W. J., K. J. Cleerman, and T. Alfrey, Jr., *SPE Trans.*, **3**, (1963), 192.

Shrenk, W. J., D. S. Chisholm, and T. Alfrey, *Modern Plastics*, **46**, (1969), 159.

Skelland, A. H. P., *Non-Newtonian Flow and Heat Transfer*, Wiley, N. Y. (1967).

Spencer, R. S. and R. M. Wiley, *J. Colloid Sci.*, **6**, (1951), 113.

Spielman, L. and O. Levenspiel, *Chem. Eng. Sci.*, **20**, (1965), 247.

Smith, J. M., *Chem. Eng.* (Lond.), (1970), 45.

Smith, J. M., *Chem. Eng.* (Lond.), (1978), 827.

Stokes, R. L. and E. B. Nauman, *Can. J. Chem. Engg.*, **49**, (1971), 187.

Szabo, T. T. and E. B. Nauman, *AIChE J.*, **15**, (1969), 575.

Trivedi, R. N. and K. Vasudeva, *Chem. Eng. Sci.*, **30**, (1975), 317.

Turner, J. C. R., *Chem. Eng. Sci.*, **26**, (1971), 549.

Uhl, V. W. and J. B. Gray (Eds.), *Mixing: Theory and Practice*, Academic Press, N.Y., (1966).

Ulbrecht, J., *Chem. Eng.*, **286**, (1974), 347.

Ultman, J. S. and M. M. Denn, *Trans. Soc. Rheol.*, **14**, (1970), 307.
Vallentin, F. H. H., *Chem. Eng.*, (1967), 99.
Walters, K. and J. G. Savins, *Trans. Soc. Rheol.*, **9**, (1965), 407.
Waters, N. D. and M. J. King, *Q. J. Mech. Appl. Maths.*, **24**, (1971), 331.
White, E. T., *Imp. Coll. Chem. Eng. Soc. J.*, **14**, (1962), 72.
White, J. L. and B. L. Lee, *Trans. Soc. Rheol.*, **18**, (1974), 467.
Wohl, M. H., *Chem. Eng.* **75**, (1968), 113.
Yap, C. Y., I. Patterson, and P. J. Carreau, unpublished work, (1978).
Zaloudik, P., *Br. Chem. Eng.*, **14**, (1969), 657.
Zwietering, T. N., *Chem. Eng. Sci.*, **11**, (1959), 1.