distributions of non-reactive, diffusive tracer were applied for comparison of mixing performance of investigated impellers.

A very complicated, transient and three-dimensional analysis of mixing with chemical reaction was recently presented by Kaminoyama and Kamiwano [38]. In this study, reaction and mixing process of highly viscous Newtonian and pseudoplastic liquid was considered in a vessel stirred with a double helical ribbon impeller. The authors correctly predicted dynamic changes of flow patterns and concentration distributions of diffusing and reacting solutes: iodine and either sodium thiosulfate or disodium phosphate. The influence of the impeller rotational speed on the decolouration time was also correctly predicted. The last example clearly shows the abilities of the modern computation technique in solving problems of laminar mixing.

2.4. Efficiency of Mixing.

Among criterions of mixer performance proposed in the literature, energetic cost of mixing is the ultimate one when a device for mixing of very viscous liquids is to be chosen. A development of a general procedure which allows evaluation and comparison of the energetic efficiency of mixing in various mixers types was always a challenging task for researchers.

Gray [39] compared efficiency of batch mixing in different mixers by comparing the mixing time values measured at the same power input and identical viscosity. The condition of identical power input into compared systems enables direct comparison of energy required for batch mixing: the energy ratio is simply equal to the mixing time ratio. The mixing time was defined as a time necessary for obtaining a visually uniform mixture throughout the mixer vessel after introduction of dyed solution into the clear content of the vessel. In practice the measurements of the mixing time in the systems to be compared are performed at different power input and different viscosity. In such a situation the mixing time should be recalculated. In the regime of laminar mixing a power input and mixing time can be expressed as follows:

$$Po = \frac{P}{\rho \cdot n^3 \cdot d^5} = \frac{const_1}{Re} = \frac{const_1 \cdot \mu}{\rho \cdot n \cdot d^2} \qquad (2.51)$$

$$n \cdot t_m = const_2 \ . \qquad (2.52)$$

Thus, comparison at the power level $\mathbf{P}_1$ and for the same liquid mixed (characterized by dynamic viscosity μ_1) requires the rotational stirrer speed:

$$n_1 = \sqrt{\frac{P_1}{const_1 \cdot \mu_1 \cdot d^3}}\ , \tag{2.53}$$

what results in the mixing time

$$t_{m1} = \frac{const_2}{n_1}\ . \tag{2.54}$$

The values of $\mathbf{t_{m1}}$ can be directly compared for different mixers.

Using this method Gray [39] found that helical ribbon and off-centered helical screw agitators are much more efficient than: curved rods and flat turbines, centered helical screws, and curved blade turbines in mixing of Newtonian liquids for viscosities greater than 20 Pa·s.

Gray's study was a starting point for a more general and reliable study of Hoogendoorn and Hartog [40]. These authors tested nine different types of agitators in batch wise mixing of very viscous, Newtonian liquids. Hoogendoorn and Hartog [40] determined the mixing time by applying two different techniques of measurements:

- injection of a small quantity of heated liquid and measuring dynamic changes of temperatures at several points in the vessels,
- decolouration of the mixer content as the effect of a single, instantaneous, homogeneous chemical reaction proceeding between initially unpremixed reactants.

Hoogendoorn and Hartog [40] used one general definition of the mixing time and checked experimentally that this mixing time can be evaluated using either the thermal or decolouration method.

For a number of impellers (three inclined paddles on one shaft, helical screw, helical-ribbon, marine-type propeller, anchor agitator) working in the laminar regime, the authors confirmed validity of equations (2.51) and (2.52). Eliminating revolution speed, **n**, from these equations, replacing formally the impeller diameter, **d**, with **D·(d/D)** and taking into account that for a given mixer type **d/D=const** Hoogendoorn and Hartog [40] obtained a dimensionless expression:

$$\frac{t_m^{\,2} \cdot P}{\mu \cdot D^3} = const\ , \tag{2.55}$$

where the value of constant in equation (2.55) is dependent on the type of the mixer and the vessel geometry. Thus, for a given mixer geometry the power per unit volume required to obtain a certain mixing time $\mathbf{t_m}$ is proportional to the viscosity and independent of the size of the vessel; the mixing time for a given viscosity is inversely proportional to the square root

of the power per unit volume. The value of the constant in equation (2.55) can be used to compare energetic costs of mixing required to obtain a certain level of homogeneity. However, when different types of mixers are to be compared, the values of the group $(t_m^2 \cdot P)/(\mu \cdot D^3)$ should be compared at the same values of the generalized Reynolds number:

$$Re_G = \frac{\rho \cdot (D/t_m) \cdot D}{\mu} \qquad (2.56)$$

defined by Hoogendoorn and Hartog [40]. An example of such comparison is presented in [40], indicating the superiority of mixers with an intensive axial flow through the entire vessel (three inclined blade paddles, screw or propeller agitators in a draught tube) over other type mixers (i.e. anchor agitator, Rushton turbine) in mixing of very viscous liquids. The helical ribbon agitator was found to be less efficient than the agitators with a draught tube but more efficient than the anchor and turbine agitators.

Novak and Rieger [41] applied a similar procedure to show that a helical screw impeller with a draught tube as well as multiple paddle and helical screw impellers mounted in an off-centered position are more efficient than anchor and turbine agitators.

A simpler method was presented by Zlokarnik [43] who proposed using the working sheet for determination of optimum working conditions on the homogenization. The working sheet is constructed by plotting the modified power number

$$\Pi_1 = Po \cdot Re^3 \cdot \frac{D}{d} = \frac{P \cdot D \cdot \rho^2}{\mu^3} \qquad (2.57)$$

versus modified mixing time number

$$\Pi_2 = \frac{n \cdot t_m}{Re} \cdot \left(\frac{d}{D}\right)^2 = \frac{t_m \cdot \mu}{D^2 \cdot \rho} \; . \qquad (2.58)$$

A mixer with smaller Π_1 for a given Π_2 is superior from the point of view of energetic costs. In conclusion it should be pointed out that the methods proposed by Gray [39], Hoogendoorn and Hartog [40] and Zlokarnik [43] enable a precise comparison of performance of different mixers and determination of optimum working conditions. A disadvantage of these methods is related to the fact that there is not commonly accepted definition of the mixing time. Thus the mixing times, measured by various researchers may differ considerably - some examples are shown in table 2.I. This problem creates difficulties when one wants to use the literature correlations for t_m to characterize performance of various mixers; often the comparison is impossible without additional measurements.

Table 2.I. Comparison of $n \cdot t_m$ as reported by the literature for the helical ribbon agitator; $d/D \approx 0.95$.

literature source	$n \cdot t_m$	measurement method	the mixing time defined as the time at which
Gray [39]	25.3	colour addition and visual observation	visually homogeneous mixture is obtained
Hoogendoorn and Hartog [40]	65.0	decolouration reaction and visual observation	differences between the local concentrations and the final concentration step are less than 25%
Novak and Rieger [41]	62.1	addition of salt solution and conductivity measurement	fluctuations of electrical conductivity are less than ±2% of the total conductivity change
Takahashi et al. [42]	239	addition of tracer liquid containing small capsules of liquid crystal and visual observation	flow lines of tracer liquid can not be recognized by naked eye.

Another concept of evaluating efficiency was proposed by Le Goff [44]. This author postulated to compare energy consumption in the real process of mixing including convection and diffusion with the energy required by a "Maxwell demon" to homogenize the mixture on the molecular scale. Le Goff [44] assumed that each particle to be moved from point **i** to point **j** separated by distance l_{ij} in time t_m should receive kinetic energy:

$$E_{ij} = \frac{1}{2} \cdot m_p \cdot v_{ij}^2 = \frac{1}{2} \cdot m_p \cdot \left(\frac{l_{ij}}{t_m} \right)^2 , \qquad (2.59)$$

where m_p is a particle mass. The particles positions are rearranged in a way minimizing the overall distance travelled by the "Maxwell demon". The total energy per unit volume required to mix two completely segregated fluids **A** and **B** of equal densities was found to be:

$$e_m = 2 \cdot \rho \frac{V_A \cdot V_B}{V^2} \cdot \left(\frac{l_m}{t_m} \right)^2 , \qquad (2.60)$$

where l_m denotes the mean distance between particles **A** and **B**. Then efficiency of mixing can be defined as the ratio of the minimum energy input and the real energy input:

$$\text{efficiency} = \frac{e_m}{e} . \qquad (2.61)$$

Efficiencies computed from this expression are extremely small because e_m does not account

for viscous friction. The idea has now only a historical significance.

A more consistent way of quantifying mixer performance is based on interpreting mixing as generation of intermaterial area per unit volume.

Spencer and Wiley [15] defined mixing efficiency as the ratio of the minimum power input required to achieve a certain degree of mixing (defined as the increase of the intermaterial surface area ratio) to the overall power input necessary for both: liquid mixing and transport

$$\text{efficiency} = \frac{P_M}{P_M + P_T} . \tag{2.62}$$

In the case of the continuous flow coaxial cylinder mixer the $\mathbf{A/A_0}$ ratio (the increase of surface ratio) was specified for material leaving the cross-section annulus midway between the cylinders where the $\mathbf{A/A_0}$ is smallest. The power required for mixing was

$$P_M = \frac{9 \cdot \mu \cdot Q^2}{4 \cdot V} \cdot \left[\left(\frac{A}{A_0} \right)^2 - 1 \right] \tag{2.63}$$

and the power required for transport

$$P_T = \frac{12 \cdot \mu \cdot Q^2}{V} \cdot \left(\frac{L}{d} \right)^2 , \tag{2.64}$$

where **L** is the length of the cylinders and **d** is separation between the cylinders. The efficiency for this specific mixer is thus equal to:

$$\text{efficiency} = \left\{ 1 + \frac{16}{3} \cdot \left(\frac{L}{d} \right) \Big/ \left[\left(\frac{A}{A_0} \right)^2 - 1 \right] \right\}^{-1} . \tag{2.65}$$

Equation (2.65) shows that the ratio **L/d** should be kept as small as possible to keep high efficiency in this specific mixer. The method based on equation (2.62) can, however, give completely wrong results when different mixers are to be compared; notice also that decreasing the power required to achieve certain level of homogenization - $\mathbf{A/A_0}$ (for instance better orientation of slabs) results in decreasing the efficiency when the power required for transport is kept constant. Thus, the first attempt to define the energetic efficiency seems to be unsuccessful.

A more reliable definition was proposed by Mohr [16]:

$$\text{efficiency} = \frac{\text{theoretical power to attain the desired result}}{\text{actual power to attain the desired result}} , \tag{2.66}$$

where the theoretical power requirement can be calculated under the following assumptions:

1. the shear is constant in the system,

2. the shear acts in one direction,

3. there is a plug flow in a continuous mixer.

As pointed out by Mohr [16] the actual power requirement is greater than the theoretical one due to deviation from the above assumptions. Clearly, this definition is more reliable than the previously discussed one, however satisfying of the assumption of a homogeneous shear (points 1 and 2) is not equivalent to the achievement of the most efficient mixing as it will be discussed below.

The general approach to the problem of mixing efficiency was formulated by Ottino and Macosko [45] and further developed by Ottino and co-workers [46, 47]. The idea of Ottino is based on the expressions from (2.22) to (2.26). The rate of area stretch $\overline{\overline{\mathbf{D}}}:\hat{\mathbf{n}}\hat{\mathbf{n}}$ formally has a maximum value $\left(\overline{\overline{\mathbf{D}}}:\overline{\overline{\mathbf{D}}}\right)^{1/2}$ for only one orientation of the intermaterial area with respect to the principal axes of deformation; this allowed Ottino et al. [47] to define the local efficiency of mixing:

$$eff(\vec{X},t) = -\frac{\overline{\overline{D}}:\hat{n}\hat{n}}{\sqrt{\overline{\overline{D}}:\overline{\overline{D}}}} = \frac{1}{\eta}\cdot\frac{d\eta}{dt}\Big/\sqrt{\frac{\epsilon}{2\cdot\mu}} \,. \tag{2.67}$$

Efficiency defined by equation (2.67) is equal to zero when no mixing occurs despite providing energy into the system and tends to the upper bound for a perfect orientation of the intermaterial area. In fact the efficiency equal to one seems to be impossible; in practice the highest value of the local rate of area stretch characterizing, for example, a two-dimensional stagnation flow is equal to $\sqrt{\epsilon/\mu}/2$, so the highest value of the local efficiency is equal to $\sqrt{2}/2$. A direct application of equation (2.67) is possible only in very simple flows (simple shear, elongation [47]). It is more practical to relate efficiency of mixing to the model of lamellar structure using relations (2.33)÷(2.35) and to apply the concepts of striation thickness, a local value of the intermaterial surface area and the characteristic stretching function $\alpha(\vec{\mathbf{X}},\mathbf{t})$. Thus, in the microflow element ζ_x

$$\alpha(\vec{X},t) = -\frac{d\ln s}{dt} = \frac{d\ln a_V}{dt} = -\overline{\overline{D}}:\hat{n}\hat{n} = eff(\vec{X},t)\cdot\sqrt{\overline{\overline{D}}:\overline{\overline{D}}} = eff(\vec{X},t)\cdot\alpha_{max} \tag{2.68}$$

which can be rewritten as:

$$\frac{\partial \ln a_V(\vec{X},t)}{\partial t} + \vec{v}\cdot\nabla \ln a_V(\vec{X},t) = eff(\vec{X},t)\cdot\alpha_{max} \,. \tag{2.69}$$

The last relationship is a base of any calculations of the average value of mixing efficiency in relation to intermaterial area per unit volume. As shown by Ottino et al. [47] for systems

of constant volume (see figure 2.12) integration of equation (2.69) over the entire volume yields:

$$\frac{d}{dt}\left\langle \ln a_V \right\rangle_V = \left\langle eff(\vec{X},t)\cdot\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_V . \quad \textbf{(2.70)}$$

In this case the average value of mixing efficiency can be defined as - see [47]:

$$\langle eff(t)\rangle_V = \frac{\left\langle eff(\vec{X},t)\cdot\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_V}{\left\langle\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_V} . \quad \textbf{(2.71)}$$

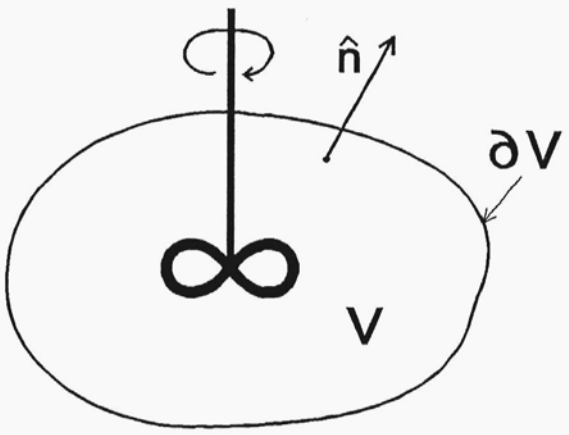

Figure 2.12. A closed volume mixer.

Basing on the results of Hoogendoorn and Hartog [40], Ottino and Macosko [45] recalculated the mean efficiency using an arbitrary chosen final value of an intermaterial surface area ratio

$$\left\langle a_V(t_m)\right\rangle_V / \left\langle a_V(0)\right\rangle_V = 10^5 . \quad \textbf{(2.72)}$$

Eventually, they obtained:

$$\left\langle eff(t_m)\right\rangle_V \cong \ln 10^5 \cdot t_m \Big/ \sqrt{\frac{P}{2\cdot\mu V}} , \quad \textbf{(2.73)}$$

where the power consumption and mixing time are given respectively by equations (2.51) and (2.52). The calculated efficiencies were ranging from 0.17% to 2.7% and the resulting hierarchy of mixers was identical with that proposed by Hoogendoorn and Hartog [40].

For continuous flow systems (see figure 2.13) the average value of mixing efficiency defined as an average value over a cross-sectional area at surface **A** [47] is given by:

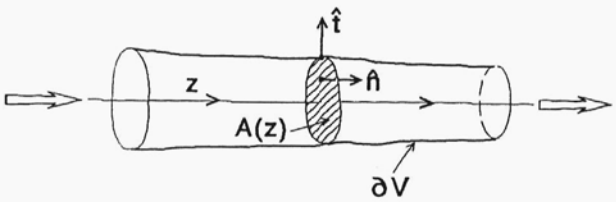

Figure 2.13. A continuous flow mixer.

$$\langle eff(z)\rangle_A = \frac{\left\langle eff(\vec{X},t)\cdot\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_A}{\left\langle\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_A} . \quad \textbf{(2.74)}$$

Assuming no slip condition and steady flow, integration of equation (2.69) over cross-sectional area yields:

$$\frac{d\left\langle\left\langle \ln a_V\right\rangle\right\rangle_A}{dz} = \frac{d}{dz}\left(\frac{\left\langle v_n\cdot\ln a_V\right\rangle_A}{\left\langle v_n\right\rangle_A}\right) = \frac{\left\langle eff(\vec{X},t)\cdot\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_A}{\left\langle v_n\right\rangle_A} = \frac{\langle eff(z)\rangle_A\cdot\left\langle\left(\overline{\overline{D}}:\overline{\overline{D}}\right)^{1/2}\right\rangle_A}{\left\langle v_n\right\rangle_A} , \quad \textbf{(2.75)}$$

where $\mathbf{v_n}$ is the normal velocity component. Ottino [48] applied this theory to evaluate

efficiency of a Kenics Static Mixer and an ISG Mixer. Following Tadmor and Gogos [3], Ottino [48] used the approximate relations for mixing in static mixers:

$$\frac{\langle\langle a_V \rangle\rangle_A}{\langle\langle a_{V0} \rangle\rangle_A} = 2^N \quad \text{- Kenics Mixer ,} \tag{2.76a}$$

$$\frac{\langle\langle a_V \rangle\rangle_A}{\langle\langle a_{V0} \rangle\rangle_A} = 4^N \quad \text{- ISG Mixer ,} \tag{2.76b}$$

where **N** is a number of mixing units. Pressure drop in a static mixer can be expressed with reference to the pressure drop in a tube of the same diameter and for the same flow rate:

$$\frac{\Delta p_{mixer}}{\Delta p_{tube}} = K_n(Re) \ , \tag{2.77}$$

where the value of $\mathbf{K_n}$ depends on the mixer type and Reynolds number. Expression (2.77) enables calculation of power input for Newtonian liquids from:

$$P = 8 \cdot \pi \cdot \mu \cdot z \cdot \langle v_z \rangle_A^{\,2} \cdot K_n(Re) \ . \tag{2.78}$$

Finally, taking into account that the distance, **z**, can be expressed as a product of **N** and the length of a single flow unit, **L**, Ottino [48] obtained from expressions (2.75), (2.76) and (2.78) an equation for efficiency, which for Newtonian liquids reads:

$$\langle eff(z) \rangle_A = \langle v_z \rangle_A \cdot \frac{d}{dz} \ln \langle\langle a_V \rangle\rangle_A \cdot \left(\frac{2 \cdot \mu \cdot A \cdot z}{P} \right)^{1/2} = \frac{\ln j}{2} \cdot \frac{R}{L} \cdot \frac{1}{\sqrt{K_n(Re)}} \ . \tag{2.79}$$

The resulting efficiency for the Kenics Mixer (**j=2, $\mathbf{K_n}$=5, R/L=0.31**) was equal to 4.8%, whereas for the ISG Mixer (**j=4, $\mathbf{K_n}$=156, R/L=0.46**) was equal to 2.5%.

Ottino's theory of energetic efficiency provides a very consistent background for estimation of energetic performance of mixing devices. Unfortunately, the procedure proposed to calculate mixing efficiency directly from knowledge of the intermaterial area distribution in the system has serious limitations. Firstly, in most cases it is extremely difficult to calculate the intermaterial area; in fact exact mapping of all interfaces in space and time has to be performed. This, in the case of complex flows creates numerical problems. Secondly, it is also difficult to measure $\mathbf{a_V}$ directly. Some knowledge on $\mathbf{a_V}$ can be obtained from calculated or measured distributions of the striation thickness using expression (2.29).

Bertrand et al. [49] managed to compute distributions of **s** and the rate of deformation in a cross-section of the ISG Static Mixer but did not calculate the efficiency. Saito and Kamiwano

[30] measured the striation thickness in the batch mixer agitated by either screw or helical ribbon impeller. These measurements were performed at relatively small area when compared to the whole system and at one direction of the cutting plane. This is a very common situation when optical measurements are interpreted.

The only reliable estimations of mixing efficiency as defined by equations (2.67), (2.71) or (2.74) can be made by means of a proper mathematical description of micromixing allowing to relate conversion or selectivity of homogeneous chemical reactions to the history of stretch parameter. Such investigation was undertaken by Ottino [46] who used the lamellar model to recalculate mixing efficiencies from the conversion of a single instantaneous reaction. However, the computations were conducted for mixing in the turbulent regime, where the lamellar structure mixing model is completely inadequate (the laminar structures are not persistent) - see Bałdyga and Bourne [33].

2.5. Stability of Laminar Flows.

The rheological properties and the compatibility of mixed liquids can affect the mixing process and the structure of resulting mixture. The problem was investigated mainly in the context of droplet dispersion in the two-phase systems. Only a few papers discussed mixing of completely miscible liquids of widely different dynamical properties. An interesting paper addressing this problem was published by Ranz [28], who anticipated the possibility of formation of periodic, segregated structures during mixing of liquids widely differing in viscosity and density. These structures are formed from striations of the "minor" component undergoing tensile deformation superimposed by the "major" component.

Looking more generally, the first publications on the hydrodynamic instability were presented in the Fluid Mechanics literature by Taylor [50] and Tomotika [51].

Taylor [50] showed experimentally that a drop of lubricating oil immersed in syrup subjected to the hyperbolic shear field was deformed into a cylindrical thread while the apparatus was running. When the apparatus which was used to produce flow was suddenly stopped, the final thread gradually broke up into a number of small drops of equal size. Taylor [50] suggested that the observed dispersion was related to the equilibrium between the interfacial surface tension and the viscous forces acting in both liquids. Tomotika [51] inspired by Taylor analyzed theoretically stability of a filament of a viscous liquid surrounded by another viscous liquid. For this purpose he used a method of small perturbations and linear stability analysis. The method of small perturbations assumes that the velocity components and pressure can be