

## **2. Literature review.**

Mixing of very viscous liquids is an important engineering problem in industries which range from plastics production and processing through rubber, glass, ceramics, paint to food production and biotechnology.

In polymer processing [1,2,3] mixing appears in relation to such processes as: mixing a monomer and an initiator with a polymer in polymerization reactors, reaction injection molding, mixing of different grades of polymer in extruders, thermal homogenization of polymers preventing building up internal stresses.

Homogenization of very viscous glass melts [4] is a crucial stage in production of optical glasses and during melting of glasses with volatile components.

In fermentation processes [5,6,7] broths containing polysaccharides or filamentous microorganisms are very viscous, which makes them difficult to mix and aerate.

### **2.1. Mixing Indices.**

The composition uniformity of plastics or glasses and good homogenization of the reactor content in the case of reactors designed to handle viscous reagents are critical requirements in industrial applications. The ideal uniformity is of course impossible, what one, however, wants to know is how much the mixture differs from completely homogeneous one. To this end a quantitative measure of the state of unmixedness or mixing index should be first defined. The basic concepts in this subject were introduced by Danckwerts [8,9].

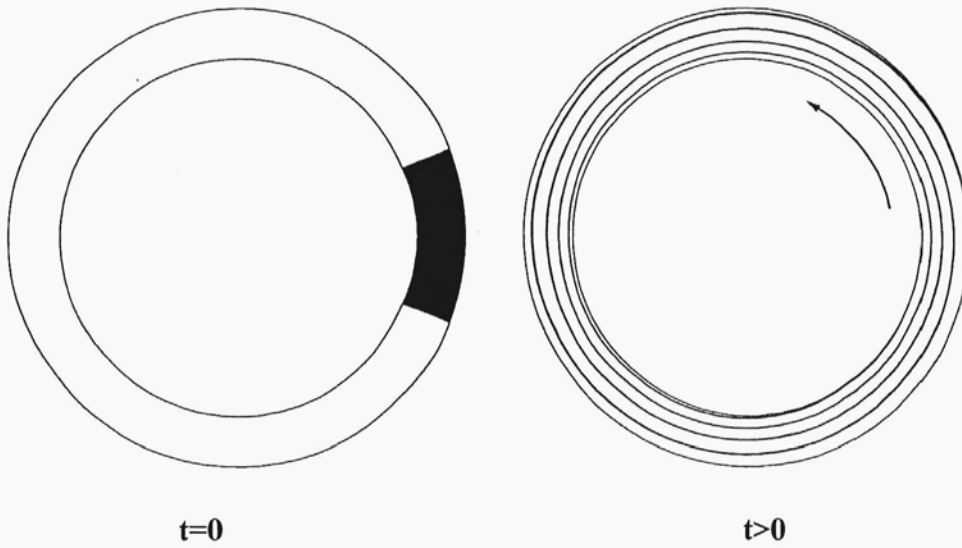
Following the review by Nauman and Buffham [10] let us assume that concentration of a mixture component  $c(\vec{x})$  can be somehow determined at every point  $\vec{x}=(x_1, x_2, x_3)$  in the system. Then one can characterize the spatial distribution of the component in the system by a "vector correlation coefficient":

$$g(\vec{r}) = \frac{\overline{[c(\vec{x}) - \bar{c}] \cdot [c(\vec{x} + \vec{r}) - \bar{c}]}}{\overline{[c(\vec{x}) - \bar{c}]^2}}, \quad (2.1)$$

where overbars represent averages over many "points". The concept of a "point", "concentration at a point" etc. were introduced by Danckwerts [9]. Accordingly, the concentration is averaged over a region small in comparison with the whole system, but large enough to be independent of statistical fluctuations related to the molecular structure of the fluid, and thus much larger than the molecular length scale. The definitions of a "point" and a "concentration

at a point" are in fact identical with the general concepts of phenomenological limit i.e. with treating a fluid as a continuum.

A function  $g(\vec{r})$  represents the statistical correlation in concentration between points separated by vector  $\vec{r}$  and its magnitude is related both to the absolute value and the direction of  $\vec{r}$ . It is obvious that if  $|\vec{r}| \rightarrow 0$  then  $g(\vec{r}) \rightarrow 1$ . For random mixtures created usually by turbulent flows, increasing the distance between points decreases the value of correlation coefficient; thus when  $|\vec{r}| \rightarrow \infty$  then  $g(\vec{r}) \rightarrow 0$ . This may not be true in the case of highly structured mixtures created by laminar flows, where  $g(\vec{r})$  appears to be a more or less periodic function of  $\vec{r}$  - see figure 2.1.



**Figure 2.1. Mixing in laminar rotational Couette flow.**

Equation (2.1) allows to define a "reactor integral scale of segregation" - see [10]:

$$L = \int_0^{x_{\max}} g(\vec{x}) d|\vec{x}|, \quad (2.2)$$

where the upper limit of the integral denotes the maximum absolute value of  $\vec{x}$  in the reactor. This parameter is highly dependent on the direction of  $\vec{x}$  and its value mainly depends on convective mixing. As it was shown by Nadav and Tadmor [11], in the case of structure consisting of two types of regions characterized by two characteristic length values  $\delta_1, \delta_2$  and two values of concentration  $c_1, c_2$  - figure 2.2, the characteristic scale of segregation measured along the abscissa equals:

$$L = \frac{1}{2} \cdot \frac{\delta_1 \cdot \delta_2}{\delta_1 + \delta_2}. \quad (2.3)$$

According to this equation if either  $\delta_1$  or  $\delta_2$  approaches zero what is equivalent to obtaining a uniform structure, then  $L$  will tend to zero. Inversely, if either  $\delta_1$  or  $\delta_2$  approaches infinity, then  $L$  will be twice smaller than the length of the finite segregated region.

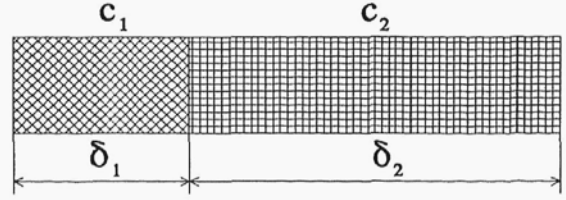


Figure 2.2. Two component structure.

Due to difficulties in estimation of  $g(\vec{r})$  in the case of complex mixtures the definition (2.2) does not have practical applications. Mohr et al. [12] introduced a simpler concept of a "striation thickness", particularly useful in characterizing mixtures possessing a layered structure. For a specified direction, the striation thickness can be defined as the distance separating a pair of like interfaces. For the simple mixing process shown in figure 2.1, the striation thickness measured in the radial direction as well as the radial segregation scale will decrease in time.

It is rare but not impossible that processes occurring on the molecular level such as diffusion and chemical reaction may increase the scale of segregation - [13].

To characterize the level of mixedness on the molecular scale Danckwerts [9] proposed the following definition of an "degree or intensity of segregation":

$$I_s = \frac{\overline{(f - \bar{f})^2}}{\bar{f} \cdot (1 - \bar{f})}, \quad (2.4)$$

where  $f$  denotes the concentration fraction  $c/c_0$ . In the case of complete segregation the dimensionless concentration  $f$  takes the values 0 or 1 at any point in the system and the intensity of segregation is equal to 1. When the process of molecular diffusion starts then the value of  $I_s$  decreases. As soon as the homogenization is complete on the molecular scale then  $f = \bar{f}$  at every point in the system and the intensity of segregation equals 0. Hydrodynamic mixing can indirectly affect the intensity of segregation due to decreasing the average path length for molecular diffusion and increasing the concentration gradients.

A complete knowledge of the spatial distribution of species in the system is not required when  $I_s$  is to be calculated. In reality the probability density function (PDF) of concentration  $f(c)$  is usually used to compute the concentration variance. Hiby [14] gives a review of several methods of measuring  $f(c)$  and estimating on this basis the deviation from homogeneity.