

- 3) Then rotation with a constant speed or oscillation with a constant frequency and amplitude was initiated. The movement of the inner cylinder was carried out at least half an hour longer after the moment when the complete decolouration of phenolphthalein was observed.
- 4) At the end, the resulting mixture was let off by the discharge pipe into a beaker and thoroughly mixed with a screw stirrer. Samples of this solution were analyzed by means of HPLC to determine the final ester concentration. The final selectivity was computed from equation (7.2).

8.2. Experimental results.

8.2.1. Effect of the Rotational Speed on the Product Distribution.

One directional rotation of the inner cylinder creates a shear flow in the annular gap between the cylinders. Neglecting the side effects, caused by the presence of reactor bottom and free surface, and assuming the fully laminar and stable flow, one can find the velocity profile from the system of Navier-Stokes equations with appropriate boundary conditions:

$$\frac{v_{\theta}^2}{r} = \frac{1}{\rho} \cdot \frac{\partial p}{\partial r}, \quad (8.1a)$$

$$0 = \frac{\partial}{\partial r} \left[\frac{1}{r} \cdot \frac{\partial}{\partial r} (r \cdot v_{\theta}) \right], \quad (8.1b)$$

$$0 = \frac{1}{\rho} \cdot \frac{\partial p}{\partial z}, \quad (8.1c)$$

$$\text{-- at } r=R_1 \quad v_{\theta} = 2 \cdot \pi \cdot R_1 \cdot n, \quad (8.2a)$$

$$\text{-- at } r=R_2 \quad v_{\theta} = 0, \quad (8.2b)$$

where n is the revolution speed of the inner cylinder, R_1 and R_2 are radii of the inner and outer cylinders, respectively. Solution of equations (8.1) and (8.2) reads:

$$v_{\theta} = 2 \cdot \pi \cdot R_2 \cdot n \cdot \left(\frac{R_2}{r} - \frac{r}{R_2} \right) / \left[\left(\frac{R_2}{R_1} \right)^2 - 1 \right]. \quad (8.3)$$

Thus, a local shear rate in the gap equals:

$$G = -r \cdot \frac{\partial}{\partial r} \left(\frac{v_{\theta}}{r} \right) = \frac{4 \cdot \pi \cdot n}{1/R_1^2 - 1/R_2^2} \cdot \frac{1}{r^2}. \quad (8.4)$$

As a result of the Couette flow, contact surfaces between mixed solutions, initially

perpendicular to the shear direction, become tangentially oriented and a lamellar structure is created in the gap - see figure 2.1. The rate at which the distance between the contact surfaces decreases depends on: radial position, revolution speed and time. Following Bergen [84], one can write the relation between a lamina thickness δ and a deflection angle β (see figure 8.4) in the following form:

$$\left(\frac{\delta_0}{\delta}\right)^2 = 1 + ctg^2\beta . \quad (8.5)$$

On the other hand, the deflection angle β can be found as:

$$ctg\beta = r \cdot \frac{d\theta}{dr} = r \cdot \frac{d}{dr} \left(\frac{v_\theta}{r} \right) \cdot t = G(r) \cdot t . \quad (8.6)$$

Elimination of β from equations (8.5) and (8.6) yields:

$$\frac{\delta}{\delta_0} = \frac{1}{\sqrt{1 + [G(r) \cdot t]^2}} . \quad (8.7)$$

Finally, differentiating expression (8.7) with respect to time results in:

$$\alpha = -\frac{1}{\delta} \cdot \frac{d\delta}{dt} = \frac{G(r)^2 \cdot t}{1 + [G(r) \cdot t]^2} . \quad (8.8)$$

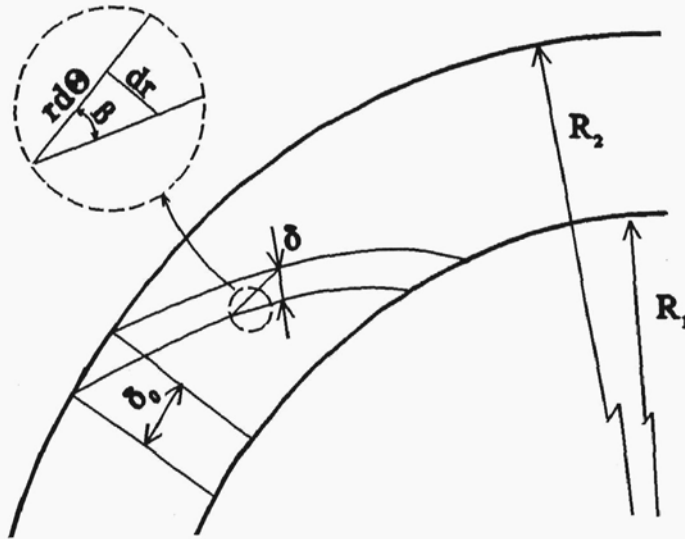


Figure 8.4. Laminar shear mixing in a concentric cylinder system.

It should be noticed, that the form of the expressions for both the lamina thickness (8.7) and the deformation rate (8.8) is identical to that obtained in the case when $G=\text{const}$; see figure 3.8 and equations (3.18)÷(3.19). In relations (8.7) and (8.8) the shear rate depends on radial position and revolution speed, according to equation (8.4).

The first series of experiments was carried out to determine the effect of the rotational speed on the selectivity of the test reactions (6.1). In all the experiments, the initial distribution of the substrates solutions was the same; the base solution occupied one eighth of the gap, the rest of the gap was filled with the acid and ester solution, as shown in figure 8.2. Tables 8.Iabc show compositions, volumes, viscosities and densities of solutions together with revolution speeds and final selectivities. Final selectivities measured in the experiments are also plotted in figure 8.5. The experiments were carried out at 18°C.

Table 8.Ia. First series of tests - the acid and ester solutions; $w_p=42\%$.

Exp.no.	HCl [mol/dm ³]	Ester [mol/dm ³]	V [dm ³]	ρ [g/cm ³]	μ [Pa·s]	KCl [g/kg]
1	0.01407	0.01416	1.743	1.0717	0.5075	5.539
2	0.01397	0.01355	1.739	1.0707	0.5124	5.515
3	0.01414	0.01386	1.741	1.0717	0.5073	5.523
4	0.01407	0.01416	1.756	1.0717	0.5075	5.539

Table 8.Ib. First series of tests - the base solutions; $w_p=42\%$.

Exp.no.	NaOH [mol/dm ³]	V [dm ³]	ρ [g/cm ³]	μ [Pa·s]
1	0.09865	0.2393	1.0717	0.5341
2	0.09887	0.2466	1.0719	0.5553
3	0.09862	0.2391	1.0717	0.5289
4	0.09865	0.2295	1.0717	0.5341

Table 8.Ic. First series of tests - final solutions after experiment.

Exp.no.	n [rev/min]	Ester [mol/dm ³]	X[%]	V [dm ³]	ρ [g/cm ³]	μ [Pa·s]
1	5	.008686	31.53	1.983	1.0709	0.5112
2	10	.008554	27.12	1.982	1.0728	0.5116
3	20	.009132	26.08	1.980	1.0719	0.4886
4	40	.009659	25.14	1.985	1.0720	0.5099

According to Kaye and Elgar [85] the flow in the annular gap is stable when:

$$Re_s = 2 \cdot \pi \cdot n \cdot R_1 \cdot (R_2 - R_1) \cdot \rho / \mu \leq \pi^2 \cdot \sqrt{R_1 + R_2} / \sqrt{2 \cdot v \cdot (R_2 - R_1)} , \quad (8.9)$$

where

$$v = 0.0571 \cdot \left(1 - 0.652 \cdot \frac{R_2 - R_1}{R_1} \right) + 0.00056 \cdot \left(1 - 0.652 \cdot \frac{R_2 - R_1}{R_1} \right)^{-1}. \quad (8.10)$$

In the case when $\mu=0.51$ Pa·s and $\rho=1072$ kg/m³, the critical value of the modified Reynolds number, Re_s , in the reactor equals 91.5, whereas in the experiments Re_s never exceeded 13.9. The visual observations of mixing during the experiments proved that the stratified structure created in the annular gap was not disturbed by Taylor vortices; the gradually thinning striations remained vertical.

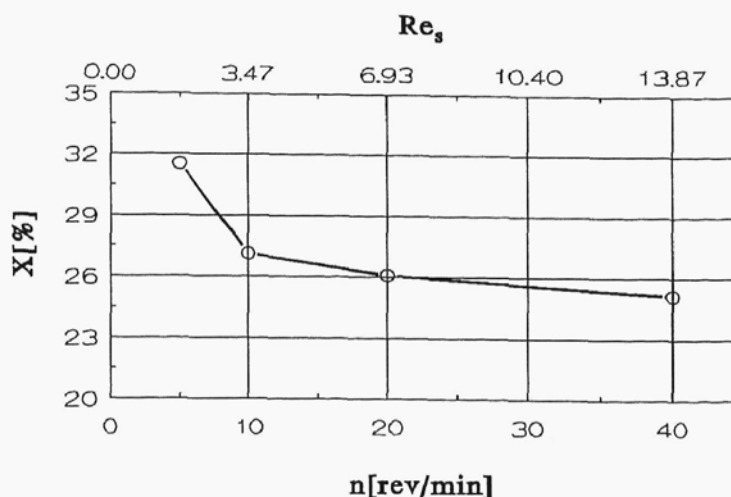


Figure 8.5. Effect of the rotational speed on the final selectivity in the batch reactor - experimental results.

It was also noticed that thinning of striations was accompanied with decolouration of phenolphthalein in the liquid initially containing sodium hydroxide. The process of decolouration was usually completed after 10 to 20 minutes from the beginning of the test; it was very difficult to determine precisely the moment of complete neutralization of NaOH.

Analysis of figure 8.5 indicates that increasing the rotational speed of the inner cylinder improves mixing in the reactor. It should be noted, however, that differences between selectivity values are very small for $n \geq 10$ rev/min, because in the Couette flow, the deformation rate for long times ($t \gg 1/G$) becomes inversely proportional to time and is not dependent on the shear rate G - equation (8.8). During the experiments G was ranging from 1.6 to 21.5 s⁻¹ so, after a few revolutions of the inner cylinder the rate of thinning was practically independent of the rotational frequency. This explains weak influence of n on the final selectivity.

8.2.2. Effect of the Initial Volume Ratio on the Product Distribution.

In the second series of tests the effect of initial volume ratio was studied for the revolution speed $n=10$ rev/min. The experiments were carried out at 18°C. Tables 8.IIabc report compositions, volumes, viscosities and densities of solutions and final selectivities