8. Investigation of Mixing with the Test Reactions in a Batch Reactor.

8.1. Experimental System and Experimental Procedure.

Experiments were conducted in a reactor consisting of two coaxial cylinders (figures 8.1 and 8.2). The outer cylinder was motionless. The inner cylinder, mounted to the top cover of the reactor by a system of two precise ball bearings, was able to rotate without radial run-out. Two different movements of the inner cylinder could be obtained in the experimental system. Firstly, rotation with a constant speed was achieved when a DC motor was placed above the reactor and fixed directly to a driving shaft. Secondly, oscillations with constant frequency and amplitude were obtained when driving force was transformed by means of a slider-crank mechanism, shown in figure 8.3. In both cases, the movement of the inner cylinder was producing a drag flow of the liquid contained in the annular gap between the cylinders. The variable speed DC motor was equipped with an optical revolution counter and an electronic controller keeping the revolution speed constant despite variations of a working load or a line voltage.

The top cover of the reactor was equipped with two stub pipes made of brass and placed on the opposite sides of the mixer axis. These pipes were used to fill the reactor with the substrates solutions. Five slots spaced 45 degrees one from another were cut in the top cover (figure 8.2). Two 1 mm thick plexiglass plates were inserted in these slots, dividing the gap between the cylinders into two separate parts and thus securing the initial separation of two different solutions poured into the reactor. In this way, seven different initial volume ratios **a** {1:7, 2:6, 3:5, 4:4, 5:3, 6:2, 7:1} could be achieved in the reactor. The plates were removed at the moment of initialization of mixing-reaction experiments.

The central part of the mixer bottom, equipped with a rubber seal, could be adjusted in the vertical direction in order to prevent mixing of the solutions underneath the inner cylinder when the reactor was being filled. The reactor bottom was also equipped with a discharge pipe located at the mixer axis and made of brass.

The inner and outer cylinders, the top cover and the bottom of the mixer were made from transparent plexiglass to allow visual inspection of mixing in the reactor.

The solutions mixed in the reactor were composed of water, polyethylenepolypropylene glycol, potassium chloride, phenolphthalein and contained substrates of competitive-parallel reactions (6.1); NaOH in the first solution and HCl plus $CH_2ClCOOC_2H_5$ in the second one.

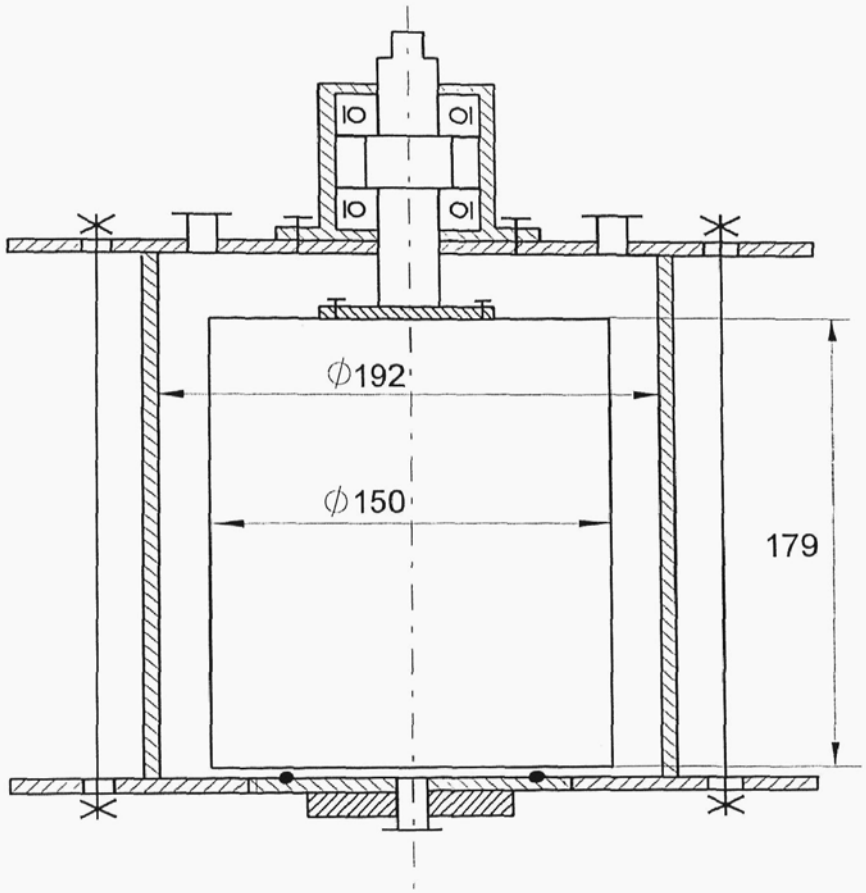

Figure 8.1. Scheme of a batch mixer.

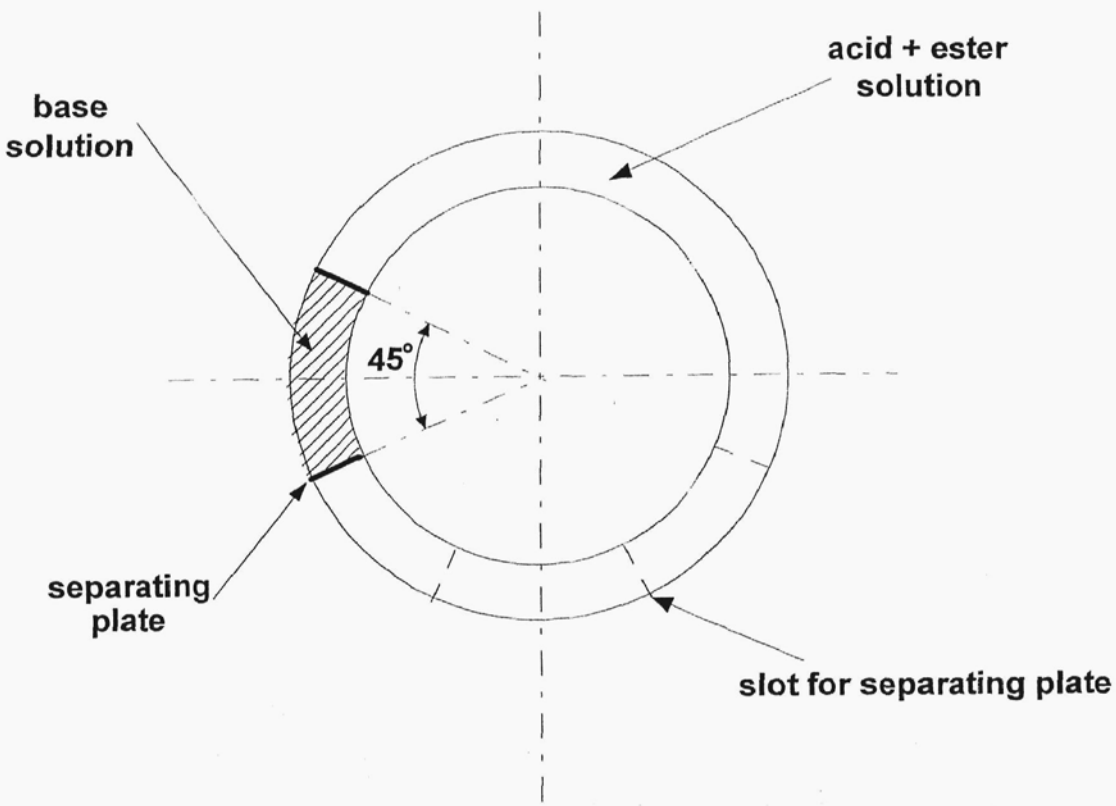

Figure 8.2. Initial distribution of solutions in a batch mixer; volume ratio 7:1.

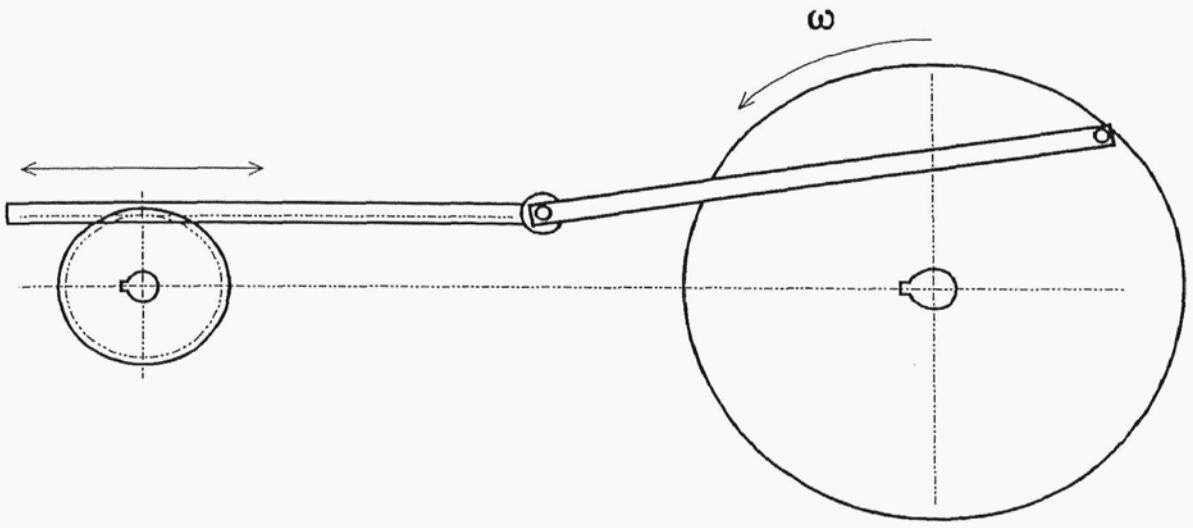

Figure 8.3. Scheme of a slider-crank mechanism.

Similarly as in the case of the semi-batch reactor the chemically equivalent amounts of base, acid and ester were used in the experiments; the initial average concentration of each substrate in the reactor was equal to 0.0125 mol/dm^3. Concentrations of the reactants were determined in the same way as described in chapter 7.1. Viscosities and densities of initial solutions and a resulting mixture were always measured at the same temperature at which tests were performed.

In order to avoid gravitational separation, while mixing in the annular gap, densities of the initial solutions were equalized by addition of potassium chloride to the less dense solution. Phenolphthalein was added to the substrates solutions in order to detect the moment of complete consumption of the limiting reactant.

The experiments were carried out in the following way:

1) After sealing the bottom of the inner cylinder (the central part of the reactor bottom was screwed up) and inserting the separating plates, the annular gap between the cylinders was simultaneously filled with the substrates solutions. The amounts of both solutions poured into the reactor were determined by weighing the beakers containing them before and after the filling operation. The level of the liquid in the gap was at least few millimeters below the upper edge of the inner cylinder in order to prevent escaping the mixed solutions from the gap during mixing.

2) After filling up the gap, the reactor bottom was slightly lowered to allow free rotation of the inner cylinder. The separating plates were carefully removed in order to minimize undesired mixing; due to high viscosity of mixed solutions the contact surfaces between liquids were practically not deviated from the initial position of the separating plates.

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:

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

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

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

- at $r = R_1$ $\qquad v_\theta = 2\cdot\pi\cdot R_1\cdot n\,,$ **(8.2a)**

- at $r = R_2$ $\qquad v_\theta = 0\,,$ **(8.2b)**

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

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

Thus, a local shear rate in the gap equals:

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

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