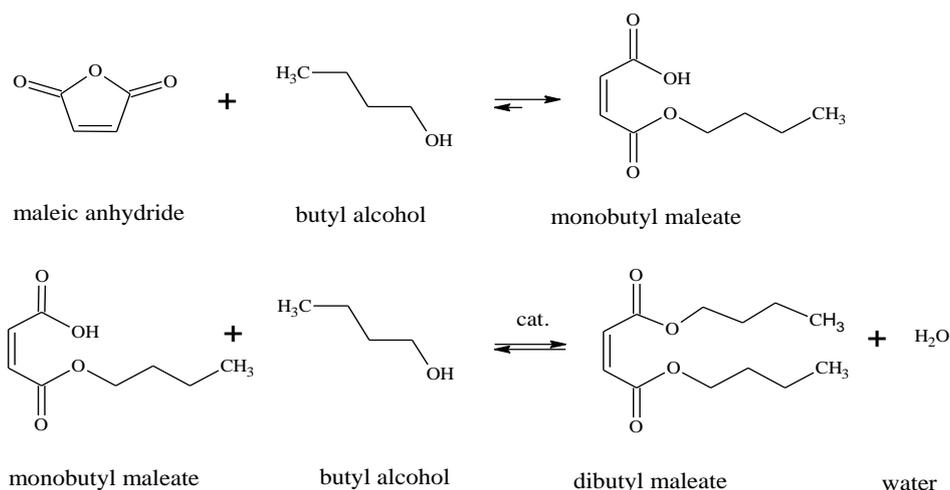


KINETICS AND MODELLING OF ESTERIFICATION PROCESS OF MALEIC ANHYDRIDE WITH BUTANOLS

Dibutyl maleate is widely used, especially as a plasticizer for plastics. It can also be used for production of protective coatings, detergents, solvents, drugs or 1,4-butanediol – which is an important intermediate in the polymer industry.

The esterification reaction of maleic anhydride with butyl alcohol occurs in two stages:



In the first, rapid and practically irreversible step is formed monobutyl maleate, while dibutyl maleate is formed in the second step. This is a slow and reversible stage therefore requires a use of a catalyst. A review of the literature (Chapter 3) shows that the synthesis of dibutyl maleate is at a technological level well understood (section 3.4), while the kinetics of this reaction is understood poorly. Of the available literature describing the synthesis of maleates (section 3.3), only one publication from 1977 describes the kinetics of the esterification of maleic anhydride with *n*-butanol, which was run without removal of water from the reaction mixture.

Due to diverse and widespread use of dibutyl maleate and so insufficient information on the kinetics of the dibutyl maleate synthesis reaction, own kinetic studies have been carried out over a very wide extent using three butyl alcohol isomers (*n*-, *i*- and *sec*-butanol) under non-catalytic conditions and in the presence of seven acid catalysts. Among them two – Nafion SAC-13 and Dowex 50WX8 – were heterogeneous catalysts which could be readily isolated from the reaction mixture and reused in the process. The characteristics of the reagents and catalysts are given in section 3.1.

The kinetic experiments were carried out in the range of temperatures 383-433 K and initial molar ratios alcohol to maleic anhydride 2,2:1-5,0:1 under condition of continuous

removal of water from the reaction mixture to eliminate the hydrolysis reaction of dibutyl maleate and to match the test conditions to the industrial conditions of the esterification process. Due to a rapid progress of the first stage of the reaction, the subject of the kinetic study was, in effect, a slow reaction of esterification of monobutyl maleate with butanol. The experimental part (Chapter 4) describes the specifics of the tests.

There have been determined a dependence of the reaction rate on temperature, reagent concentration, catalyst type and the butanol isomer. Graphs of the monoester conversion in function of the reaction time for all experiments are included in the Appendix. Results of the kinetic study are presented in Chapter 5.

It was found that primary butyl alcohols: *n*-butanol and *i*-butanol exhibited a much higher reaction activity than a secondary alcohol: *sec*-butanol (Fig. 106-113). The catalyst activity was as follows: phosphotungstic acid, sulfuric acid, methanesulfonic acid > Dowex 50WX8, Nafion SAC-13 >> tetrabutyl titanate, tetrabutyl zirconate (Fig.103-105). The determined reaction rate values are presented in Tab. 10.

In the studied range of parameters the reaction rate, r_A , is described by the formula:

$$r_A = k \cdot c_A^\alpha \cdot c_B^\beta \quad (15)$$

where: k –reaction rate constant, A - monobutyl maleate, B -butanol, α , β - fractional orders of reaction.

The dependence of the reaction rate constant on the temperature satisfied the Arrhenius equation. The determined values of exponents, pre-exponential factor and activity energy are given in Tab. 11. The effect of the concentration of the reactants and the temperature on the reaction rate showed a dependence on the type of the butyl alcohol isomer and in the reactions with primary butanols also on the type of the catalyst.

The results of kinetic studies on the synthesis of dibutyl maleate were used to model and optimize a chemical reactor (Chapter 6). An esterification column was proposed. With an assumed production capacity of 10,000 tons per year the process is proposed to be carried out in a column having from 3 to a maximum of 9 plates. A very high monoester conversion of 0.995 can be achieved in less than 5 hours in a 6-plate column having a volume of 7 m³ for a primary butanol process in the presence of homogeneous protonic acids (sulfuric acid, methanesulfonic acid or phosphotungstic acid) at a temperature of 403 K. For the non-catalytic process and for reactions carried out in the presence of organometallic catalysts or with *sec*-butanol other technological solutions should be sought, as the column volumes and residence times determined for them are not realistic.