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Short communication

Esterification of benzoic acid in microwave tubular flow reactor

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Abstract

Acid-catalyzed esterification of benzoic acid with ethanol was investigated in a continuous tubular flow reactor heated by microwaves. The microwave reactor operated at medium pressure and high temperature conditions. Esterification was catalyzed with sulfuric acid and with ion exchange resins. Kinetic parameters of esterification were determined in a stirred glass vessel using conventional heating. A mathematical model was proposed to describe temperature profiles and to predict the conversion of the reaction in the tubular flow microwave reactor. The calculated conversions of benzoic acid based on predicted temperature profiles agree with experimental data. The operating conditions in the microwave reactor allowed us to achieve high conversions at relatively low residence times. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Microwave heating; Esterification; Ion exchange resins

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1. Introduction

Since the first findings that microwaves could be used to enhance chemical reactions, microwave heating has spread to almost all areas of chemistry and to date more than 300 papers have been published in the area of microwave chemistry. It has been the subject of a number of excellent reviews [1–6]. However, a lot of the work has been empirical and qualitative. Establishing temperature effects is very important for a quantitative description of microwave heating. The measurement of temperature in the presence of a strong electric field is still problematic and can in many cases only provide average temperatures.

The aim of our work is to propose a simple mathematical model to describe temperature profiles and to predict the conversion for a tubular flow microwave reactor operating at elevated pressure. Esterification of benzoic acid with ethanol was chosen as a model reaction. Esterification was catalyzed with sulfuric acid and with ion exchange resins.

Gedye [7,8] reported high reaction rates of esterification of benzoic acid with various alcohols heated with microwaves. The reason for this is that reactions were carried out within closed vessels at elevated temperatures and pressure. Our previous work [9] confirmed that when esterification of benzoic acid with ethanol is performed at atmospheric pressure and under controlled conditions, it can be described by the same kinetics under microwave heating as under conventional heating.

Esterification of a carboxylic acid with an alcohol is extremely slow at ambient temperatures. However, heating the reaction mixture of carboxylic acid and alcohol to the atmospheric boiling point of the mixture generally still does not provide for a suitable practical rate of esterification. The extent of the reaction of carboxylic acids will be governed by the equilibrium constant, so that complete conversion cannot be obtained. The major concern for practical applications is increasing the reaction rate and establishing conditions which will allow obtaining higher conversions. The advantages of microwave heating, such as direct heating of materials, rapid start-up and the possibility of enchanced chemistry, demonstrate that microwaves could be successfully applied in the synthesis of various esters.

Microwave heating has been applied to batch and continuous flow systems. One of the limitations of microwave heating is the depth of penetration of microwaves in absorbing materials. The use of continuous flow systems, however, reduces these problems.

Chen [10] and coworkers reported that the yields of esterification of benzoic acid with methanol in a continuous tubular flow reactor heated with microwaves were lower because of the evaporation of methanol in the Teflon coil. The operating conditions in our experiments (pressure up to 7 atm)

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allowed us to carry out esterification in a continuous tubular flow reactor under higher temperatures without any evaporation of solutions. Esterification of benzoic acid with ethanol was performed with a large excess of ethanol that was used as the reactant and as the medium for microwave heating.

Esterification was homogeneously catalyzed with sulfuric acid and heterogeneously catalyzed with ion exchange resins. Such esterification reactions utilize ion-exchange resins instead of mineral acids. Ion exchange resins have many advantages over conventional catalysts: they increase the product yield, retain their activity for a long time, and do not pollute. It is also easy to separate them from reaction media. In view of results in the literature [11,12], Amberlyst 15 appears to be the best commercially available solid catalyst for this reaction and was chosen for present study.

Conversions of the reaction were calculated, based on the proposed mathematical model. Rate equations with the kinetics parameters used in the mathematical model were determined in a glass vessel under conventional heating.

2. Experimental

The tubular flow reactor was a Pyrex glass tube (inner diameter 1.07 cm, length 42 cm), placed at the axial position of the microwave oven. The microwave oven was a conventional unit (Panasonic NE-1780, Matsushita Electric Industrial Co., Osaka, Japan) with full-power level of 1700 W, operating 2450 MHz. An additional continuous water flow system was placed in the oven to absorb the excess of radiation and thus to prevent magnetron damage. Details of the equipment are presented in Fig. 1.

The temperature of the inlet and outlet flow was measured with NiCr–Ni thermocouples. The glass reactor was filled with the catalyst and a wire mesh was placed at the ends of the reactor to prevent any loss of resins and leakage of microwaves. A pressure-regulating valve was placed at the outlet of the reactor. The applied pressure of 7 atm allowed temperatures up to 140°C at a flow rate of $1\,\mathrm{l\,h^{-1}}$. Evaporation of the solution occurred at higher temperatures and bubbles disturbed the flow. The maximum temperature was also limited by the thermal stability of the resins.

All experiments were performed with a large excess (molar ratio 10:1) of pure ethanol (pro analysis, Merck, Darmstadt)) with respect to benzoic acid (pro analysis, Carlo Erba, Milan). Sulfuric acid [pro analysis, Merck, Darmstadt] was added as a homogeneous catalyst (2.1 wt.%). Amberlyst-15 [13] (Rohm and Haas, 20% DVB, particle size 0.35–1.2 mm, average pore diameter 24 nm, moisture content 53%, concentration of active sites $1.8\,\mathrm{meq\,ml^{-1}}$) was used as a strong acid ion exchange resin. Amberlyst 15 is a strong acid macroreticular ion exchange resin in hydrogen form. The analysis of the samples was performed by HPLC (Knauer, Hypersil ODS column).

3. Kinetics of esterification

Benzoic acid reacts with ethanol to form ethyl benzoate and water:

$$\mathrm{C_6H_5COOH + C_2H_5OH \underset{k_b}{\overset{k_f}{\rightleftarrows}} C_6H_5COOC_2H_5 + H_2O}$$

The kinetics parameters of esterification reaction were determined in a glass vessel (volume 200 ml) placed in a thermostated bath and equipped with a reflux and a magnetic stirrer. The speed of the magnetic stirrer was high enough to eliminate external mass transfer resistance. The experiments were performed in the temperature range from 50 to 80°C.

Esterification of benzoic acid with ethanol in the temperature range used in our experiments at atmospheric pressure is a very slow reaction and several days are needed to reach the equilibrium (Fig. 2). Ethanol was used in large excess to shift equilibrium towards the products.

McCracken and Dickson [14] concluded that esterification of acetic acid with cyclohexanol was first order with respect

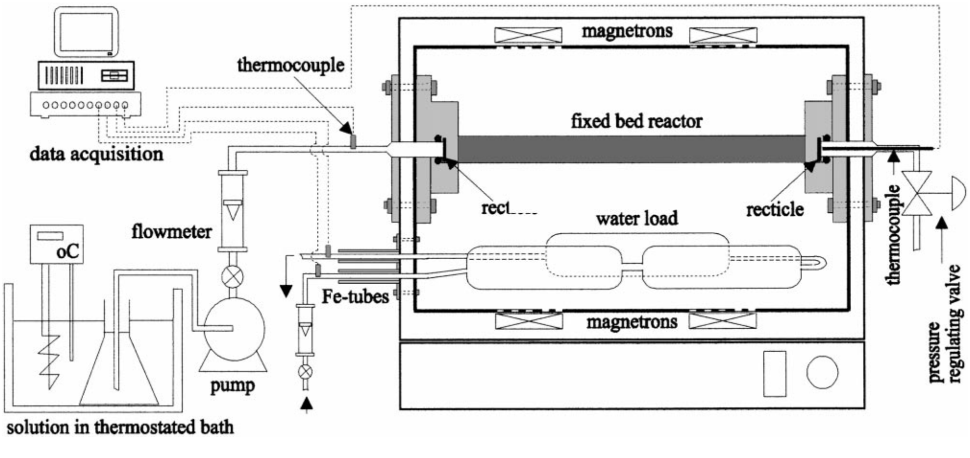

Fig. 1. Microwave tubular flow reactor: experimental setup.

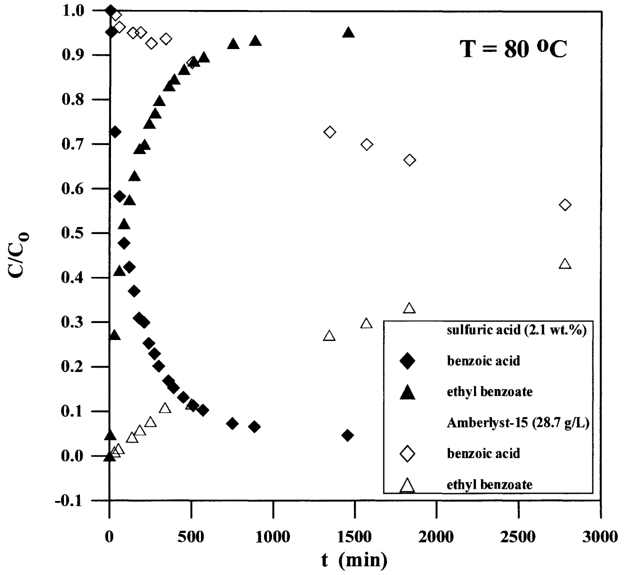

Fig. 2. Time course of benzoic acid and ethyl benzoate at 80°C under conventional heating.

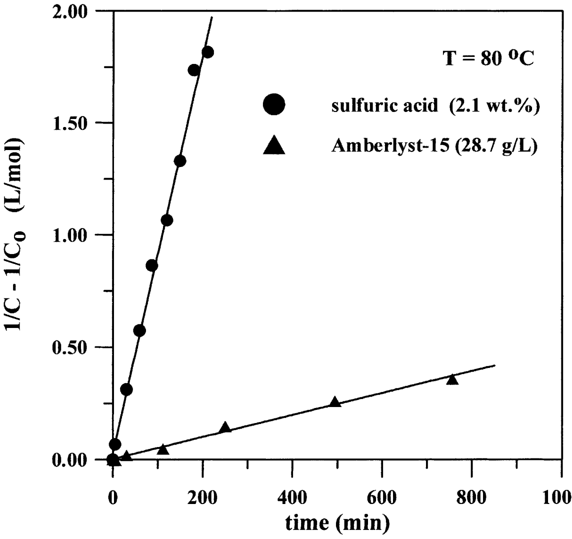

Fig. 3. $1/C_\mathrm{B}$ vs. time at 80°C under conventional heating.

to cyclohexanol and second order with respect to acetic acid. We also applied these assumptions to the esterification of benzoic acid with ethanol, which results in:

$$-\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t}=k_\mathrm{f}C_\mathrm{E}C_\mathrm{B}^2 \tag{1}$$

where k_f is the rate constant for the forward reaction, C_E is the concentration of ethanol, and C_B is the concentration of benzoic acid. When alcohol is used in large excess, the reaction rate is essentially independent of the concentration of alcohol and Eq. (1) can be changed to:

$$-\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t}=k'C_\mathrm{B}^2 \tag{2}$$

The straight lines in Fig. 3, where $1/C_\mathrm{B}$ was plotted versus time, clearly show that esterification is second order with respect to benzoic acid for both the reaction catalyzed with sulfuric acid and the one with ion exchange resins. The effects of the reverse reaction are negligible in this concentration range.

Reaction rate constant k' is the function of temperature that can be described by the Arrhenius law:

$$k'=k'_0\exp^{(-E_\mathrm{a}/RT)} \tag{3}$$

It can be seen from Fig. 4 that the plots of $\ln k'$ vs. $1/T$ are straight lines. The activation energy is $80.5\pm0.5\,\mathrm{kJ\,mol^{-1}}$ for homogeneously catalyzed esterification and $69.1\pm0.5\,\mathrm{kJ\,mol^{-1}}$ for heterogeneously catalyzed esterification. Pre-exponential factor is $1.48\pm0.02\times10^{8}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ for homogeneously catalyzed esterification and $2.47\pm0.15\times10^{5}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ for heterogeneously catalyzed esterification. The estimated Thiele modulus [15] for heterogeneously catalyzed esterification is 0.11 at 120°C, so the effect of the internal diffusion on the reaction rate is very small.

Ion exchange resins in the tubular flow reactor form fixed bed and the concentration of active acid sites is $1.8\,\mathrm{meq\,ml^{-1}}$ [13] which is considerably higher than in the batch reactor. The reaction rate of esterification depends also on the concentration of ion exchange resins. The reaction rate constant increases linearly with the amount of the catalyst, which can be seen in Fig. 5. Benzoic acid reacts with ethanol without any catalyst but the reaction is extremely slow. The reaction rate of self-catalyzed esterification can be neglected when compared to that of catalyzed reaction. Even small amounts of Amberlyst 15 greatly increase the reaction rate.

The concentration of $\mathrm{H^+}$ was $0.0404\,\mathrm{mol\,l^{-1}}$ when esterification was catalyzed with sulfuric acid. The concentration

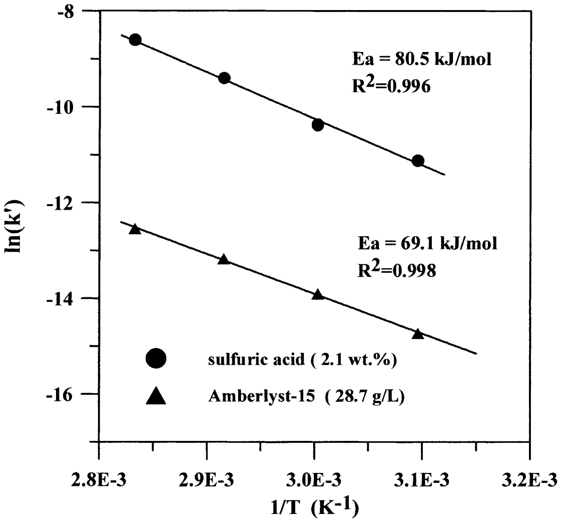

Fig. 4. Arrhenius plot for esterification catalyzed with sulfuric acid and Amberlyst 15.

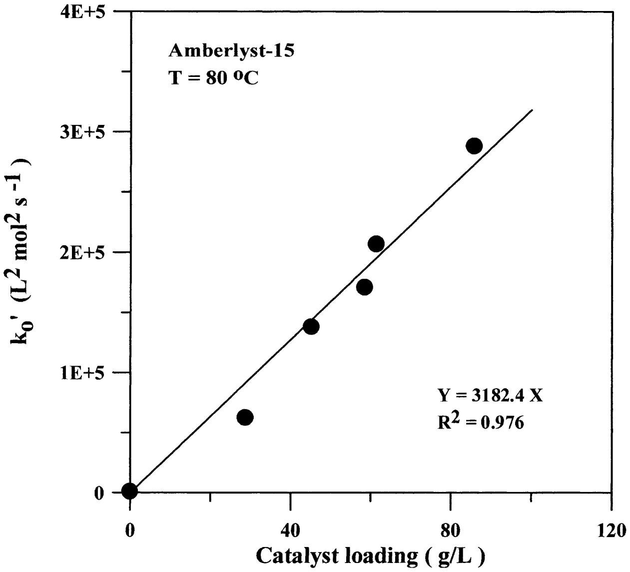

Fig. 5. Effects of Amberlyst 15 loading on reaction rate at 80°C.

of sulfuric acid in batch experiments was same as in experiments in the tubular flow reactor because even small increase of the concentration of sulfuric acid can cause dehydration of the alcohol to olefins and ethers.

Finally, the rate of disappearance of benzoic acid can be written as

$$r_B = k_0' C_B^2 \exp^{(-E_a/RT)} \tag{4}$$

where activation energy E_a and pre-exponential factor k_0' are given in text above.

4. Mathematical model

A mathematical model is proposed to describe the temperature and concentration profiles in a continuous flow reactor with a fixed bed of catalyst. It is assumed in the model that:

- the flow in the bed is of the plug type (longitudinal dispersion is neglected);
- there are no temperature and concentration gradients in the radial direction of the bed because of its small diameter.

The estimated Peclet number [16,17] for the reactor with the fixed bed of ion exchange resins is 1200; therefore the effects of axial dispersion can be neglected. The Reynolds number for homogeneously catalyzed reaction is between 1500 and 3700, so the flow of the fluid is turbulent at higher flow rates. The estimated Peclet number at higher flow rates is 100, so the effect of axial dispersion is very small. At lower flow rates, the effect of axial dispersion probably becomes more important, because the flow regime changes from turbulent to laminar.

The above assumptions were applied to the mathematical model. The mass balance for benzoic acid includes the rate of disappearance of benzoic acid, which is obtained by Eq. (4):

$$v\frac{dC_B}{dz} + r_B = 0 \tag{5}$$

The energy balance for the reaction mixture includes heat transfer to the surroundings and heat generation by the absorption of microwaves:

$$\rho c_p v \frac{dT}{dz} = U a_W (T_\infty - T) + Q_{MW} \tag{6}$$

where a_W is the specific surface of the reactor wall per volume, U is the overall heat transfer coefficient to the surroundings, T_∞ is temperature of the surrounding and Q_{MW} is the average absorbed power of microwaves per unit volume at the reaction temperature. The associated initial conditions at the inlet of the reactor are:

$$z = 0, \quad T = T_0, \quad C_B = C_{B0} \tag{7}$$

The set of differential equations with its initial conditions was solved by an appropriate numerical method.

5. Results and discussion

The prediction of temperature profiles is essential for the design and efficient operation of chemical applications. The absorbed power depends on dielectric properties of the material and on the intensity of the electric field [18]. The electric field inside the microwave oven is basically non-uniform and has a very complex pattern [19]. It depends on the design of the oven, and the size and geometry of the sample. Dielectric properties for commonly used chemicals are available in literature [20]. However, the presence of other chemicals such as ionic salts can dramatically change dielectric properties. Temperature also has a significant effect on dielectric properties. The dielectric constant and the dielectric loss of pure ethanol at 2450 MHz decrease with increasing temperature [20]; therefore, less power is absorbed at higher temperature.

The average absorbed power of microwaves per unit volume was experimentally determined for the tubular flow reactor by the temperature rise at different flow rates. Temperature dependency of the absorbed microwave power Q_{MW} for ethanol is given by:

$$Q_{MW} = (2.3 \pm 0.2) \times 10^7 \exp^{(-(2.8\pm 0.2)\times T)} \tag{8}$$

where T is temperature in degree Celsius.

The fluid-filled space outside and inside the solid particles of ion exchange resins couples with the microwaves and dry ion exchange resins also absorb microwaves and contribute to heating. The heating rate of the reaction mixture was considerably higher than the heating rate of pure ethanol (Fig. 6). Obviously, the presence of benzoic acid, reaction products (water and ester) and catalysts

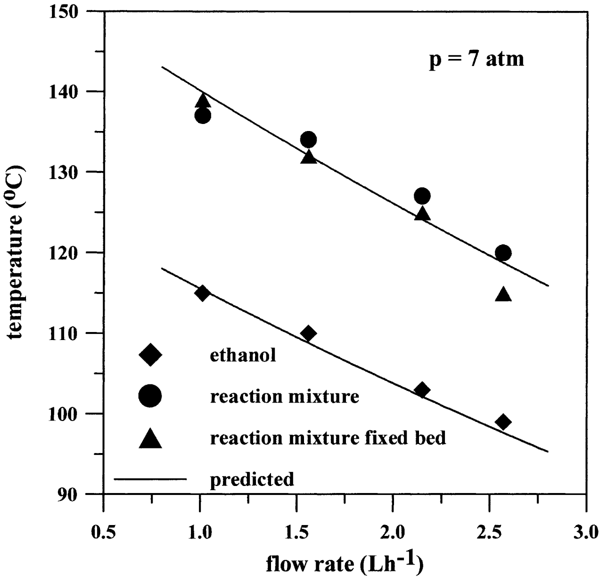

Fig. 6. Experimental and numerical data of outlet temperature at different flow rates.

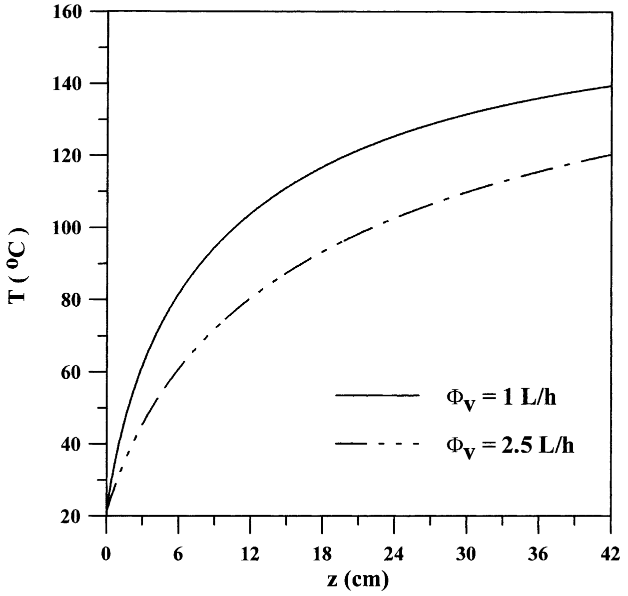

Fig. 7. Predicted temperature profiles in the tubular flow microwave reactor at different flow rates.

(sulfuric acid or ion exchange resins) changes dielectric properties of the reaction mixture and increases the absorption of microwaves. Thus, the dependency of the absorbed microwave power on temperature for the reaction mixture is:

$$Q_{\mathrm{MW}} = (2.6 \pm 0.2) \times 10^7 \exp^{(-(3.0\pm0.2)\times T)} \qquad (9)$$

Eq. (9) was also used for describing the absorption of microwaves when esterification was catalyzed with sulfuric acid, because the outlet temperatures were similar to the outlet temperature from the reactor with a fixed bed of ion exchange resins.

Outlet temperatures for the reaction mixture and pure ethanol were calculated, taking into account the temperature dependency of the absorbed power and convective heat transfer to the surroundings. The differences between the experimental and calculated temperatures can be attributed to the fact that the temperature profiles were predicted on the basis of average absorbed power per volume. The absorbed power of microwaves depends on electric field intensity, which is a strong function of the temperature and the position in the microwave oven.

Temperature profiles along the reactor were calculated taking into account the temperature dependency of the absorbed power and convective heat transfer to the surroundings. The temperature rise is much higher at the inlet part of the reactor (Fig. 7) than at the end. Absorption of microwaves is better at low temperatures, because with increasing temperature dielectric constant and dielectric losses decrease. Also heat losses become more pronounced at higher temperature. Both effects contribute to the decrease of the heating rate with increasing temperature. The outlet temperatures for ethanol and the reaction mixture were predicted (Fig. 6) on the basis of temperature profiles, considering temperature dependence of the absorbed power, which is given by Eqs. (8) and (9).

The rate equations of esterification were determined in a thermostated vessel with conventional heating. These equations can be applied to microwave heating because no specific effects of microwaves on esterification were observed. The conversion of esterification in the continuous tubular flow reactor was predicted by considering temperature profiles for esterification catalyzed with a fixed bed of Amberlyst 15 (Fig. 8) and for esterification catalyzed with sulfuric acid (Fig. 9). The agreement between the calculated

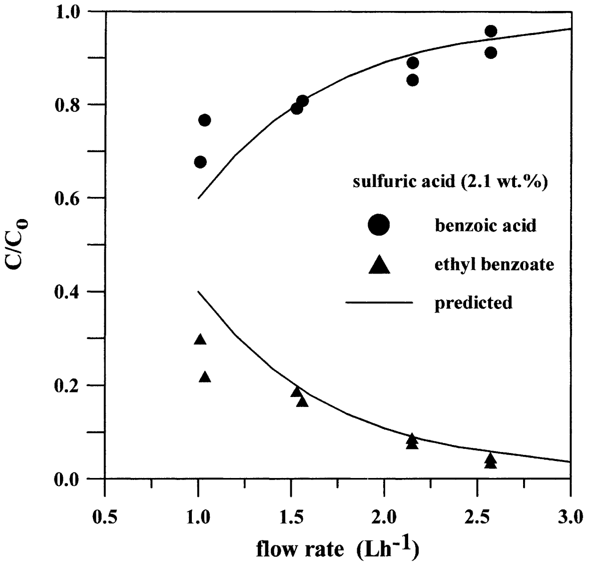

Fig. 8. Experimental and predicted outlet concentration of esterification catalyzed with sulfuric acid at various flow rates.

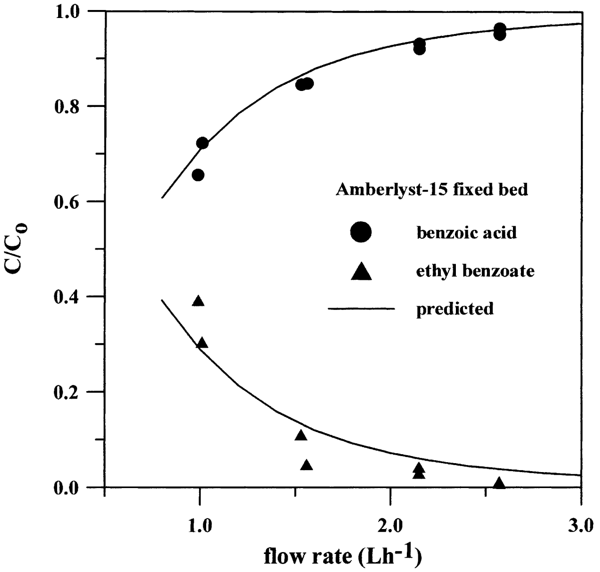

Fig. 9. Experimental and predicted outlet concentration of esterification catalyzed with fixed bed of Amberlyst 15 at various flow rates.

and measured concentrations is good taking in account that the temperature profiles are predicted on the basis of the average absorbed power. A change of temperature by 10°C increases the reaction rate of esterification by approximately two times. Experimentally obtained conversions are only lower than expected for homogeneously catalyzed esterification at the lowest flow rate. This is probably because at lower flow rates axial dispersion become more pronounced and the flow is not a ideal plug flow, so the obtained conversions are lower than those for an ideal plug flow reactor.

The conversions of the reaction in the tubular flow reactor are similar at the same flow rates for esterification catalyzed with sulfuric acid and with Amberlyst 15. The reaction rates in batch experiments were significantly lower for esterification catalyzed with Amberlyst 15 than with sulfuric acid. However, when the reaction is performed in the tubular flow reactor, the reaction rates in a fixed bed of Amberlyst 15 are higher than in the batch experiments because the concentration of acidic sites in the fixed bed is higher.

6. Conclusions

Esterification of benzoic acid with ethanol can be successfully catalyzed homogeneously and heterogeneously in a microwave tubular flow reactor. The mathematical model describes the temperature profiles in the continuous tubular flow microwave reactor with a fixed bed of catalyst. These descriptions are also the basis for the prediction of reactant conversion. Rate equations determined under conventional heating were included in the mathematical model to predict the conversion of esterification. The agreement between experimental and calculated data is good, considering that the temperature was calculated on the basis of the average absorbed microwave power per unit volume.

Esterification of benzoic acid is a slow reaction and needs several days to reach equilibrium at elevated temperatures (80°C). The operating conditions in the tubular flow microwave reactor (140°C, 7 atm) allowed us to significantly increase the reaction rate of esterification. It is also important that the outlet solution was optically clean and that no side reactions occurred.

7. Nomenclature

a_{W}	specific surface of the reactor wall ($\mathrm{m^2\,m^{-3}}$)
c_{P}	specific heat ($\mathrm{J\,kg^{-1}\,K^{-1}}$)
E_{a}	activation energy ($\mathrm{J\,mol^{-1}}$)
k	rate constant ($\mathrm{l^2\,mol^{-2}\,s^{-1}}$)
k'_0	pre-exponential factor ($\mathrm{l^2\,mol^{-2}\,s^{-1}}$)
Q_{MW}	absorbed power per unit volume ($\mathrm{W\,m^{-3}}$)
R	gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
r	rate of disappearance ($\mathrm{mol\,l^{-1}\,s^{-1}}$)
T	temperature (K)
t	time (s)
v	superficial velocity ($\mathrm{m\,s^{-1}}$)
U	overall heat transfer coefficient ($\mathrm{W\,m^{-2}\,K^{-1}}$)
z	longitudinal distance (m)
ρ	density ($\mathrm{kg\,m^{-3}}$)

Subscripts:

B	benzoic acid
E	ethanol

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