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Multi-functional trickle bed reactor for butylacetate synthesis

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Abstract

Esterification—the reaction of acetic acid and butanol in a trickle bed reactor, packed with a strong acid ion-exchange resin, operating with partial evaporation of reaction mixture into inert gas (nitrogen) stream—was investigated in this study. The experiments were carried out under atmospheric pressure. Reaction temperature was maintained in the interval from 70 to 120 °C, i.e. above the boiling point of the azeotropic mixture containing part of unreacted alcohol and both reaction products, i.e. ester and water. Partial evaporation of the reaction mixture into the inert gas (nitrogen) stream passing through the catalyst bed and consequent separation of reaction products into vapour and liquid phases shifted the chemical equilibrium of the reaction. The paper propose two different techniques for increasing the performance of trickle bed reactor for mentioned esterification: simultaneous reaction and evaporation and periodic modulation of the feed rate.

Keywords: Trickle bed reactor; Product separation; Evaporation; Esterification; Butylacetate

1. Introduction

Alkylacetate synthesis is commonly based on esterification of acetic acid with a pertinent alcohol. The equilibrium reaction is catalysed by strong acids or acidic catalysts. The resulting reaction mixture usually contains both the products, i.e. ester and water, and unconverted reactants, i.e. alcohol and acetic acid, because of the chemical equilibrium limit in the reaction system. Therefore, a set of distillation columns or other separation steps like extraction or pervaporation are usually necessary to separate all reaction components and products efficiently.

Reaction conversion can be shifted beyond its equilibrium value by combining esterification and separation into one reaction system. The reactive distillation process is an advantageous variant of such a system, see e.g. [1,2]. Another possibility is to use a trickle bed reactor, packed with a strongly acidic ion-exchange resin, operating at temperature above the boiling point of the azeotropic mixture, formed from the reaction products and/or reaction components. Such an arrangement has been investigated in the frame of this study. The advantages of this type of reaction system are demonstrated for the case of butylacetate synthesis using a trickle bed reactor, operating above the boiling point of the azeotropic mixture (90 °C). By means of partial evaporation of the reaction mixture during esterification, the conversion is shifted considerably above the equilibrium value without necessity of using large molar excess of one reactant in the feed. The advantage of such a variant was recently demonstrated also for butylacetate and ethylacetate syntheses, see [3]. A combination of a trickle bed esterification reactor and a reactive distillation

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column represents another technological possibility to overcome the chemical equilibrium limitation [1,2].

2. Experimental

The esterification of acetic acid and butanol was investigated in this study. The chemical equilibrium constant of the reaction is 4.24 (428 K) [4] and corresponding equilibrium conversion of equimolar mixture of reaction components is 67.3%. Thermal effects of the reaction are negligible its reaction enthalpy is very close to zero (−2.0 kJ/mol, 298 K). The experiments were carried out under atmospheric pressure in a laboratory glass trickle bed reactor with a temperature controlled jacket, packed with strong acidic ion-exchange resin Purolite 151 ($CH+ = 5$ eq./kg). The reaction temperature was maintained in a interval between 90 and 120 °C.

The reactor operated at temperature above the boiling point of the azeotropic mixture containing unreacted alcohol and both reaction products, i.e. ester and water. Under these reaction conditions, only part of the liquid reaction mixture was evaporated so that the products removal from catalyst active sites during reaction was possible. Partial evaporation of the reaction mixture into an inert gas (nitrogen) stream passing through the catalyst bed and consequent separation of reaction products into vapour and liquid phases shifted the chemical equilibrium of the reaction resulting in the production of concentrated ester. The influence of temperature on the reactor performance was investigated.

Additionally, strong effort was focused on the improvement of the trickle bed reaction and reaction products separation efficiency and the reactor performance optimisation by the feed rate modulation. Dynamic experiments and simulations were carried out to optimise relations between the period length, its split into “feed-on” and “feed-off” cycles and the trickle bed reactor performance (throughput of the product, concentration of key components in the outgoing stream). The overall production rate at constant mean feed rate during time was represented by mean value of acetic acid conversion calculated from outlet cup mixing composition of liquid and vaporised products weighted by mass flow rates of liquid phase and condensate from cooled gas phase.

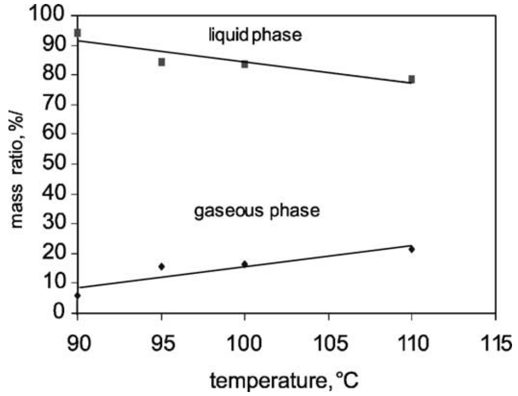

Fig. 1. Temperature dependence of reaction product split into gaseous and liquid phases $W/F = 20$ g h/mol, nitrogen flow rate = 10 l/h.

3. Results and discussion

Partial vaporisation of reaction mixture at the temperature between the temperature of butylacetate–butanol–water azeotrope (90 °C) and the temperature of acetic acid–butanol equimolar mixture (118 °C) boiling points speeds up esterification and limits ester hydrolysis. For this reason, the esterification reaction equilibrium is shifted towards products. If the trickle bed reactor operates in the temperature interval mentioned above, the reaction product is split into liquid and gaseous phases, see Fig. 1.

The effect of reaction temperature on the conversion of acetic acid and butanol equimolar mixture, measured in the liquid and vaporised parts of the product is shown in Figs. 2 and 3. It is clear that acetic acid concentration in the vapour phase is lower (conversion value is higher) in comparison with the liquid phase of the product. The experimental data clearly illustrate the benefit of simultaneous esterification and distillation of the reaction products in the form of azeotropic mixture from the reaction space in catalyst pores and, subsequently, from the liquid reaction mixture flowing as a liquid film down the bed of catalyst pellets. Vaporised azeotropic mixture was stripped out from the void space of the trickle bed by means of a nitrogen stream. In the case of total wetting of the catalyst bed, the contact of vaporised products (ester and water) with the catalyst is naturally limited and the backward reaction, i.e. ester hydrolysis, is suppressed this way.

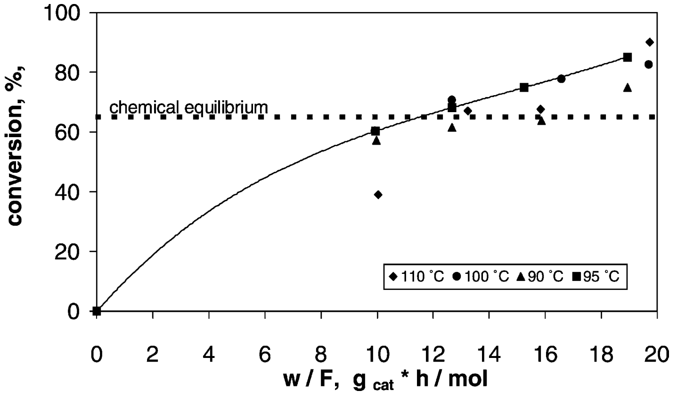

Fig. 2. Conversion of equimolar mixture of acetic acid and butanol in liquid phase vs. kinetic coordinate W/F in a trickle bed reactor at atmospheric pressure and different temperatures.

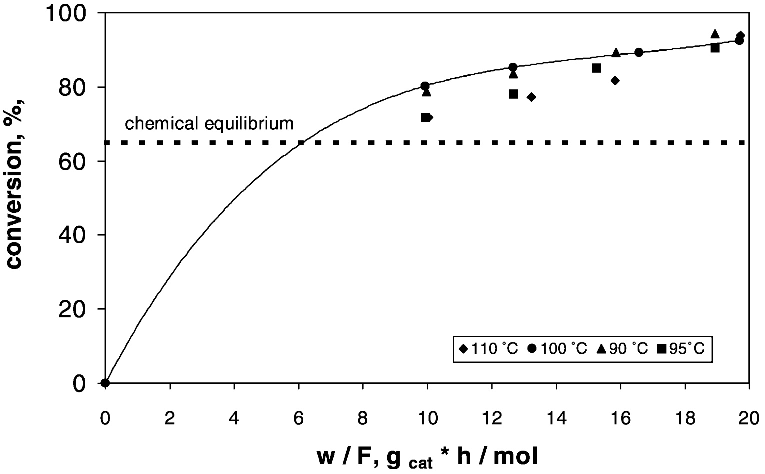

Fig. 3. Conversion of equimolar mixture of acetic acid and butanol in vapour phase vs. kinetic coordinate W/F in a trickle bed reactor at atmospheric pressure and different temperatures.

Mean value of reaction conversion was calculated on both phases amounts and compositions basis. The amount ratio of the liquid to gaseous phase at different temperatures is presented by Fig. 1. The temperature dependence of the conversion is shown in Fig. 4. This figure displays also the data from the experiment in which the reaction product was recycled into the trickle bed reactor. In fact, this set-up represents a two member trickle bed reactor cascade system. An increase of mean conversion is evident in this case.

The ASPEN Plus software was utilised for the steady state simulation of the reaction systems studied. The experimental and simulated reaction mixture

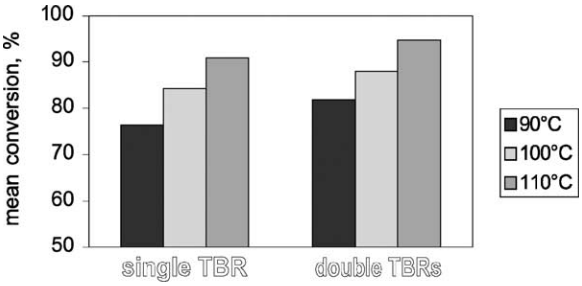

Fig. 4. Mean reaction conversion vs. temperature for single and double trickle bed reactors W/F = 20 g h/mol, nitrogen flow rate = 10 l/h.

Table 1
Comparison of measured and simulated reaction conversion for the single reactor temperature = 100 °C, nitrogen flow rate = 10 l/h W/F = 20 g h/mol

	Liquid phase conversion	Gas phase conversion	Average conversion	L/G phase ratio
Experiment	82.6	92.5	84.26	0.832
Simulation	75.7	90.0	79.44	0.75

compositions in the outlet liquid and gaseous streams as well as their ratio were in good agreement, see Table 1. The simulation results fit well in the experimental data, indicating adequacy of the mathematical model developed.

Trickle bed esterification is mass transfer limited and thus can be additionally improved by periodic operation of the reactor using modulation of the feed rate. With cyclic liquid feeding of reaction mixture at the same mean liquid flow rate as is conventionally applied in constant feeding mode of operation an increase of inter-phases mass transfer coefficients (i.e. liquid–solid and gas–solid) is typically observed [5]. In case of reaction system studied evaporation of the ternary azeotropic mixture from the catalyst pellets internal space is the rate determining step, periodical variation of the feed rate or feed flow interruption can improve the reactor throughput, increasing the external mass transfer rate via reduction of the thickness of the liquid film, descending down the catalyst bed.

Fig. 5 brings selected results measured in periodic operation mode using different periodic length for split value equal to 0.5. In every experimental series, mean conversion in dynamic operation mode (DS) has been compared to previous and subsequent conversion values measured in uniform steady state operation modes (US1 and US2, respectively) using the same mean feed rate of equimolar reaction mixture to trickle bed reactor.

An enhancement in reactor throughput in periodic operation mode in comparison to steady state operation mode depends on parameters of periodic operation mode. For example, there is an optimum value of mean reaction conversion increase in dependence on period length, see Fig. 6. The experiments have been carried out at temperature 95 and 110 °C when 16 and 22% of reaction mixture partially evaporates. Similar results has been measured at different period length and its split, see Fig. 7.

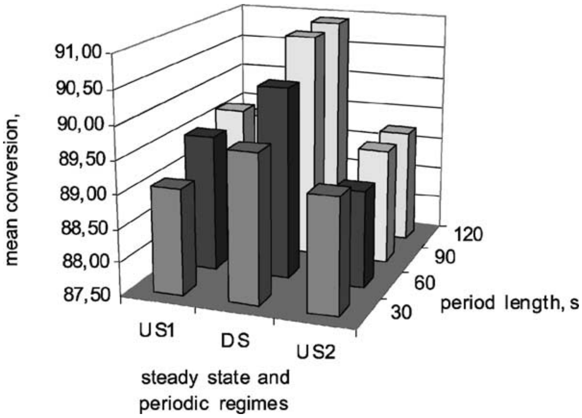

Fig. 5. Effect periode length during feed rate modulation on reaction conversion temperature = 95 °C, W/F = 20 g h/mol, nitrogen flow rate = 10 l/h, split = 0.5.

It is evident, the highest increase in mean conversion value was observed at period length 120 s for split value 0.5. This result is in a good agreement with draining time of liquid from the catalyst bed (110 s) after feed-off to the trickle bed reactor. The draining time is a useful characteristic parameter which can be easily measured and its application for data scaling up is to be expected.

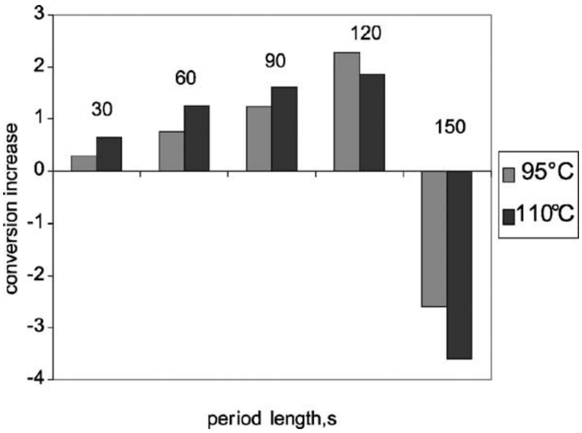

Fig. 6. Periodic operation mode increase for different period length and temperature in contrast to steady state operation mode of trickle bed reactor split = 0.5 W/F = 20 g h/mol.

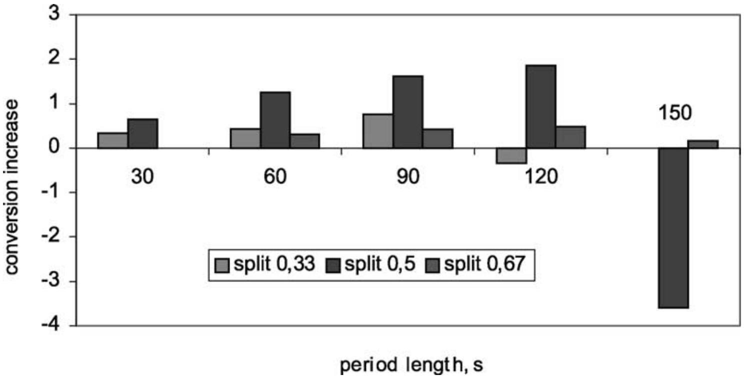

Fig. 7. Periodic operation mode increase for different period length and split in contrast to steady state operation mode of trickle bed reactor temperature = 110 °C, W/F = 20 g h/mol.

4. Conclusions

Experimental data illustrate the benefit of simultaneous esterification and partial evaporation of the reaction products in the multi-functional trickle bed reactor. A vaporised azeotropic mixture can be stripped out of voidage of catalyst bed using gas stream. In case of total wetting of the catalyst, bed contact of vaporised products (ester and water) with catalyst is naturally limited and thus, the backward reaction, i.e. ester hydrolysis is suppressed. This shifts the chemical equilibrium conversion to high values.

Rate determining step of the process is reaction mixture evaporation from liquid hold up and from the internal pores of catalyst pellets. An enhancement of the external mass transfer rate of reaction products—ester and water—from liquid to vapour phase by periodic operation mode in comparison to steady state operation mode was demonstrated in this study. Its extent depends on parameters of periodic operation mode like period length and split.

Acknowledgements

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