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Esterification of propionic acid under microwave irradiation over an ion-exchange resin

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Abstract

Esterification of propionic acid with ethyl alcohol over an ion-exchange resin catalyst was studied under microwave dielectric heating. Experiments were carried out in a single-mode microwave loop reactor, equipped with a heating band as well to directly compare the efficiency of the conventional convective/conductive heating and microwave dielectric heating. Series of kinetic experiments were carried out with both conventional and dielectric heating at the reaction temperature of 105 °C and total pressure of 7 bar. Different initial molar ratios of propionic acid-to-ethanol (from 1:2 to 2:1) were investigated. Initial molar ratios of acid-to-alcohol significantly affected the final yield of the desired product ethyl ester of propionic acid, ethyl propionate. The highest product yield was observed with equimolar initial ratio, compared to 1:2 and 2:1 initial molar ratios of acid-to-alcohol. However, the kinetics and equilibrium of this reaction were unaffected by the method of heating (microwave or conventional).

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Keywords: Esterification; Ion-exchange resin; Microwave dielectric heating

1. Introduction

Process intensification aims at transforming current practices in chemical engineering and bringing forth new developments in equipment, processing techniques and operational methods. The goal is more compact, safer, energy efficient and environmentally friendly processes.

Microwave irradiation is becoming an increasingly interesting method to heat materials in chemical laboratories, offering a clean, cheap, convenient, selective and instantaneous method of heating. Since 1986, when Gedye and coworkers [1] published the first pioneering report about utilizing microwave irradiation in chemical synthesis, increasing amount of articles concerning microwaves has been published [2–13]. However, it can be stated that at present moment microwave irradiation in catalytic chemical reactions still remains largely unexploited and all the potential of microwaves in chemical catalytic processes has not yet been discovered.

An esterification reaction is a reaction between an alcohol and a carboxylic acid, leading to the formation of an ester and a water molecule. Organic esters are a very important class of chemicals having applications in a variety of areas in chemical industry such as perfumes, flavours, pharmaceuticals, plasticisers, solvents and intermediates [14]. One major drawback of the reaction is that it is equilibrium-limited. Therefore, the goal was to investigate whether from the equilibrium point of view more favourable reaction conditions could be established in connection to the MW dielectric heating of the reaction mixture.

2. Experimental

2.1. Experimental and reactor set-up

Esterification of propionic acid (Acros, 99%) with ethyl alcohol was carried out in a single-mode microwave loop reactor (1100 ml) (Fig. 1) under microwave and conventional heating. An ion-exchange resin Amberlyst 15 (Fluka) was utilized as the catalyst and the catalyst mass was 5 g. The initial acid-to-alcohol molar ratio was varied, 1:1 (50%

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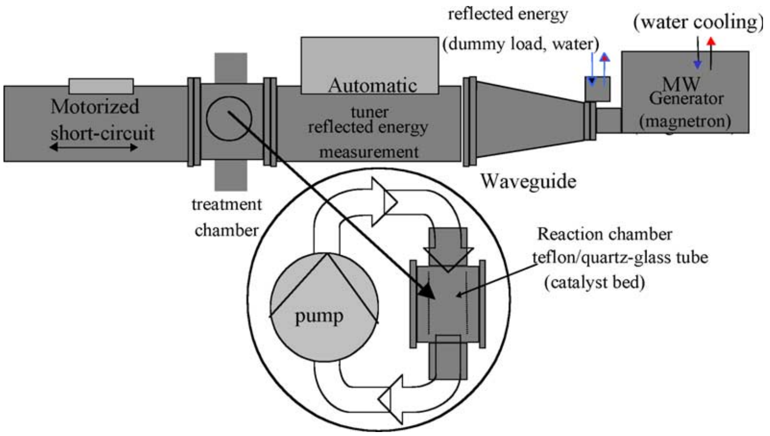

Fig. 1. A schematic picture of the microwave radiation generator and the control appliances of the multi-purpose reactor system.

acid and 50% alcohol), 1:2 (33% acid and 67% alcohol), 2:1 (67% acid and 33% alcohol), 2:3 (40% acid and 60% alcohol) and 3:2 (60% acid and 40% alcohol), respectively. The reaction temperature was 105 °C, at a microwave power input of 850–900 W, total pressure of 7 bar was applied (vapour pressure of reactants 2.96 bar and N_2 pressure 4.04 bar). The experiments were carried under isothermal conditions and with forced cooling as well, upon which a temperature gradient over cavity of 30 °C was established. The loop flow rate was 1 l/min. The samples drawn from the reactor were analysed by means of a gas chromatograph (GC) equipped with FID detector and DB–1 (100% dimethylpolysiloxane) column (length 30 m, diameter 0.25 mm, thickness 0.5 μm). The specific heating rate of the mixture was studied by means of a fiber optic temperature sensor (FISO Technologies). A scaled amount of liquid was placed into quartz glass test tube together with the thermoelement and temperature profiles as well as the absorbed energy level were recorded as a function of time.

2.2. Catalyst characterization

The catalyst particles were studied by scanning electron microscopy (SEM). A 360 (LEO Electron Microscopy Ltd.) scanning electron microscope equipped with a secondary and backscattered electron detector was used for imaging spent ion-exchange resin Amberlyst 15 exposed to microwave and conventional heating.

3. Results and discussion

3.1. Effect of initial acid-to-alcohol molar ratio under microwave heating

The effect of initial acid-to-alcohol molar ratio under microwave dielectric heating was investigated. The effect of initial molar ratio of ethanol and propionic acid on final yield of desired product ethyl propionate was significant. The highest yield of ethyl propionate was observed with equimolar mixture of ethyl alcohol and propionic acid (Fig. 2). Nearly the same product yield was obtained with initial molar ratio of propionic to ethyl alcohol 3:2 and 2:3. However, significantly lower product concentration was obtained when the initial molar ratio of propionic acid to ethyl alcohol was 1:2 and 2:1 (Fig. 2).

3.2. Effect of initial acid-to-alcohol molar ratio under conventional heating

The effect of initial acid-to-alcohol molar ratio was studied under conventional heating as well. A trend, similar to that observed under microwave irradiation could be seen. The highest product concentration was observed at an equimolar mixture compared to the 1:2 and 2:1 mixtures of propionic acid to ethyl alcohol (Fig. 3).

3.3. Comparison of microwave and conventional heating

No significant acceleration of the reaction rate, neither shift in the equilibrium concentration was observed under microwaves compared to conventional heating (Figs. 2 and 3) (Table 1). The fact that the equilibrium remained unaffected was, nevertheless, expected since the laws of thermodynamics should prevail: Microwave dielectric heating was not expected to be associated with any ‘‘magical’’ phenomena. Based on the obtained results we can conclude that the kinetics and equilibrium of this reaction is unaffected by the

Table 1
The equilibrium constants for the esterification reaction of propionic acid and ethyl alcohol over ion-exchange resin Amberlyst 15 (molar ratios: acid to alcohol)

Initial molar ratio	$K_{\text{equilibrium}}$	
	Microwave heating	Conventional heating
1:1	4.43	4.90
1:2	5.18	4.46
2:1	4.40	4.82
2:3	4.76	–
3:2	4.81	–

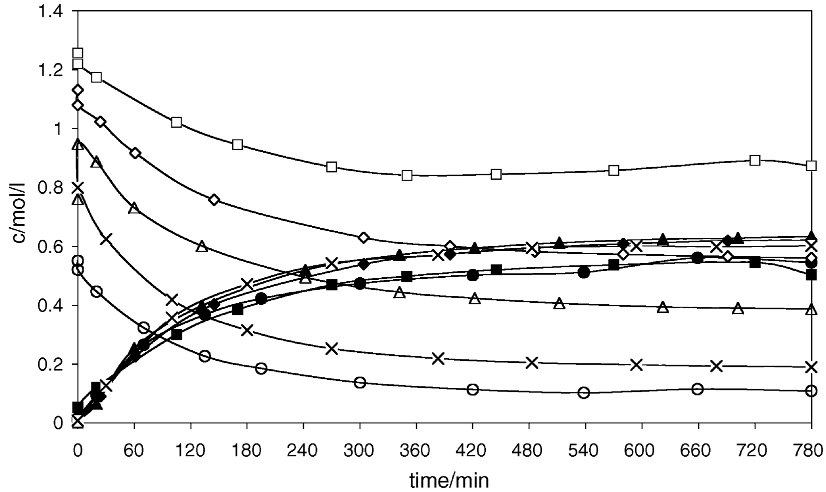

Fig. 2. Concentrations of ethyl alcohol and ethyl propionate versus time under microwave heating. The symbols: initial molar acid-to-alcohol ratios (ethyl alcohol: (□) 1:2, (◇) 2:3, (△) 1:1, (×) 3:2, (○) 2:1; ethyl propionate: (■) 1:2, (◆) 2:3, (▲) 1:1, (×) 3:2, (●) 2:1). The concentrations of propionic acid have been omitted for readability.

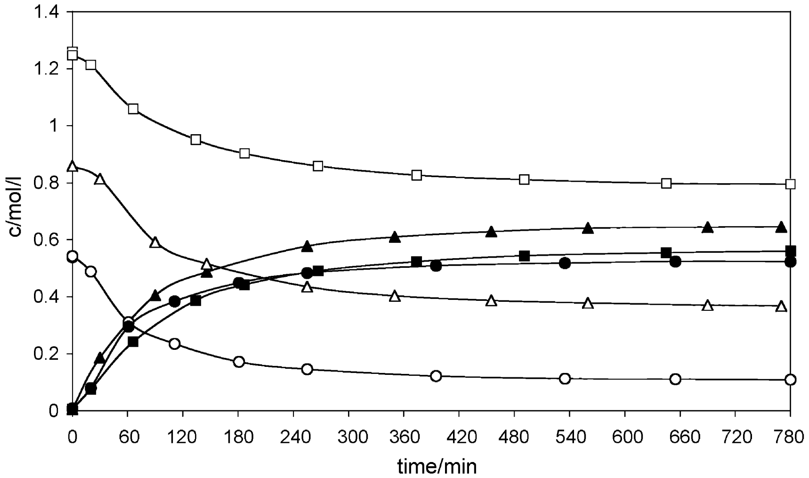

Fig. 3. Concentrations of ethyl alcohol and ethyl propionate versus time under conventional heating. The symbols: initial molar acid-to-alcohol ratios (ethyl alcohol: (□) 1:2, (△) 1:1, (○) 2:1; ethyl propionate: (■) 1:2, (▲) 1:1, (●) 2:1).

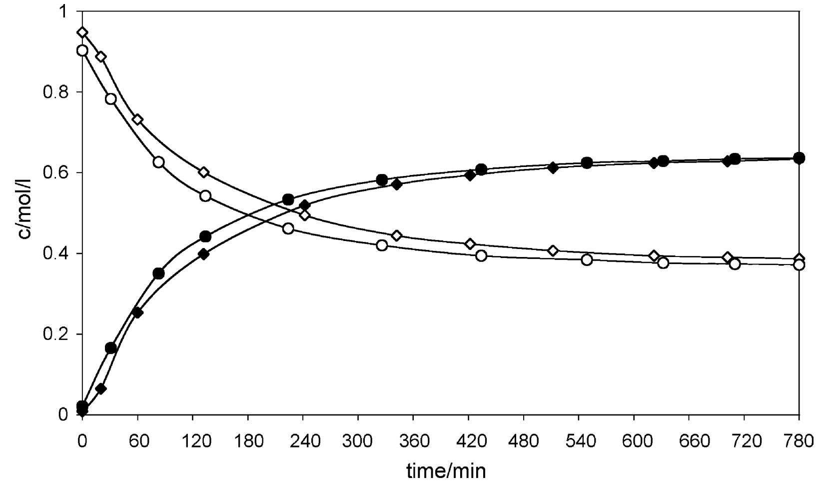

Fig. 4. Concentrations of ethyl alcohol and ethyl propionate versus time under microwave heating with and without forced cooling (ethyl alcohol: (◇) forced cooling, (○) without forced cooling, ethyl propionate: (◆) forced cooling, (●) without forced cooling).

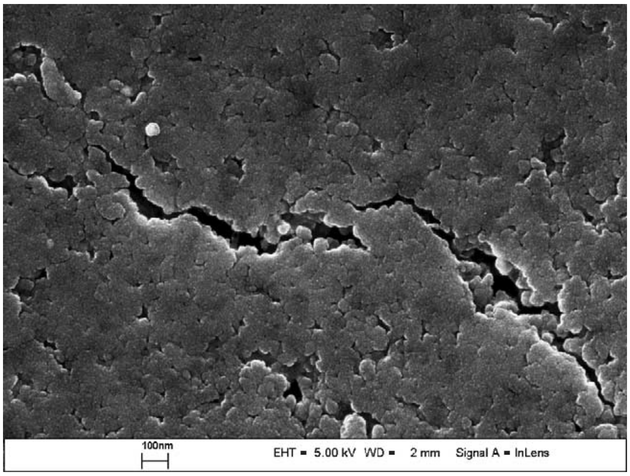

Fig. 5. SEM image of spent ion-exchange resin catalyst (Amberlyst 15) subjected to microwave heating.

method of heating. This conclusion is in agreement with the literature [15]. However, microwave irradiation allows more rapid heating to the reaction temperature compared to the conventional conductive/convective heating. In conclusion, microwave irradiation has potential as a more clean, economic, selective, convenient and instantaneous method of heating, although for a proper comparison between microwave and conventional heating the cumulative electrical energy fluxes should be measured in the future. One of the main goals of this investigation was to gain experience in the operation of our tailor-made, unique apparatus for comparison of microwave dielectric and conventional heating.

3.4. *Effect of forced cooling under microwave heating*

The effect of forced cooling on kinetics and equilibrium was investigated. In case of forced cooling, the temperature gradient before and after the cavity was 30 °C, without forced cooling the temperature gradient before and after cavity was 15 °C due to the heat losses in the loop. However, no significant enhancement of the reaction rate, nor a shift in the equilibrium was obtained by forced cooling (Fig. 4).

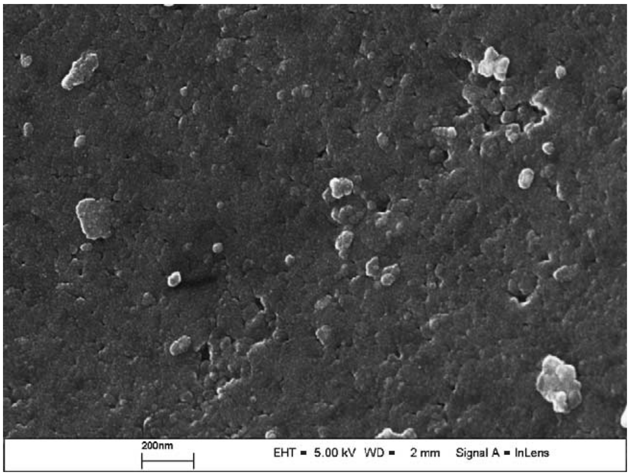

Fig. 6. SEM image of spent ion-exchange resin catalyst (Amberlyst 15) subjected to conventional heating.

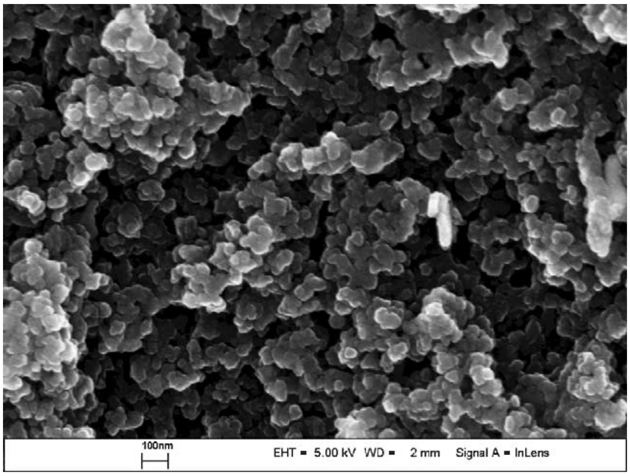

Fig. 7. SEM image of spent ion-exchange resin catalyst (Amberlyst 15) subjected to conventional heating.

4. Catalyst characterization

4.1. *Scanning electron microscopy*

An ion-exchange resin Amberlyst 15 used during the reaction exposed to microwave and conventional heating was studied by means of scanning electron microscopy (SEM).

In the catalyst exposed to microwave irradiation cracks were observed on the surface of the catalyst (Fig. 5), while in the catalyst subjected to conventional heating, no cracks were formed (Fig. 6). Slight melting of the catalyst particles occurred under microwave irradiation, as well, which could not be observed under conventional heating (Figs. 7 and 8).

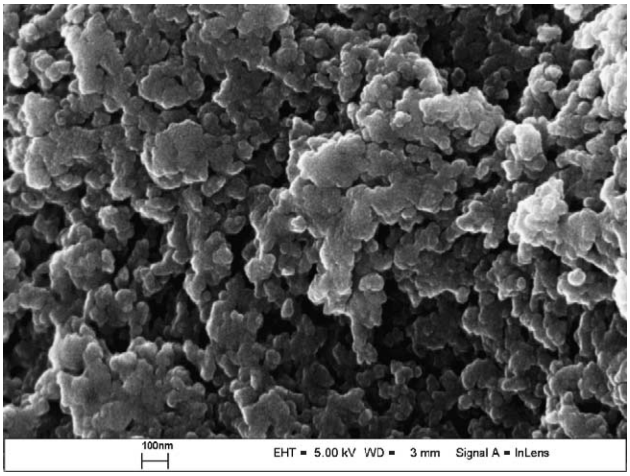

Fig. 8. SEM image of spent ion-exchange resin catalyst (Amberlyst 15) subjected to microwave heating.

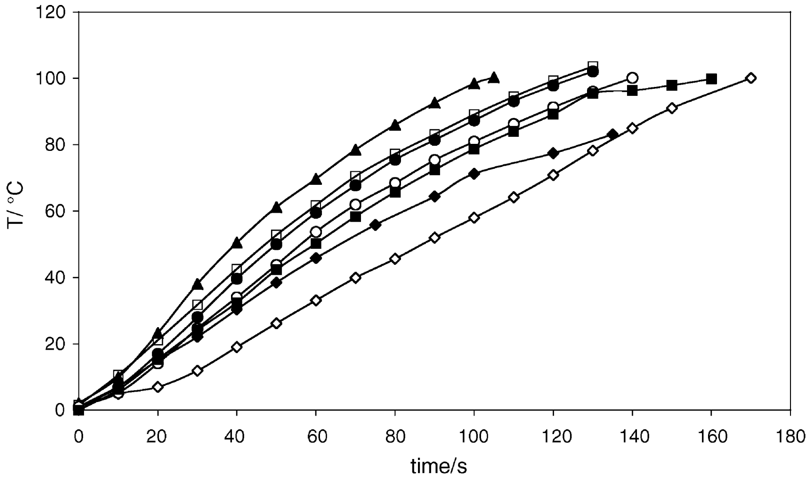

Fig. 9. Temperature rice versus time under microwave dielectric heating (power in-put 30 W) (▲) equimolar, (◆) ethyl alcohol, (◇) water, molar ratios of acid-to-alcohol: (□) 3:2, (■) 2:3, (○) 3:2, (●) 2:3.

5. Conclusions

Esterification of propionic acid with ethyl alcohol over an ion-exchange resin catalyst was studied under microwave dielectric and conventional heating. The effect of the initial molar ratio of propionic acid to ethyl alcohol on the final yield of the desired product ethyl propinate was significant, both under microwave and conventional heating. An equimolar ratio of acid-to-alcohol increased the yield of the final product compared to the initial molar ratios 2:1 and 1:2 of propionic acid to ethyl alcohol. However, the kinetics and equilibrium of this reaction was unaffected by the method of heating. Forced cooling of the reactant-mixture during the course of the reaction did not result into increase of the reaction rate neither to a shift in the equilibrium, as well. Catalyst surface cracking and negligible melting was observed in the catalyst subject to microwave irradiation. Interestingly, the heating rate of equimolar mixture by microwave irradiation was the most rapid, as can been seen in (Fig. 9). On the other hand ion-exchange resin catalyst (Amberlyst 15) and propionic acid are essentially microwave transparent.

As a summary, one can conclude that it is possible to carry out esterification reactions by means of microwave dielectric heating. Although, no significant enhancement was obtained in comparison of conventional heating, nevertheless, a rapid temperature gradient in the catalyst bed can be established and, therefore, the liquid bulk can be maintained at a much lower temperature. This concept is expected to be beneficial in carrying out chemical reactions where competitive or consecutive side reactions lead to by-products and thus cause deteriorating selectivities. Keeping the bulk of the liquid at lower temperatures could prevent then formation of such undesired side products. Such studies are currently in progress in our laboratory.

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