

EFFECTS OF PULSED ELECTRIC FIELD ON THE ESTERIFICATION REACTIONS

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ABSTRACT. The effects of alternative pulsed electric fields on the esterification reactions between acetic acid and different alcohols were investigated in this paper. The aim of this study was the synthesis of some esters using a new and ecological method. Only acetic acid and different alcohols were used as raw materials and an alternative pulsed electric field as accelerator. Also, the enzymatic synthesis of esters was performed in order to draw a conclusion on the effectiveness of the new proposed method. Gas chromatography analysis showed that the esterification was considerably enhanced by an alternative pulsed electric field. The highest amounts of ester were obtained for *n*-propyl acetate, significantly higher than in the case of enzymatic synthesis. The synthesis of *i*-butyl and *i*-amyl acetate using the alternative pulsed electric field shows the formation of lower amounts of ester, probably due to the conformation of the molecule. Using raw materials of natural origin (acetic acid and alcohols obtained, for example, by fermentation) in the presence of an alternative pulsed electric field, natural esters are obtained and they can be used without restrictions in pharma, food, perfume or cosmetic industry.

Keywords: esterification reactions, pulsed electric field, enzymatic synthesis, food industry, natural esters

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INTRODUCTION

In pharma, food, perfume or cosmetic industry, a large number of odors and flavoring compounds are used [1]. Among these, the most commonly products used are esters; they are generally obtained by removing a molecule of water as a result of the reaction between a carboxylic acid and an alcohol or phenol. On the other hand, esters can also be synthesized by Tishchenko reaction or by the addition of a carboxylic acid to an alkene, but there are many other chemical methods that are less used [2, 3]. If esters must be used in pharma and food industry, they are mandatory obtained using enzymes as catalysts, the most preferred being lipases [4]. Also, esters can be obtained using transesterification reaction, or assisted by microwaves, visible light, pulsed electric fields [5 - 10].

There are two ways to obtain natural esters by chemical synthesis, starting from raw materials of natural origin: by chemical reaction using enzymes as catalysts or by chemical reaction using a pulsed electric field as a catalyst [11]. Considering that obtaining esters by enzymatic methods involve high costs, the aim of this study was to apply and test a new esterification method using only acid and alcohol as raw materials, and a rectangular pulsed electric field (20 kHz) as catalyst. The synthesized esters were *n*-propyl acetate, *i*-butyl acetate and *i*-amyl acetate. These three esters were chosen because they have applications in pharma, food industry and in cosmetics [12-14]. In order to draw a conclusion on the effectiveness of the new proposed method using the pulsed electric field as catalyst, the enzymatic synthesis of these esters was performed.

RESULTS AND DISCUSSIONS

n-Propyl acetate synthesis

In Figure 1 (A,B,C), the results obtained in the esterification reaction of acetic acid with *n*-propanol are shown. The reactions were performed in the presence of an alternative pulsed electric field (20 kHz) as catalyst compared with the enzymatic synthesis.

The amount of ester obtained in the case of pulsed electric field synthesis for all 3 molar ratios and at every sampling hour is higher compared to the amount of ester obtained after enzymatic synthesis. The amounts of *n*-propyl acetate obtained after 26 hours using a pulsed electric field as catalyst are 108.8 mg (1:2), 202.2 mg (1:1) and 199.3 mg (2:1), significantly higher than the ones obtained enzymatically: 92.9 mg (1:2), 104.1 mg (1:1)

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and 113.3 mg (2:1). The highest amount of *n*-propyl acetate, 202.2 mg, was obtained when the molar ratio between reactants was 1:1 in the case of synthesis using an alternative pulsed electric field. This result indicates a higher efficiency compared to other molar ratios and the excess of reactants to increase the reaction efficiency is not required.

If the syntheses were performed using excess, either acid or alcohol, significant changes have been observed 26 hours later, especially in the case of pulsed electric field method, so the amount of ester obtained using excess alcohol is around two times lower compared to the quantity obtained in equimolar ratio.

Using an excess of acid, a decrease around 5% was observed; thus, the optimal molar ratio between reactants for the synthesis of *n*-propyl acetate was 1:1.

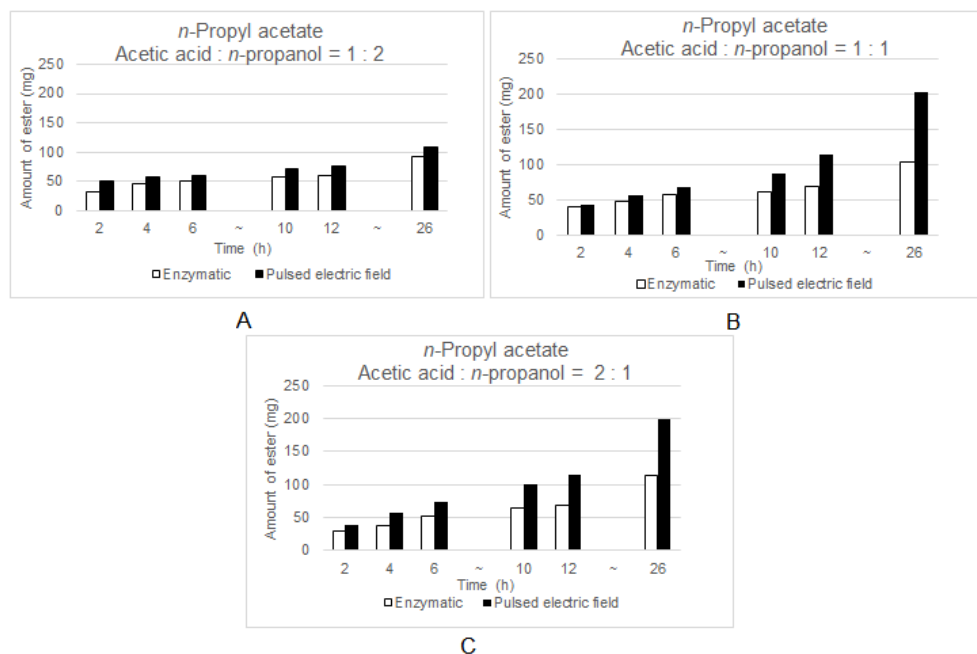


Figure 1 (A,B,C). The amount of *n*-propyl acetate obtained for molar ratio acetic acid : *n*-propanol 1:2, 1:1 and 2:1

For the enzymatic synthesis of *n*-propyl acetate, the optimal molar ratio under the selected reaction conditions is 2:1. In the case of alcohol excess, the amount of ester decreases around 20%, and in the case of the equimolar ratio the amount of ester is about 10% lower than in the case of the optimal molar ratio 2:1.

i-Butyl acetate synthesis

In Figure 2 (A,B,C) the results obtained in the esterification reaction of acetic acid with *i*-butyl alcohol are shown. All reactions were performed in the same conditions as the previous ones.

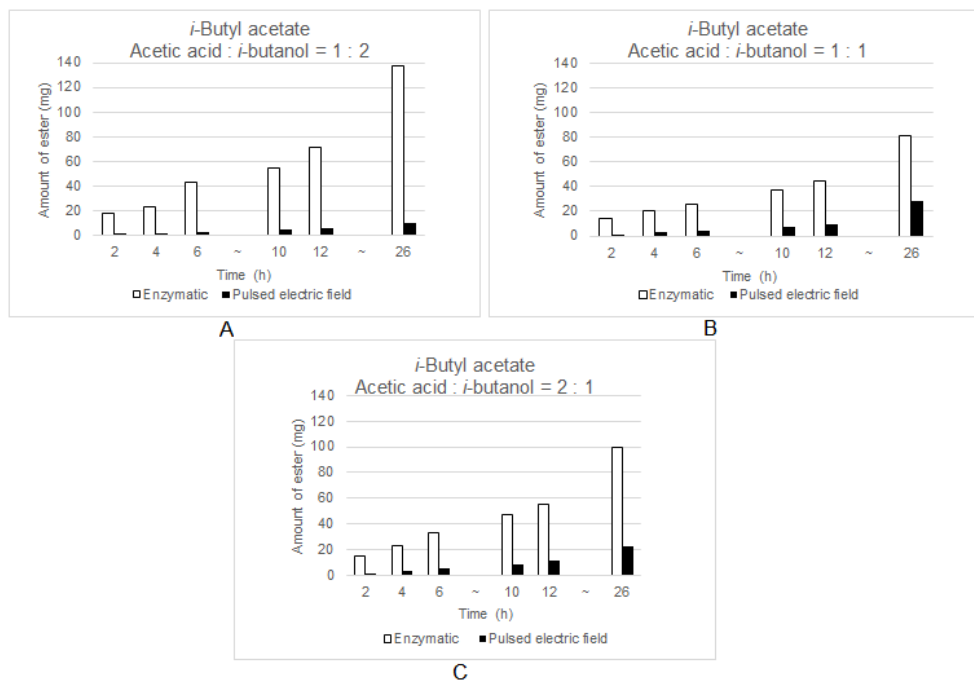


Figure 2 (A,B,C). The amount of *i*-butyl acetate for molar ratio acetic acid : *i*-butanol 1:2, 1:1 and 2:1

It can be observed that in the case of all three molar ratios and at every sampling hour the amount of *i*-butyl acetate obtained using pulsed electric field as catalyst for synthesis is lower compared to the amount of ester obtained enzymatically. The amounts of *i*-butyl acetate obtained after 26 hours using a pulsed electric field as catalysts are 10.5 mg (1:2), 28.1 mg (1:1) and 22.9 mg (2:1), lower than the ones obtained enzymatically: 137.5 mg (1:2), 81.5 mg (1:1) and 99.1 mg (2:1). The highest amount of ester was obtained when the molar ratio between reactants was 1:1 in the case of pulsed electric field synthesis. This result indicates a higher efficiency compared to other molar ratios, with no need for excess reactants to increase the reaction efficiency. If the syntheses were performed using a reactant excess, either acid or alcohol, significant changes are observed after 26 hours, especially in the case of pulsed

electric field method, so the amount of ester obtained using excess alcohol was around three times lower compared to the quantity obtained in equimolar ratio. When an excess of acid was used, it was observed a decrease around 25%; thus, the optimal molar ratio between reactants for the synthesis of *i*-butyl acetate in pulsed electric field was 1:1. The enzymatic synthesis of *i*-butyl acetate proved to be more efficient, the optimal molar ratio under the selected reaction conditions being the molar ratio 1:2. In the case of excess acid the amount of ester decreases around 25% and in the case of the equimolar ratio the amount of ester was about 35% lower compared to the optimal molar ratio (1:2).

i-Amyl acetate synthesis

In Figure 3 (A,B,C), the results obtained in the esterification reaction of acetic acid with *i*-amyl alcohol are shown. All reactions were performed in the same conditions as the previous ones. The synthesis of *i*-amyl acetate by the two presented methods were similar to the reactions of obtaining *i*-butyl acetate, which practically confirms the unfavorable influence of the branched chain on the development of these reactions in the pulsed electric field.

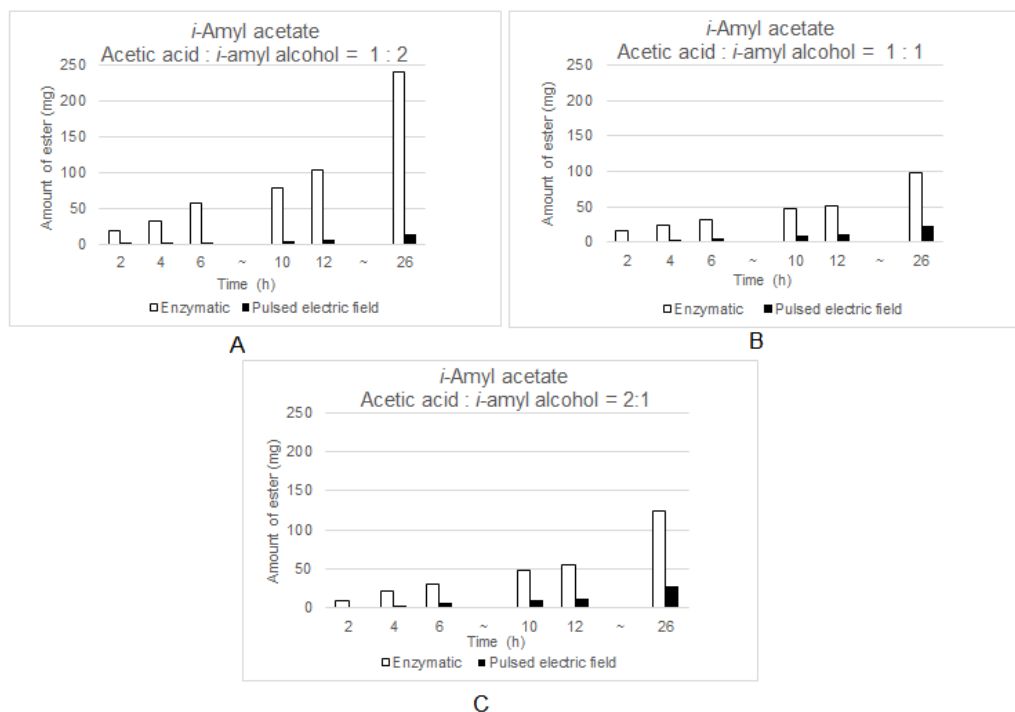


Figure 3 (A,B,C). The amount of *i*-amyl acetate for molar ratio acetic acid : *i*-amyl alcohol 1:2, 1:1 and 2:1

The amounts of *i*-amyl acetate obtained after 26 hours using a pulsed electric field as catalyst are 14.7 mg (1:2), 24.0 mg (1:1) and 27.2 mg (2:1), lower than the ones obtained enzymatically: 239.1 mg (1:2), 99.0 mg (1:1) and 124.1 mg (2:1). The highest amount of ester was obtained when the molar ratio between reactants was 2:1 in the case of pulsed electric field synthesis. If the syntheses were performed using excess of alcohol, significant changes were observed after 26 hours, especially in the case of the pulsed electric field method; therefore, the amount of ester obtained was approximately 2 times lower compared to the amount obtained when the molar ratio was 2:1.

In the case of *i*-amyl acetate synthesis using the reactants in equimolar ratio, it was observed a decrease around 15%, thus resulting that the optimal molar ratio between reactants for the synthesis of *i*-amyl acetate using the pulsed electric field was 2:1.

The enzymatic synthesis of *i*-amyl acetate proved to be more efficient, the optimal molar ratio under the selected reaction conditions being the ratio of 1:2. Using an excess of acid the amount of ester decreases around 50%, and in the case of the equimolar ratio the amount of ester was about 60% lower compared to the optimal molar ratio of 1:2.

It can also be seen that after 12 hours of reaction there is no directly proportional increase in the amount of ester with the number of hours indicating an equilibrium.

CONCLUSIONS

Experimental determinations have shown that the pulsed electric field has an impact regarding the esterification reaction of acetic acid with different alcohols. Due to the orientation of the molecular dipoles in alternative pulsed electric field, the probability of effective collisions with the formation of reactive products is increased. In case of branched alcohols, due to the interactions that manifest themselves between the branched chains, the catalytic effect is less pronounced.

In this study, three esters of acetic acid with linear and branched aliphatic alcohols were synthesized in the presence of a pulsed electric field and enzymatically. The synthesis of some esters using a pulsed electric field as catalysts was demonstrated for the first time, the obtained results being a starting point in the synthesis of "green" esters.

The highest amounts of ester, in the case of pulsed electric field synthesis, were obtained for *n*-propyl acetate, significantly higher than in the case of enzymatic synthesis. The synthesis of *i*-butyl and *i*-amyl acetate in pulsed electric field synthesis shows the formation of lower amounts of ester, probably due to the branched chain of the alcohol.

According to the literature data, a such behavior can be explained taking into consideration the difference between values of the relative polarization of the molecules for the 3 studied alcohols. The greater relative polarization, the more effect of the pulsed electric field is more intense, orienting the alcohol molecules in favorable positions of effective clashes, which materializes by obtaining higher quantities of ester compared to the reactions in which alcohols with lower relative polarizations are used (branched chain alcohols with bigger molecules) [15].

Therefore, starting from raw materials of natural origin, it was demonstrated that natural esters can be obtained using the method presented in this study and it can be used in the food industry because the use of electricity as a catalyst is a natural process, thus it does not have any harmful effect.

On the other hand, flavorings used in the food industry are obtained exclusively enzymatically, which means a higher production cost due to the high price of enzymes as well as the necessary equipment. Therefore, the price of the finished product (flavor) will be higher.

In conclusion, starting from raw materials of natural origin and using as catalyst an alternative pulsed electric field, natural esters can be obtained with a significantly lower production cost than in the case of obtaining esters for the food industry using enzymes as catalysts.

EXPERIMENTAL SECTION

Materials

The reagents used for these studies are commercial and they have been used without further purification: acetic acid (99%, Chimreactiv), *n*-propanol (99%, Merck), *i*-butanol (99%, Merck), *i*-amyl alcohol (99%, Merck), acetone (99%, Merck), decane (99%, Merck), enzyme: lipase *Candida antarctica* - lipase B (Genofocus).

Enzymatic synthesis

In 5 mL Eppendorf tubes predetermined volumes of acetic acid and alcohol (*n*-propanol, *i*-butanol and *i*-amyl alcohol) corresponding to the molar ratios of acid: alcohol = 1:2, 1:1 and 2:1 were added, and then the enzyme *Candida antarctica* lipase B was added, representing 1% of the reaction mass.

The reactions were incubated at 50°C, 1000 rpm and samples were collected at predetermined time intervals: 2, 4, 6, 10, 12 and 26 hours.

Synthesis using a pulsed electric field as catalyst

In a 30 mL glass mini-reactor (figure 4), predetermined volumes of acetic acid and alcohol (*n*-propanol, *i*-butanol and *i*-amyl alcohol) corresponding to the studied molar ratios (acid : alcohol = 1:2, 1:1 and 2:1) were added for a total volume of 25 mL reaction mass. A stainless steel electrode connected to an electronic power amplifier which generates high voltage (5000 V) with a frequency of 20 kHz (rectangular signal), it was inserted inside the glass reactor that on the outside of it is provided with a thin copper sheet sheath that constitutes the external electrode connected to the ground of the device.

The reactions were incubated at 50°C with stirring at 1000 rpm and samples were collected at predetermined time intervals: 2, 4, 6, 10, 12 and 26 hours.

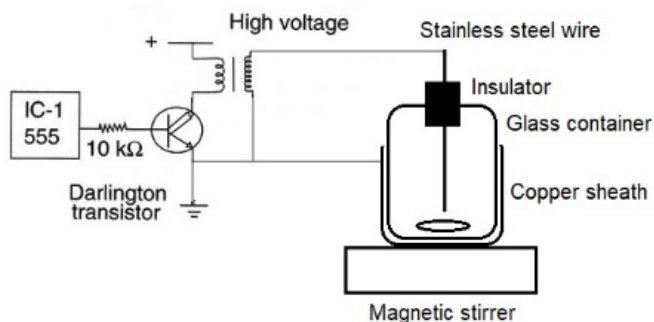


Figure 4. Device used for synthesis of esters using a pulsed electric field.

The amount of esters (mg) obtained for all the reactions (pulsed electric field and enzymatic synthesis) was monitored by flame ionization gas chromatography using acetone as solvent, and decane was used as the internal standard. Chromatographic analyses were performed using a Varian 450-GC chromatograph with autosampler and the parameters used were: injector temperature: 250°C, detector temperature: 300°C, temperature range: from 40°C to 80°C (10°C/min), carrier gas pressure (hydrogen): 10 psi. The mixture (1000 µl) subjected to GC analysis consisted of: 100 µl of reaction mass, 880 µl acetone and 20 µl decane (internal standard).

Confirmation of acetates formation was performed using the classical spectral methods (data not shown):

- Fourier-transform infrared spectra (FT-IR) for the obtained samples were performed using a Bruker Vertex 70 spectrometer (Bruker Daltonics GmbH, Germany) equipped with a Platinum ATR spectrometer, Bruker Diamond Type A225/Q1.

- Mass spectra were recorded with GC-MS Thermo-Scientific TRACE 1310 gas chromatograph, ITQ1100 Ion Trap MS. The parameters used in the GC-MS analysis were: transfer line temperature: 310°C, injector temperature: 250°C, the gas flow was 1ml/min in the reading range 50-500 m/z.

- NMR spectra were recorded with the Bruker FOURIER 300 NMR spectrometer in CDCl₃.

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