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EFFECTS OF AUDIO FREQUENCY ELECTRIC FIELDS ON THE ESTERIFICATION REACTIONS OF ACETIC ACID WITH C4-C8 BRANCHED ALCOHOLS

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ABSTRACT. The esterification reactions, which lead to esters with a big diversity of uses across numerous industries, is one of the most important reactions in organic synthesis. Within these esterification reactions, a variety of strategies have been used to improve conversion, reaction rate, and equilibrium. This paper investigated the effects of the audio frequency electric fields on the esterification reactions of acetic acid with C4-C8 branched aliphatic alcohols. The aim of these studies was to synthesize a few acetic acid esters in an environmentally and friendly manner utilizing a new method. The only raw materials used were acetic acid, C4–C8 branched aliphatic alcohols and an audio frequency electric field acting as an accelerator. In order to determine the efficacy of the suggested approach, these esters were also synthesized without applying the audio frequency electric field. Analysis using gas chromatography technique revealed that the audio frequency electric field significantly increased esterification yields. The highest yields of ester were obtained for 2-octyl acetate, exhibiting a notable increase in comparison to the synthesis that did not employ the application of an audio

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frequency electric field as an enhancer of the reaction rate. The proposed new method, as well as the employing of raw materials of natural origin, allows the production of esters in an environmentally friendly manner and with reduced costs. These esters can be used without any restrictions in a variety of industries, including food, pharmaceuticals, and cosmetics.

Keywords: *audio frequency electric field, esterification reactions, natural esters, food and pharmaceutical industry, green method*

INTRODUCTION

A wide range of flavors and fragrances are used in the pharmaceutical, food and drink industries. [1]. The most utilized substances in these industries are esters, which are typically obtained through Fischer esterification. However, there are numerous alternative methods, including Tishchenko condensation and the addition of a carboxylic acid to an alkene, which are less prevalent. [2, 3]. Also, the most recent techniques of ester synthesis are transesterification reaction, assisted by microwaves, pulsed electric fields or visible light [4 - 9].

If the esters should be utilized within the food or pharmaceutical industries, it is imperative that they are derived from natural sources. Two main methods exist for the synthesis of natural esters, the first one employing chemical reaction, typically utilizing enzymes (especially lipases) as catalysts, and the second one conducted in the presence of an electromagnetic field which serves as catalyst [10-11].

The most utilized enzymes used in the synthesis of esters belong to the *Candida, Hanseniaspora, Kluyveromyces or Pichia* families.

Although the use of enzymes in esterification reactions is a natural process, allowing the resulting esters to be classified as “natural” (and thus eligible for unrestricted use in food), the high cost of these enzymatic biocatalysts will inevitably result in elevated final production costs [10].

In the light of these findings, a novel synthesis method was proposed that employs an audio frequency electric field as a catalyst. This method enables the classification of the resulting esters as “natural,” provided that the raw materials are of natural origin, as the audio frequency electric field has been found to have no adverse effects. The esterification process in the presence of an electric field has the advantage of requiring only the necessary reactants, such as alcohol and acid. If these are obtained by fermentation, the resulting esters would be 100% natural, devoid of any synthetic by-products and are suitable for the use in the food industry or in the manufacture of pharmaceutical products [12]. Within this study, the synthesized esters were: *2*-butyl acetate, *2*-pentyl acetate, *2*-hexyl acetate, *2*-heptyl acetate and *2*-octyl acetate (Figure 1). The selection of these esters was based on their potential applications in the pharmaceutical, food, and cosmetic industries [13-22].

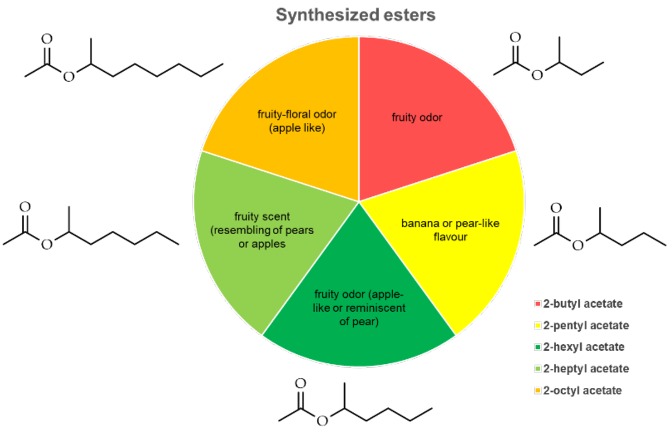

Figure 1. The esters obtained in this study and their flavoring characteristics.

RESULTS AND DISCUSSIONS

In these investigations, two frequencies (3 kHz and 6 kHz) and two temperatures (20°C and 50°C) were used to synthesize five acetic acid esters with branched aliphatic C4–C8 alcohols in the presence of an audio frequency electric field. The results are expressed as yields of esters obtained after 24 hours at the 2 frequencies used, compared to the ones obtained without applying the audio frequency electric field.

According to the experimental determinations, the esterification reaction of acetic acid with branched alcohols was positively impacted by the audio frequency electric field. The application of the audio frequency electric field leads to a better orientation of the molecular dipoles of acetic acid and alcohols increasing the probability of effective collisions, which raises the yields of ester.

It is already well known that the temperature has a big impact on the esterification reactions. In particular, the yields of ester are diminished when lower temperatures are employed in the esterification reaction in comparison to the yields obtained when higher temperatures are utilized. As a result, the yields of esters obtained when the reactions were performed at 20°C were lower than those obtained when the syntheses were performed at 50°C.

The optimal frequency that produced the highest yields of ester was 6 kHz for both scenarios (when the syntheses were conducted at 20°C and 50°C). This phenomenon can be attributed to the fact that the effect of the applied audio frequency electric field is more pronounced when a higher frequency is employed, orienting the alcohol molecules in favorable positions for efficient collisions with the acid molecule, which ultimately results in the attainment of higher yields of ester at the two used temperatures.

When the reactions were carried out at 20°C (Figure 2) and 3 kHz, the yields of ester varied in the range 1.1% - 6.4%, the highest one registering for *2*-octyl acetate, while in the case of using 6 kHz, the yields of esters varied in the range 1.3% - 7.0%, the highest one registering also for *2*-octyl acetate. In the case of the reactions conducted without applying the audio frequency electric field, it was observed that the yields of ester were lower than in the case of using it, more precisely, they varied in the range 0.9% - 5.7%.

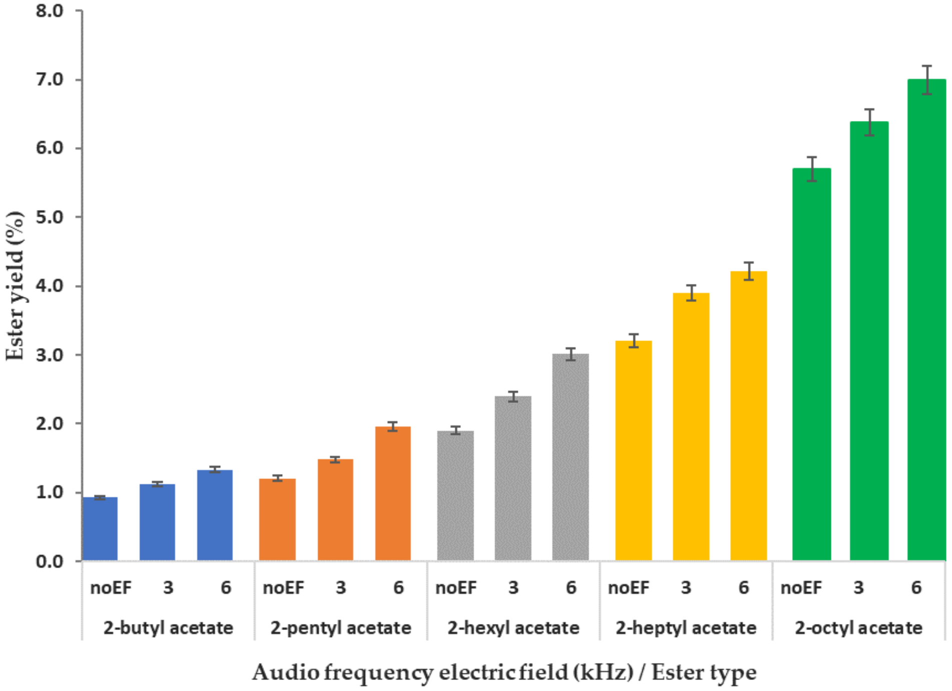

Figure 2. Effect of the audio frequency electric field (kHz) on the ester yield in esterification reactions operated at 20°C. (noEF—in the absence of an electric field).

The reactions performed at 50°C (Figure 3) and 3 kHz showed that the yields of ester varied in the range 4.9% - 14.1%, the highest one registering for *2*-octyl acetate. When 6 kHz was used, the yields of ester varied in the range 5.7% - 17.8%, the highest one registering also for *2*-octyl acetate. The reactions performed without applying the audio frequency electric field showed that the yields of ester were lower than in the case of using it, more precisely, they varied in the range 4.1% - 10.5%.

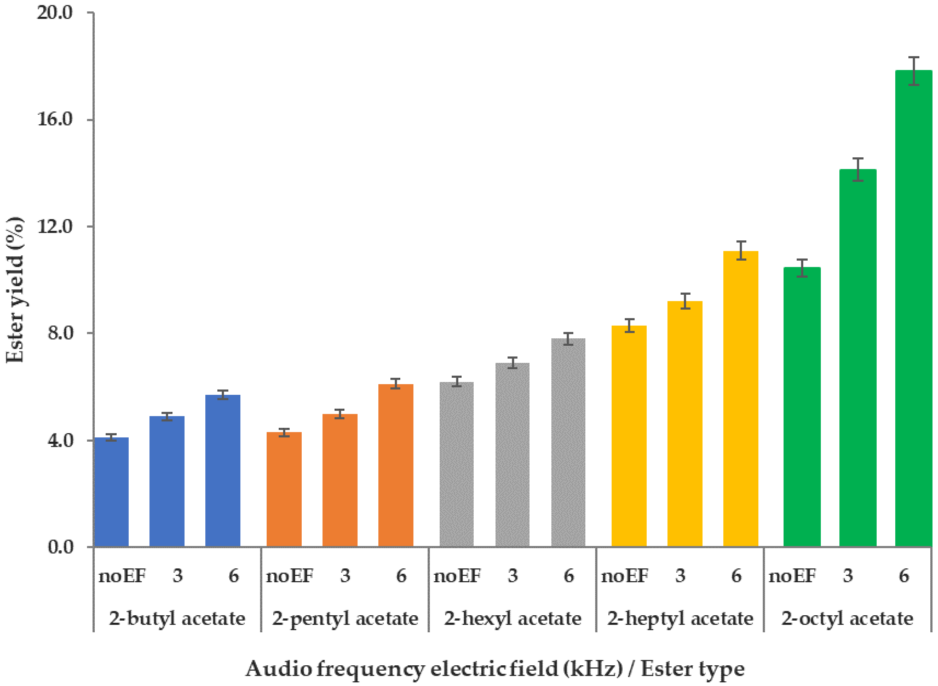

Figure 3. Effect of the audio frequency electric field (kHz) on the ester yield in esterification reactions operated at 50°C. (noEF—in the absence of an electric field).

In comparison to the yields of esters obtained in the case of standard esterification (the electric field has not been applied), it can be concluded that the application of an audio frequency electric field resulted in higher ester yields for all reactions, irrespective of temperature or frequency.

It can also be concluded that the optimum frequency (within this study) was 6 kHz for all the reactions carried out and that the highest yields of ester were obtained for 2-octyl acetate.

Mechanism of esterification using the audio frequency electric field as catalyst

The esterification reaction typically requires the use of a catalyst, usually an acid, in order to increase the yield of the reaction. However, in the presence of an audio frequency electric field, the reaction can be positively influenced by polarizing the reactant molecules, reducing the activation energy and favoring molecular orientation.

The proposed mechanism of the esterification reaction using an audio frequency electric field as a catalyst can be divided into six steps as follows:

1. Polarization of the reactants: the application of an audio frequency electric field has the effect of polarizing the reactant molecules, making the carboxylic acid more electrophilic and the alcohol more nucleophilic due to the alignment of their dipole moments.

2. Nucleophilic attack: the polarized alcohols are easier to attack the carbonyl carbon of the carboxylic acid, with the formation of tetrahedral intermediates, more specifically, the audio frequency electric field increases the electrophilicity of the carboxylic acid and the nucleophilicity of the alcohol, which makes nucleophilic attack more favorable and simpler.

3. The formation of a tetrahedral intermediate is a subsequent consequence of the nucleophilic attack. This intermediate is stabilized by the audio frequency electric field, which aligns the dipoles and reduces the activation energy.

4. A proton transfer occurs within the tetrahedral intermediate, leading to the formation of a more stable intermediate. The audio frequency electric field plays a stabilizing role in this process, facilitating the transfer of protons.

5. Dehydration: The application of an audio frequency electric field serves to facilitate the elimination of a molecule of water from the tetrahedral intermediate. This is achieved by stabilizing the transition state and thereby reducing the activation energy that is required in this instance.

6.The final stage is the ester formation and the release of water. Throughout this process, the audio frequency electric field orients and stabilizes the molecules, enhancing the reaction yield even in the absence of a catalyst.

The effect of the audio frequency electric field can be summarized as follows: the polarization of the reactant molecules is achieved, increasing their reactivity; this is accomplished by making the carbonyl carbon more electrophilic and the alcohol’s oxygen more nucleophilic. Furthermore, the stabilization of intermediates and transition states is facilitated, reducing the activation energy and additionally, orienting the reactant molecules in such a way that makes the reaction more favorable and efficient [11], [23].

CONCLUSIONS

The results of experimental syntheses demonstrated that the audio frequency electric field has a beneficial effect on the esterification reactions of acetic acid with branched alcohols.

Within these studies, five esters of acetic acid with C4-C8 branched aliphatic alcohols were synthesized for the first time using an audio frequency electric field as enhancer of the reaction yields, the proposed method being a sustainable way in the synthesis of “green” esters.

The highest yields of ester were obtained for *2*-octyl acetate in the case of the synthesis using the audio frequency electric field, which were significantly higher than within the synthesis without applying it. Although the synthesis of the other esters proceeded with lower yields of esters, in all situations the yields were higher than in the standard esterification case (without the application of an audio frequency electric field).

The methodology outlined in this study demonstrated efficacy in the production of natural esters which can be used in a variety of industries, including food, pharmaceuticals, and cosmetics, without any restrictions due to the non-harmful effect of the catalyst, which is an audio frequency electric field.

EXPERIMENTAL SECTION

Materials

The reagents used for the below mentioned synthesis are commercial and they had been used without further purification: acetic acid (99%, Merck), *2*-butanol (99%, Merck), *2*-pentanol (99%, Merck), *2*-hexanol (99%, Merck), *2*-heptanol (99%, Merck), *2*-octanol (99%, Merck), acetone (99%, Merck) and nitrobenzene (99%, Merck).

Synthesis using the audio frequency electric field as catalyst

The experimental setup for the synthesis was reported in our previous work [24].

The device used during this study consists of a reaction vessel represented by a cylindrical capacitor connected to the secondary coil (with high number of turns) of a resonant transformer with an open ferrite core. The capacitor has a capacity of 100 pF, as determined by the LCR-meter 880 BK Precision. This capacitor is provided with external copper thermostatic jacket as armature which is also the external cylindrical electrode connected to the ground of the device. The dielectric medium comprises the reaction mass and the glass vessel in which the physical-chemical phenomenon occurs.

The reaction vessel/reactor is made of glass and is provided with a stainless-steel central electrode. An electric field is established between this central electrode and the external thermostatic coil, which will be maintained at a constant intensity of 13.5 kV/cm throughout the experiments by adjusting the amplitude of the input signal. The electric capacity of the reactor and the inductance of the transformer's secondary coil combine to create a parallel LC circuit that can be adjusted to a desired frequency of 1–10 kHz by adjusting the ferrite core. The electrostatic voltmeter with very high impedance is used to measure the intensity of electric field (of the order of kV/cm). A sinusoidal signal generator with adjustable frequency (1 – 10 kHz) and amplitude (0 – 1 V) provides the amplifier's input signal.

The primary coil of this resonant transformer consists in a low number of turns connected in series with an equivalent capacitor made by the connection in parallel of 1 to 19 fixed condensers of 0.1 μF each one. The working capacity of this equivalent capacitor depends on the number of fixed capacitors connected, and each fixed capacitor can be individually inserted into the circuit by manipulating 19 ON-OFF contacts. This creates a series LC circuit that is adjusted at resonance of the working frequency by varying the above-discussed equivalent capacity and it is the load of the power amplifier built using TDA2003 integrated circuit. The correct tuning of this resonant circuit on the working frequency is estimated by ensuring that the filament lamp connected in series has the maximum illumination.

Predetermined volumes of alcohol and acetic acid in a 1:1 molar ratio were added to the 30 mL glass mini-reactor to create a total volume of 20 mL reaction mass. The reactions were incubated at 20°C and 50°C, with stirring and samples were collected, for each reaction, 24 hours later. All the esterification experiments were carried out in duplicate, and the mean values were taken into consideration.

The obtained esters were subjected to gas chromatography (data not shown), using a Varian 450 Chromatograph (Varian Inc., Utrecht, The Netherlands) equipped with a flame ionization detector (FID), and a 15 m x 0.25 mm VF-1ms non-polar capillary column with a 0.25 μm film thickness.

The GC analysis conditions were: oven temperature 50°C (0.5 min) – 75°C (1 min), with a heating rate of 3°C/min, injector temperature 300°C, detector temperature 350°C, and carrier gas flow (hydrogen) 2.0 mL/min. Samples were diluted with acetone and a quantitative analysis was performed using nitrobenzene as an internal standard, and the ester yield was determined based on GC data. All gas chromatographic analyses of the samples were performed in triplicate.

The structure of the esters was validated by GC-MS using a Hewlett-Packard HP6890 gas chromatograph and HP5973 mass spectrometer (Agilent Technologies, Santa Clara, California, USA) with electron ionization (EI) of 70 eV. Prior to analysis, the ester samples were diluted 1:10 in acetone. A DB-WAX high-polarity, polyethylene glycol (PEG) capillary column (30 m*0.25 mm*0.25 µm film thickness) (Agilent Technologies J&W Scientific INC.) was used. The analysis conditions were: oven temperature from 50°C to 250°C with a rate of 5°C/minute, a final hold of 5 min, and a flow rate of 1 mL/min. The MS conditions were: source temperature was set at 230°C, quadrupole detector temperature was set at 150°C. The MS detector was set in scan mode and the mass range of compounds was from 50 to 600 amu and started to register after 3 minutes of solvent delay. MS software used was: Chemstation Data Analysis (Agilent Technologies, Santa Clara, California, USA) and AMDIS (NIST, Gaithersburg, MD, USA).

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