IOSUD - Universitatea Politehnica Timişoara
Şcoala Doctorală de Studii Inginereşti

SYNTHESIS OF ESTERS FOR FOOD AND PERFUMERY INDUSTRIES USING AN ELECTROMAGNETIC FIELD

PhD Thesis – Abstract

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In the perfumery and food industry, flavoring and odorant agents (natural or synthetic) play an essential role, as their use in these products brings significant benefits, such as:

- achieving the desired organoleptic properties of a food product or a perfume;

- improving/enhancing an existing aroma that, due to the technological process, may suffer degradation, finally leading to unsatisfactory organoleptic properties;

- commercial purposes: the use of different flavors in perfumes or foods can decisively influence the buyer's decision to purchase that product, making it more attractive from a sensory perspective;

- economic considerations: the use of aromas obtained through chemical synthesis is much more cost-effective than using natural flavors [1].

A compound or a mixture of compounds (natural or synthetic) added to a food product in order to provide a specific aroma or to improve an existing one is called a flavoring agent, while odorants are natural, semi-synthetic, or synthetic chemical substances used for their olfactory properties [1].

The food and fragrance industries have experienced impressive development in recent decades, leading to an increasing demand for flavoring and odorant compounds in these industries [2].

Since obtaining aromas and odorants (for use in the perfumery and food industries) by extracting them from natural sources is a laborious, difficult, and costly operation, the use of various synthesis methods (chemical, enzymatic, electromagnetic field-assisted, etc.) for these compounds has become increasingly important both practically and economically [2].

While the perfume industry can utilize chemically synthesized flavoring and odorant compounds, the food industry is restricted to using only natural ones. These must be obtained either through extraction from natural sources (such as fruits, vegetables, and plants) or by synthesizing them from raw materials of natural origin using a natural catalyst, such as enzymes or electromagnetic fields. [2, 3].

Even though a wide variety of chemical compound classes are used in these industries, esters represent a commonly used group of substances due to their organoleptic properties (pleasant smell and taste, generally associated with fruits) and because their production processes are easier compared to other compounds with flavoring or odorant properties. For example, some of the most used esters in the food industry are isoamyl esters, particularly isoamyl acetate, due to its characteristic and strong banana-like aroma. In 2020, isoamyl acetate sales were estimated at approximately $205 million, while in 2030, sales are estimated to reach approximately $455 million [4, 5].

Esters represent a widely used class of compounds in the food, perfumery, and cosmetics industries because, from an organoleptic and sensory point of view, they provide a floral or fruity aroma and scent. Thus, the use of esters in food products either enhances their aroma or replaces the base flavor, while in the perfume or cosmetics industries, these compounds improve the organoleptic characteristics of the final products [2, 3].

Although there is a big variety of esters used in the perfumery and food industries, the most preferred ones are those with organoleptic properties similar to certain plants or fruits (figure 1), such as:

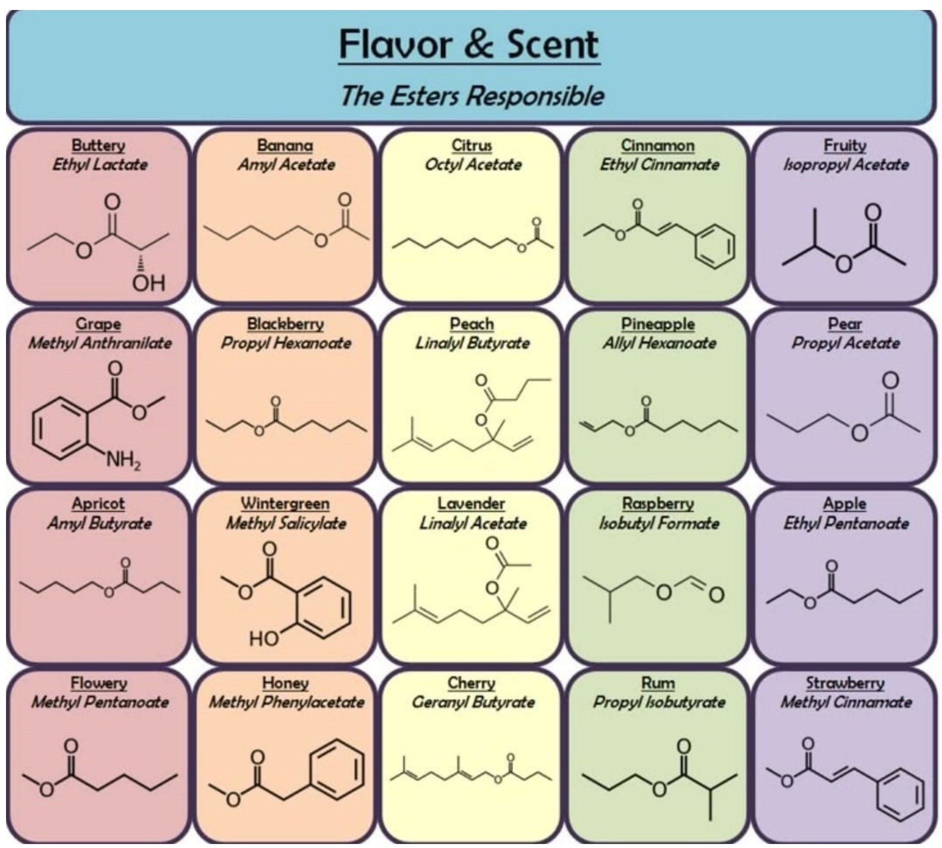

Figure 1. Esters used in the perfumery and food industry (figure adapted from [6])

Esters can be obtained through various synthesis methods, but the most common and simplest method is the Fischer esterification (figure 2), which involves the reaction between a carboxylic acid and an alcohol (usually in the presence of an acid catalyst), resulting in the formation of an ester with the elimination of a water molecule [7, 8].

This thesis is based on a series of reactions performed through Fischer esterification, but instead of a classic acid catalyst, an environmentally friendly approach is employed, specifically, using an audio frequency electric field as catalyst.

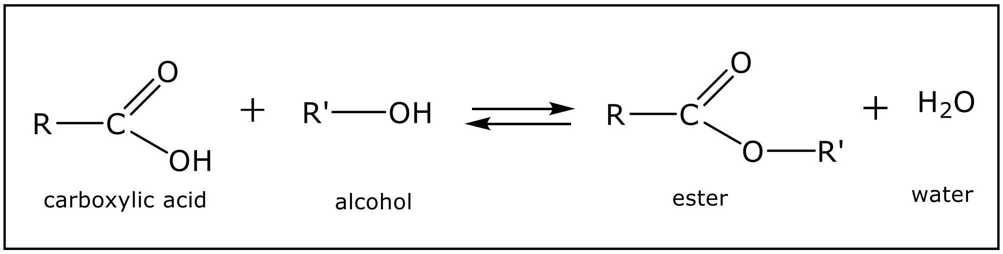

Figure 2. Esterification reaction

The subject of this doctoral thesis is based on the increasing need to produce these esters for the food and perfumery industries, respecting the essential requirement that they must be natural. Thus, the research conducted for this thesis was guided by the following specific objectives:

1. Design, development, and practical implementation of the experimental esterification device using an audio frequency electric field

Specific activities:
- designing and constructing an experimental device;
- device calibration and optimization;
- testing the performance of the developed device.

2. Synthesis of acetic acid esters with linear and branched chains

Specific activities:
- esterification of acetic acid with linear aliphatic C4-C8 alcohols;
- esterification of acetic acid with branched aliphatic C4-C8 alcohols;
- assessing the efficiency of the method at two different temperatures and two different operating frequencies.

3. Proposal of a possible reaction mechanism

Specific activities:
- formulating a probable reaction mechanism;
- evaluating the influence of the audio frequency electric field on the esterification reaction.

4. Assessment of the environmental sustainability of the proposed original synthesis method

Specific activities: evaluating the ecological character of the method using the AGREE software.

This doctoral thesis is structured into two parts:
- part I, which includes the literature review, consisting of chapters 1, 2, 3, and 4.
- part II, which comprises the experimental studies, consisting of chapters 5, 6, 7, 8, 9, 10, and 11.

Chapter 1 provides a brief introduction to the significance of flavoring and odorant compounds in the food and perfumery industries, focusing on esters.

Chapter 2 discusses classical esterification methods, including chemical methods such as Fischer esterification, Tishchenko condensation, transesterification, and the addition of a carboxylic acid to an alkene, as well as enzymatic methods and ultrasound-assisted synthesis techniques.

The objective of chapter 3 is to review modern techniques for ester synthesis, specifically those methods that utilize an electromagnetic field as a “catalyst.”

Chapter 4 presents the motivation, purpose, and objectives of the research conducted in this doctoral thesis.

Chapter 5 focuses on the design, development, and practical implementation of the experimental esterification device using an audio frequency electric field.

Chapter 6 covers the gas chromatographic methods used for the qualitative and quantitative analysis of the synthesized esters.

Chapter 7 presents the proposed original working method, and the results obtained for the synthesis of linear esters of acetic acid with linear C4-C8 alcohols: *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-heptanol, *n*-octanol, using this method and the experimental device presented in chapter 5.

Chapter 8 evaluates the applicability of using the method presented in chapter 7 also for the synthesis of branched-chain esters of acetic acid with C4-C8 branched alcohols: *2*-butanol, *2*-pentanol, *2*-hexanol, *2*-heptanol, *2*-octanol, using the same experimental device presented in Chapter 5.

Since the obtained results indicated a positive influence using the audio frequency electric field on the esterification reactions, an evaluation of the catalytic effect of this field applied to the esterification reactions presented in this thesis, as well as the proposal of a reaction mechanism, is carried out in chapter 9.

In chapter 10, an evaluation regarding the ecological aspects of the proposed method has been carried out and the results confirmed that the method proposed in this thesis fulfills the principles of "Green Chemistry" and thus the method can be considered as environmentally friendly.

Finally, chapter 11 highlights the final conclusions of these studies as well as the original contributions of the thesis.

The first specific objective of the thesis was the design, development and practical realization of the original experimental device for esterification in audio frequency electric field (chapter 5). The design and practical realization of the experimental device was the essential element of the present research, without which the main aim of the thesis could not have been achieved. According to figure 3, this device consisted of:

- resonant transformer - generates the high voltage that will provide the audio frequency electric field used in the esterification reactions;
- the audio frequency amplifier - amplifies the audio frequency signal supplied by the signal generator up to an attack level of the primary coil of the resonant transformer;
- audio frequency amplifier power supply;
- electrostatic voltmeter (for which a **patent** has been obtained) - allows to measure the high voltage of the order of kV at the terminals of the LC circuit, where C is the electrical capacity of the esterification reactor [9];
- 19 fixed capacitors - can be inserted one at a time into the circuit and provide series LC tuning of the primary low-voltage coil of the resonant transformer on the working frequency set for each individual experimental protocol;
- copper serpentine allowing the temperature condition of the reaction mixture wrapped around the glass mini-reactor;
- the reaction vessel - the glass mini-reactor in which the reaction takes place and is basically a cylindrical capacitor connected in parallel with the high-voltage coil of the resonant transformer;
- digital multimeter - monitors the intensity of the electric current supplying the audio frequency amplifier, thus making it possible to calculate the power absorbed by this experimental device from the power supply;
- incandescent bulb - allows visual estimation of the intensity of the audio frequency

current feeding the primary circuit of the resonant transformer;

- magnetic stirrer - ensures homogenization of the reaction mixture.

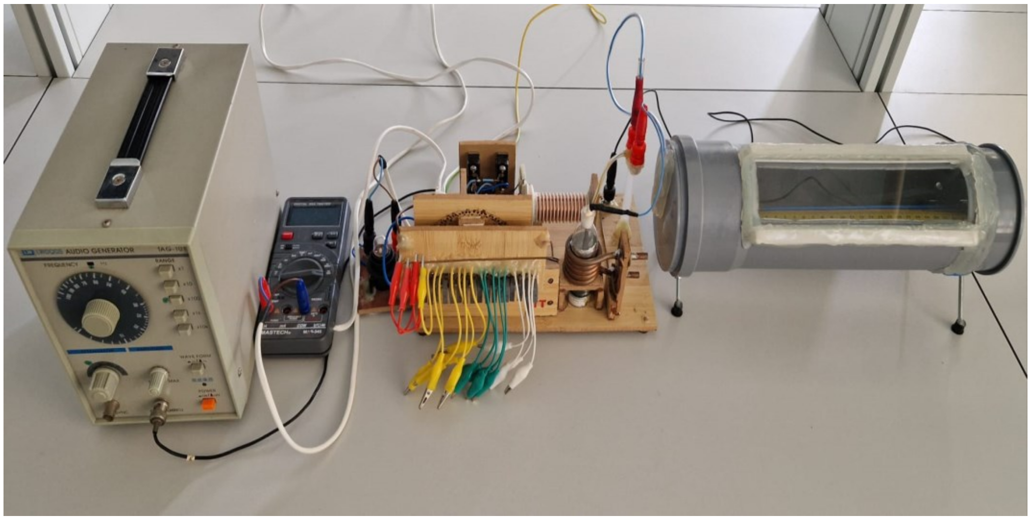

Figure 3. Device used for the "green" synthesis of esters using an audio frequency electric field (figure adapted from [10])

Once the first objective was successfully achieved, the next step was to test the experimental device by synthesizing some esters of acetic acid with C4-C8 linear aliphatic alcohols (chapter 7). In all reactions studied, the ester yields were higher when the audio frequency electric field was used as catalyst compared to reactions carried out in its absence. For the reactions carried out at 20°C and 3 kHz, ester yields varied in the range 2,5% - 11,3%, the highest reaction yield being recorded for *n*-octyl acetate. When reactions were performed using 6 kHz, the ester yields varied in the range 3,5% - 12,0%. In the case of the reactions carried out without the application of the audio frequency electric field, the ester yields obtained were lower (1,7% - 10,5%). Increasing the reaction temperature at 50°C, the reaction yields increased, so that at 3 kHz they varied in the range 12,5% - 24,9%, and the highest reaction yield was recorded for *n*-octyl acetate. When an electric field of 6 kHz audio frequency was used, the yields varied in the range 13,4% - 27,9%, and the highest yield was also obtained for *n*-octyl acetate. When the reactions were carried out in the absence of an audio frequency electric field, the ester yields were lower, varying in the range 8,9% - 17,5%. The frequency at which the highest yields were obtained was 6 kHz (in this study) for all reactions carried out, regardless of the working temperature. Due to the orientation of the molecular dipoles in the audio frequency electric field, the probability of effective collisions was higher and thus higher ester yields were obtained [10].

Since the results obtained for the syntheses of linear chain esters proved to be successful, the experimental device was also tested for obtaining branched-chain esters, specifically esters of acetic acid with branched C4-C8 alcohols (chapter 8). Also in this case, the ester yields obtained via esterification using the audio frequency electric field as catalyst were also higher than for the syntheses without its application. When the reactions were carried out at 20°C and 3 kHz, the ester yields varied in the range 1,1% - 6,4%, the highest one registering for *2*-octyl acetate, while when using 6 kHz, the ester yields varied in the range 1,3% - 7,0%, the highest one registering for *2*-octyl acetate, as well. In the case of reactions carried out without the application of the audio frequency electric field, it was observed that the ester yields were lower than the ones obtained when using the electric field, they varying in the range of 0,9% - 5,7%. The reactions carried out at 50°C and 3 kHz showed that the ester yields varied in the range 4,9% - 14,1%, the highest one being recorded for *2*-octyl acetate. When operated at 6 kHz, the ester yields varied in the range 5,7 % - 17,8 %, the highest one obtained being for *2*-octyl acetate. The reactions performed without the application of the audio frequency electric field showed that the ester yields were lower than with its use, specifically, they varied in the range 4,1% - 10,5%. The highest ester yields were obtained for *2*-octyl acetate, and the frequency at which the yields were highest (in the present study) was 6 kHz [11].

Due to the fact that the obtained results indicated a positive influence of the audio frequency electric field on the esterification reactions, another proposed objective was to identify a probable reaction mechanism, more specifically to evaluate the catalytic effect of the audio frequency electric field on the performed esterification reactions (chapter 9). The main effects of the application of this field are: polarization of acid and alcohol molecules, reduction of energy activation, as well as favorable orientation of reactant molecules leading to a more efficient reaction and higher ester yields [12].

Finally, as "Green Chemistry" has developed more and more over the years, and since the year 2000, the "greenness" of chemistry has received an increasingly important statute, a study was carried out on the environmental aspects of the proposed new synthesis method using the AGREEprep software, as well as the analytical technique (gas chromatography) using the AGREE analytical GREEnness software (chapter 10). The obtained results showed a high score for both the synthesis method (0,66) and the analytical technique (0,7), results which confirm the "greenness" of the 2 methods [13, 14].

The main original contributions of these studies are:

1. general aim of the thesis:
- to synthesize flavor and odorant compounds (in this case esters) using a new method;
- to design a plant to synthesize these compounds in an environmentally friendly manner;
2. to propose a design of the experimental device
3. testing the experimental device;
4. the choice of the synthesized esters (esters of acetic acid with linear and branched C4-C8 alcohols), and determination of the method and working parameters;
5. carrying out the experiments;
6. performing chromatographic analyses for qualitative and quantitative analysis of the synthesized esters;
7. interpretation of the obtained experimental results;
8. proposal of a possible reaction mechanism and evaluation of the catalytic effect of the use of the audio frequency electric field as a "catalyst" of the esterification reaction;
9. validation of the proposed method highlighting its advantages compared to the synthesis by the classical route, performed only by heating the reaction mass at the temperatures presented in the study without using an acid catalysts;
10. validation of the method from a "Green Chemistry" point of view, evaluating its "greenness".

In conclusion, the general objectives of the study, presented above, have been fully achieved and it can be stated that this thesis has reached the aim for which it was conceived, to design an experimental device allowing the environmentally friendly synthesis in audio frequency electric field of odorant and flavoring compounds (in this case esters) usable in the food and perfumery industry, respecting the essential condition that they must be natural/identically natural.

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