ULTRASOUND ASSISTED SYNTHESIS OF *ISO*AMYL ACETATE CATALYSED BY ACIDIC ION EXCHANGE RESIN

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Esterification of acetic acidic with isoamyl alcohol in heterogeneous phase was performed in the presence of acidic ion exchange resin. A method of enhancing the performance of resin is the use of ultrasounds. In the present paper a study on ultrasound-assisted esterification catalyzed by cation exchange resin for flavor esters preparation using a continuously micro-reactor is presented. The method is efficient and friendly for the environment, and it has shown significant improvements compared to conventional method.

Keywords: isoamyl acetate, ultrasound, ion exchange resin, heterogeneous esterification

1. Introduction

Isoamyl acetate is a strong flavor used in the food industry, the banana flavor, chemically obtained from an alcohol and an organic acid in the presence of an acid catalyst or by extraction from natural sources. The isoamyl alcohol ester, especially isoamyl acetate, has numerous industrial applications [1]. As an artificial flavor, it has uses in foods with an artificial flavor of banana and pear, for the preservation of carbonated juices, as an additive added to cigarettes, is used also as solvent for tannins, nitrocelluloses, lacquer, celluloses and camphor. The isoamyl acetate also finds applications in the production of celluloid cements, waterproof lacquer, silk, leather or artificial pearls, for photographic films, metallic paints and bronzing liquids [2-4].

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Esterification reactions are normally carried out using acid catalysts (hydrochloric acid, sulfuric acid, chlorosulfonic acid, *p*-toluenesulfonic acid etc) in the homogenous phase [5]. The disadvantages of these catalysts are the separation of products from the reaction mixture with loss of catalyst, corrosion and environmental problems [2]. Isoamyl acetate has also been synthesized in lipase-catalyzed processes in organic solvents, in solvent-free systems, with supercritical carbon dioxide and recently also in ionic liquids media [6-8]. These methods have disadvantages like unsatisfactory yields, low purity, longer reaction times and high temperatures offering sometimes an uneconomical approach [7, 9, 10]. Lately, heterogeneous technological production with the application of ion exchange resins became more attractive when compared to classical homogeneous esterification due to economic benefits, the easier separation of product and catalyst recovery [11].

The most widely used reactor design for isoamyl acetate synthesis is batch reactor, but due to their low amount produced caused by volumetric limitations in size, packed bed reactors are preferred at industrial scale. Microreactors are gaining importance in a wide range of industries, because of advantages like better selectivity, improved yields over shorter periods of time, increased process control, greater safety, flexible production, and the opportunity to tap into previously avoided or novel chemistries, the possibility of numbering up instead of the usually problematic scale-up. Catalytic packed bed microreactors, continuously operated have gained a lot of attention, since they offer easier product recovery, extended operational life of the catalyst, and, in some cases, also diminishes the possibility for reverse reaction to occur [12-14].

To intensify the resin catalysed esterification an ultrasound assisted system can be used [15, 16]. In liquids, ultrasonic energy can be applied with different ultrasonic equipment like ultrasonic bath, ultrasonic probes, a tube type ultrasonicator or flat plate ultrasonicator [17, 18]. The alternate compression and rarefaction cycles of acoustic waves propagation in liquid defines the cavitation phenomenon [19]. This phenomenon is described as the generation of micro bubbles or cavities. These bubbles grow to a maximum size in the end collapsing violently leading to a large energy dissipation locally, with high temperatures and pressures. The presence of solid particles near the collapsing bubbles in the liquid can produce an asymmetric collapse. Therefore, in heterogeneous systems, using solid catalysts, due to the resistance of surface to the liquid flow, the collapse of a cavitation bubble is asymmetrical. This resistance led to a break of liquid from the side of the bubble causing the formation of high-pressure liquid jet directed at the surface. This phenomenon increases the mass transfer rates through the interfacial film and thus the reaction rates are enhanced [20]. The advantages of ultrasounds are better processing time, increasing the product quality, reducing chemical and physical hazards, higher productivity, yield and selectivity [21].

The purpose of our research is to study the intensification with ultrasound of the esterification process in a continuously operated microreactor using acidic cation-exchange resin. Combining ultrasonication with the continuous esterification process is an added novelty to the conventional method of synthesis of isoamyl acetate. The esterification reaction of acetic acid with *iso*amyl alcohol was performed using an ion exchange resin – Dowex 50W(X8) as catalyst. In addition, effects of temperature, ultrasonic power and duty cycle on heterogeneous esterification process were undertaken.

2. Materials and methods

2.1.Materials

All chemicals used for esterification: *iso*amyl alcohol (Merck), acetic acid (Merck), *iso*amyl acetate – standard for GC analysis (Aldrich) were analytical grade and were used as supplied. For the retention of water, molecular sieves of the type 3 Grace Davison SYLOBEAD MS 564 C was used. The resins used as catalyst were purchased from Aldrich. Dowex 50W(X8) 50 – 100 mesh is a strongly acidic cation styrene-divinylbenzene resin. The catalyst was used after it has been dried at a temperature of 100 °C for 2 h. Drying at much higher temperatures could lead to the loss of active sulfonic acid sites of the catalyst [22].

2.2.Esterification of acetic acid with isoamyl alcohol methods

The conventional esterification reactions of acetic acid with *iso*amyl alcohol were carried out using a 1 mL continuous reactor equipped with a thermostat device, presented in our previous paper [4]. The equipment consists of a micro-reactor holding resin, molecular sieves dehydrator, heating/cooling jacket, pump, US control panel, thermostat, ultrasonic probe device. Ultrasound was introduced via a probe system (Vibracell VCX-750), using different ultrasound pulses and amplitudes. The water was removed from the system by passing the reaction mixture through acolumn containing 3A molecular sieve (2.3 g molecular sieve, with a water-holding capacity of 22% wt., enough to retain the whole water formed during the esterification). The reagents are mixed, heated at the working temperature and pass through the resin fixed bed from the reactor. The reactions were performed at various reaction temperatures, with acid-to-alcohol molar ratio 1:2, at different reagent flow rates. using different ultrasound pulses and amplitudes. The reaction was carried out in a loop system for two hours, and samples were taken in duplicate, every hour. The *iso*amyl acetate concentration was determined by gas-chromatographic analysis (GC analysis).

2.3. GC Analysis

Quantitative analysis of the esters was performed using an HP 6890 gas chromatograph equipped with flame ionization detector (FID). The oven is set to heat the column from 50°C to 250°C with a gradient of 10 °C/min. Helium is used as column carrier gas (flow rate 1 mL/min). *n*-Butanol is used as the internal standard for determining ester concentrations. The volume of the injected mixture was 1 μL. Individual standards of isoamyl alcohol and isoamyl acetate were analyzed and their retention time was recorded and the ester samples were compared under similar conditions. The ester concentration was determined using a calibration curve of pure isoamyl acetate with concentration ranging from 5 to 60 mg ester/g. Samples were diluted 1:10 with a standard solution of 5% n-butanol in methanol before analysis. The samples were analyzed in duplicates.

3. Results and discussions

3.1. Conventional vs ultrasound assisted esterification reactions

The acidic ion-exchange resin, Dowex 50(X8) was selected as solid catalyst. The composition and structure of an ion-exchange resin are important factors in establishing its catalytic efficiency. The catalytic activity for this catalyst was tested in the conventional and ultrasound assisted reactions between acetic acid and *iso*amyl alcohol and the variation of the isoamyl acetate concentration in time is depicted in Fig. 1.

In order to study the influence of ultrasound on esterification process, reaction was performed using isoamyl alcohol to acetic acid molar ratio of 2:1, at the temperature of 50°C in a loop reactor [4] with acidic exchange resin as catalyst. The ultrasound assisted experiments using Dowex 50(X8) lead to a higher isoamyl acetate concentration than conventional esterification process. It has been observed that the application of ultrasounds enhances the concentration of the ester to about 30% in 2 h. Also intensifying the process with ultrasounds a better ester concentration was obtained in a shorter time. Therefore, using ultrasound for increasing the conversion and reducing the process time to reach equilibrium for isoamyl acetate ester is quite effective as shown in Fig. 1.

The most important phenomena when using ultrasounds is cavitation. The formation of microjets and the mass transfer increase effect lead to the growth of product concentration. The cavitation causes the locally rise of temperature and pressure generating shock waves and microscopic turbulence. In consequence, due to cavitation generated in ultrasound system, these effects enhance the mass transfer and the diffusion of reactant molecules on the active catalytic sites.

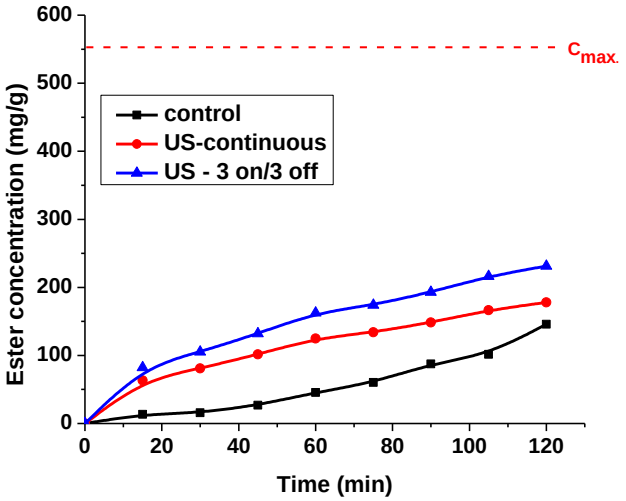

Fig. 1. Comparison between conventional and ultrasound assisted esterification (50 ° C, sonication probe at 4.5 cm from reactor, 20% amplitude, catalyst loading 0.067 g/mL).

Further, the microjets formed when bubble implodes helps for interface renewal. All these effects are responsible for the improvement in the ester concentration [23].

3.2. The influence of ultrasonic power

An important factor that influences the cavitation properties is the amount of energy that is transmitted in the reaction liquid. Bubble dynamics studies show that their distribution as a function of size, maximum lifetime, bubble number, and collapse pressure are complex functions that affect the rate of power dissipation. Also, the increase of temperature in the volume of liquid is a function of the power dissipation rate, which leads to changes in gas solubility and vapor pressure that affect the ease of generating cavitation phenomenon, as well as the final intensity of collapse [24]. To study the effect of the ultrasound power, experiments were performed by varying the amplitude from 20 to 35 % to find the best power needed in order to achieve efficient cavitation for the esterification. In Fig. 2 the results for the Dowex 50(X8) catalyzed experiments are presented. The ultrasonic power corresponding to each amplitude was read on the Vibracell device.

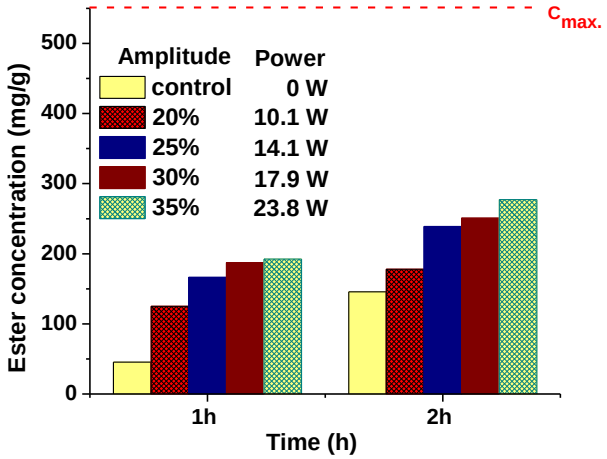

Fig. 2. Effect of the ultrasound amplitude on the ester concentration (50 °C, sonication probe at 4.5 cm from reactor, catalyst loading 0.067 g/mL, pulse 3 on / 3 off).

Other constant parameters were alcohol to acid ratio of 2 : 1, reaction temperature of 50 °C, and duty cycle of 50%. As shown in Fig. 2, with the increase of amplitude the energy input in the reaction system increases, too, leading to a higher number of cavitation bubbles and therefore to improved cavitational effects. At a sub-microscopic scale, this leads to turbulence due to the high speed of bubble generation, increasing the interfacial area. A larger interfacial area produces a greater diffusion of reactants to the catalytic sites providing a higher conversion. The higher the ultrasonic power, the much larger the amount of ultrasonic cavitation bubbles are generated in the reaction mixture. [25-27]. As a consequence, the increase in ultrasound amplitude leads to an increase in the ester concentration.

3.3. Influence of duty cycle

Intensification with ultrasounds produces high local temperature and pressure, thus, constant irradiation might cause shredding of resin balls [19]. Also, applying ultrasound in a continuous mode will harm the transducers and high temperatures might cause grading of horn tip [28]. For this reasons, it is recommended to use ultrasound irradiation in a pulse mode. Duty cycle has an important role in ultrasound assisted processes and it is suggested to carry out reactions up to a favorable concentration of ester. The effect of duty cycle on esterification was studied by varying the on-off time of ultrasonic irradiation on the reaction mixture. Fig. 5 presents the effect of ultrasound duty cycle on the ester concentration over time. The ultrasonic power corresponding to each duty cycle was read on the Vibracell device. The ultrasonic pulses applied for the esterification reaction were 3 sec on/ 3sec off (50%), 3 sec on/ 6sec off (33.4%),

and 3 sec on/ 9sec off (25%). The other conditions were kept at the optimum values of temperature 50 °C, alcohol to acid mole ratio of 2:1, catalyst loading 0.067 g/mL. The reported results establish that duty cycle is an important parameter affecting the concentration of isoamyl acetate. Fig. 3 depicts that using pulses of 3on/3off increases the ester concentration, after one hour of reaction, from 50 $mg_{ester}/g_{mixture}$ to 250 $mg_{ester}/g_{mixture}$.

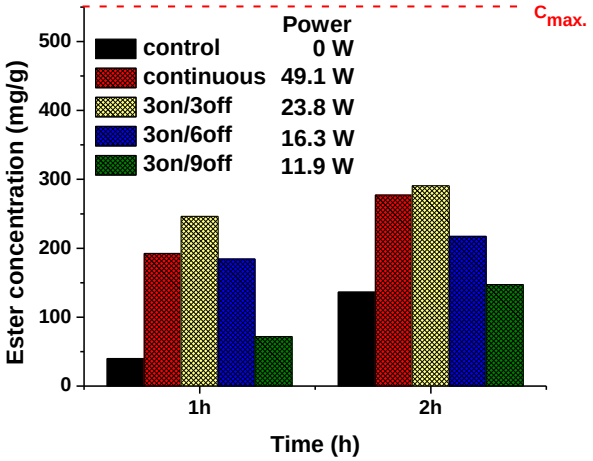

Fig. 3. Concentration of the isoamyl acetate ester over time (1: 2 molar ratio acid to alcohol at 50 ° C with 0.067g/mL acid ion exchange resin), conventional and ultrasonic heating (sonication probe at 4.5 cm reactor, different pulses).

Further increasing the off cycle of the ultrasound irradiation from 3 sec off to 6, respectively 9 sec off, leads to smaller increase in the concentration of isoamyl acetate. At higher duty cycle, because of the high amount of energy, the increase of ester concentration is smaller. This clearly demonstrated that an extended time of ultrasound irradiation may not be sufficient to improve the mass transfer between the reagents and the resin [20]. On further increase of duty cycle from 50 % to 100 %, the ester concentration decreases from 300 mg/g to 287 mg/g. This diminution in concentration can be due to excessive bubbles generated that are susceptible to coalesce and form bigger and more stable bubbles. This creates a barrier to dissipative energy transfer inhibiting effective diffusion of reactant species [27]. Finally, 50% duty cycle was selected as optimum for this reaction, which gives 300 $mg_{ester}/g_{mixture}$ after 2 h of reaction.

3.4. Influence of temperature

Temperature is an important parameter for the esterification reaction. Temperature increase helps to increase the reactant solubility, reduces the viscosity of the reaction medium, facilitates molecular collisions at the interface,

increases mass transfer and facilitates interactions between the reactants and the catalyst [20].

To investigate the influence of temperature on ultrasound-assisted esterification between isoamyl alcohol and acetic acid, the reactions were carried out at different temperatures, range from 50 to 70°C. The reaction conditions were kept constant: isoamyl alcohol to acetic acid ratio 2 : 1, catalyst loading 0.067 g/mL, added molecular sieves, the amplitude of the ultrasound horn was at 35% with duty cycle of 50 %. The results obtained are shown in Fig. 4, which shows that the temperature of 50 °C was observed as the optimal temperature in terms of increase in ester concentration. The ester concentration reached 277 mg/g in 120 min at 50 °C compared to that obtained at 70°C (247 mg/g).

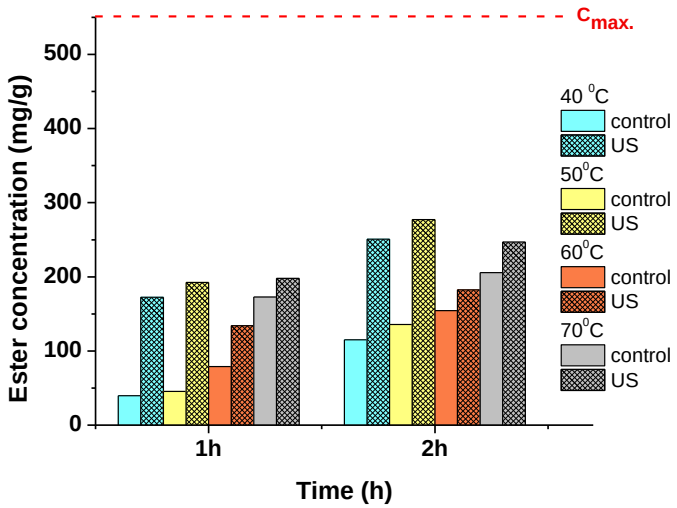

Fig. 4. Concentration of isoamyl acetate ester over time (1: 2 molar ratio acid to alcohol with 0.067 g/mL acid ion exchange resin), ultrasound at various reaction temperatures (sonication probe at 4,5 cm from the reactor, amplitude 35%, pulse 3 on / 3 off).

The reduction in cavitational intensity at higher temperature above 60 °C is responsible for negative impact on ester concentration. This poorer effect of ultrasound at higher temperatures can be attributed to the cushioning effect of vapour contained inside the bubble during cavitation. The intensity of cavitation is negatively influenced by the temperature increase due to the formation of vaporous cavities which gives a less violent collapse based on the cushioning effect. As a result of these counteracting mechanisms, it is expected to find an optimum temperature, that give a maximum enhancement in the rate of reaction [20,29]. At 50 °C the use of acoustics leads to a higher ester concentration after one hour reaction. At low temperatures, the number of bubbles generated is small, but they collapse violently, increasing the mass transfer between the reactants and the catalyst [23]. The higher effect of the cavitation at lower temperature can be

observed in the difference between control and ultrasound experiments at 40 and 50 °C. The ester concentration obtained from the ultrasound assisted reactions after 2 h increased by 2.2 times at 40 °C and 2 times at 50 °C than those for the control experiments. In the case of the reactions performed at 60 and, respectively, 70 °C the increase in ester concentration for the ultrasound assisted experiments were only by 1.2 times higher. At 70 °C, there is a reduction in surface tension and viscosity, also the formation and upcoming collapse of bubbles is disturbed. Thus, at higher temperatures the mass transfer improvement due to cavitation is reduced as bubbles collapse with less intensity [25].

3.5. Influence of flow rate (residence time)

An important parameter for the characterization of the technology of continuous esterification reactions, catalyzed by acidic resins, is the flow rate. Studying the effect of flow rate permits the design of more efficient continuous flow reactors. The flow rate and the volume of the reactor are important parameters when describing the residence time. For this study, three different reactants flow rates: 0.16, 0.3 and 0.5 mL/min were used, as showed in Fig. 5. The reaction conditions were kept constant: isoamyl alcohol to acetic acid ratio 2 : 1, catalyst loading 0.067 g/mL, added molecular sieves, the amplitude of the ultrasound horn was at 35% with duty cycle of 50 %.

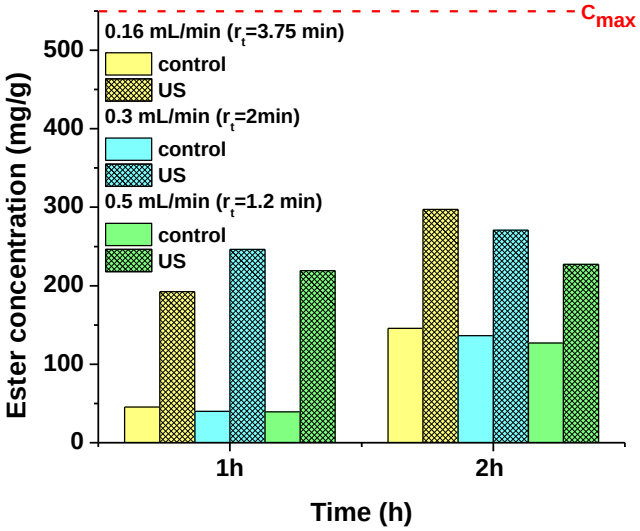

Fig. 5. Concentration of isoamyl acetate ester over time (1: 2 molar ratio acid to alcohol with 0.067 g/mL acid ion exchange resin), ultrasound at various reaction temperatures (sonication probe at 4,5 cm from the reactor, amplitude 35%, pulse 3 on / 3 off).

Flow rate have an important role in in the micro-mixing level and gives information about shear stress generated. The results indicate that

the flow rate is highly important for reaction optimization. Decreasing the flow rate leads to an important increase of the ester concentration. The highest ester concentration (300 mg/g) was achieved with a flow rate of 0.16 mL/min. The lowest concentration of ester was obtained for the highest flow rate (0.7 mL/min) that means the shorter residence time, respectively. Lower flow rates guarantee a more efficient mass transfer due to a longer contact time between the reactants involved and the acidic catalyst. For all three flow rates, ultrasound intensified reactions lead to a higher isoamyl acetate concentration.

4. Conclusions

The present research was highlighted on intensifying the esterification process of the ion exchange resin catalyzed synthesis of isoamyl acetate. This ester possesses commercial value as banana flavor, which is widely used in different industries. Ultrasound assisted synthesis of isoamyl acetate by the reaction between acetic acid and isoamyl alcohol using as catalyst an acidic ion exchange resin in presence of ultrasound irradiation was successfully performed in a continuous micro-reactor. Highest ester concentration was achieved at ultrasound amplitude of 35 % and duty cycle 50 %. The ester concentration increased with an increase in temperature over the range of 40-50 °C and decreased on further increase in temperature. Optimal concentration of isoamyl acetate was obtained at a lower flow rate. Thus combined use of ultrasound method with heterogeneous catalyst seems to be a promising alternative for the synthesis of isoamyl acetate. The results show a favorable perspective of the ultrasound technique to improve the process efficiency and reduce the reaction time when using Dowex 50(X8).

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