Green synthesis of banana flavor using different catalysts: a comparative study of different methods

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ABSTRACT

Esterification of isoamyl alcohol with acetic acid was studied using different ion-exchange resins, namely Amberlyst 15 dry, Amberlyst 16 wet, Amberlite 120-IR. Esterification was carried out using different esterification methods that are quite new (ohmic, ultrasonic probe, and ultrasonic bath) and the results were compared with microwave-assisted esterification (MAE). The highest isoamyl acetate yield (99%) was obtained by MAE, using a mixture of acetic acid and isoamyl alcohol (mole ratio of 1:2) after 2 h of reaction time. In this process, 2% Amberlyst 15 dry was used. MAE had the least specific energy consumption (0.42 kWh/g isoamyl acetate) and specific CO2 emission (34 g/g isoamyl acetate). According to the images obtained by scanning electron microscopy, lower amounts of Amberlyst 15 dry beads were destroyed by MAE method compared to other esterification methods. In conclusion, MAE proved to be an economic and environmentally-friendly method for esterification of different flavoring compounds.

1. Introduction

Short-chain esters are compounds with widespread applications that dominate the food and cosmetic industries because of their unique characteristics in flavor and fragrance (1). Banana flavor (isoamyl acetate) is one of the most widely-used short-chain esters in food preparations, in addition to the cosmetic and pharmaceutical industries (2, 3). The annual demand for isoamyl acetate is more than 195,000 lb (4).

So far, several synthetic routes and catalysts have been used for synthesizing acetate esters. Even though
lipases have been widely studied to define their roles in the synthesis of acetate esters, the use of acetic acid as an acyl donor (direct esterification) can be further explored for the catalyzed synthesis of lipase acetate esters. Relevant attempts have not been reasonably successful as yet (2, 5). These shortcomings of direct lipase esterification have led scientists to experiment with several heterogeneous catalysts.

The most common route for its direct synthesis is the use of homogenous acid/base catalysts (6). The raising of awareness about the residues of homogenous catalysts has commonly led producers to a tendency to replace them with heterogeneous catalysts. Ion-exchange resins, as heterogeneous catalysts, have been used for catalyzing different reactions such as esterification, transesterification, alkylation, acylation, and other transformations (7, 8). Microwave-assisted esterification (MAE) can be programmed to use heterogeneous catalysts. These catalysts have especially become important in Green Chemistry (9, 10). Microwave radiation, as a method, is trending among scientists who intend to heat materials inside chemical compounds. It is a cheap, clean, selective, instantaneous and convenient heating method (11). Micro wave radiation causes a rapid superheating of localized materials. This occurs due to ionic conduction or dipole rotation, thereby causing molecules to move more dynamically (12). Accordingly, a greater intensity of molecular movements can lead to a larger number of energetic collisions, and thus the reaction rate and yield are enhanced (13).

The synthesis of isoamyl acetate has been evaluated via different esterification methods (5, 14). However, the synthesis of isoamyl acetate via different ion-exchange resins in a solvent-free MAE system has not been the subject of research so far. Therefore, this study utilized the MAE system to operate on isoamyl alcohol alongside acetic acid in a solvent-free environment. Furthermore, the effect of different reaction parameters, i.e. the type of ion-exchange resin, its concentration, and the mole ratio of the substrates were investigated. Ultimately, the MAE was compared to ohmic, ultrasonic bath, ultrasonic probe, and magnetic stirrer esterification methods.

### 2 Materials and methods

#### 2.1. Materials

Acetic acid (>99%), methanol (>99%), isoamyl alcohol (>99%), and n-butyl acetate (>99%) were purchased from Merck (Darmstadt, Germany). Novozyme 435 (Candida antarctica lipase B) and Lithium chloride (LiCl) were purchased from Sigma–Aldrich (St. Louis, MO). Commercial ion-exchange resins, namely Amberlyst 15 dry (A-15 dry), Amberlyst 16 wet (A-16 wet), and Amberlite 120-IR (A-120 IR) were purchased from Fluka (Buchs, Switzerland). Physical specifications of these ion-exchange resins are presented in Table 1.

#### 2.2. Optimization of MAE

A modified microwave was used according to the method reported by Zare et al. (15). Different parameters were optimized, including ion-exchange resin type, catalyst concentration, and mole ratio of the substrates. The systematic experimentation involved changing one working parameter at a time while keeping the others constant.

The first set of experiments was conducted with the intention of comparing the catalytic performance of different ion-exchange resins (A-15 dry, A-16 wet, and A-120 IR) and Novozyme 435 in the MAE. The reaction mixture consisted of 1 mol isoamyl alcohol and 1 mol acetic acid to make a total liquid weight of 25 g. Then, the ion-exchange resin (4%) was added to the reaction at a speed of 100 rpm under the microwave power level of 200 W for 150 min (15 min intervals). Temperature of the reaction was set at 75°C. The temperature was monitored (with an accuracy of ± 1°C) using an infrared thermometer (TM-960 Lutron, Taipei, Taiwan). Also, time-temperature profiles of different esterification methods (mole ratio of 1:2; 2% (w/v) Amberlyst 15 dry; 100 rpm) are shown in Figure 1. Samples were withdrawn periodically from the reaction mixture and were analyzed by gas chromatography (GC).

The catalyst concentration and its effects on MAE of isoamyl acetate were studied in the range of 0.5, 1, 2,
4, and 6% A-15 dry. Constant reaction conditions were 1 mol isoamyl alcohol and 1 mol acetic acid, Amberlyst 15 dry as catalyst, agitation speed of 100 rpm, and microwave power level of 200 W.

The acetic acid:isoamyl alcohol mole ratio varied among 1:1, 2:1, and 1:2 which were calculated with respect to a constant total weight of 25 g in a solvent-free system. Constant reaction conditions were 2% (w/v) Amberlyst 15 dry. They also involved an agitation speed of 100 rpm and microwave power level of 200 W.

2.3. Catalysts reusability

Reusing the A-15 dry was examined to determine its stability during optimum MAE reaction conditions. This involved 2 mol isoamyl alcohol and 1 mol acetic acid, 2% (w/v) Amberlyst 15 dry, an agitation speed of 100 rpm and microwave power level of 200 W. The A-15 dry was reused six times and was studied to understand its effect on isoamyl acetate yield. After each usage, the A-15 dry was separated by means of filtration, washed with hexane and reused. Catalysts were fixed on the specimen holder by aluminum tape and sputtered by gold in a sputter coater (Polaron). All specimens were examined using scanning electron microscopy (SEM) (Cambridge, UK) under high vacuum conditions at an accelerating voltage of 20.0 kV and working distance of 3–24 mm.

2.4. Comparison of different esterification methods

2.4.1. MAE

The reaction mixture had a total weight of 25 g (1 mol of acetic acid and 2 moles of isoamyl alcohol). Accordingly, A-15 dry (2%) was added to initiate the reaction at a speed of 100 rpm under microwave power level of 200 W for 150 min. The reaction temperature was initially set at 75°C.

2.4.2. Magnetic stirrer-assisted esterification (MSAE)

Experimental conditions of MSAE were similar to those used for MAE. However, a magnetic stirrer (Labinco model LB1, DG Breda, Netherlands) was used instead of the microwave oven.

2.4.3. Ohmic-assisted esterification (OAE)

Ohmic-assisted esterification was according to method of Zare et al. (15).

2.4.4. Ultrasonic probe-assisted esterification (UPAE)

The experimental reaction operated under similar conditions for UPAE and MAE. An ultrasonic probe (Bandelin HD 3200, Bandelin Electronics, Berlin, Germany) was used in this study with a constant power of 200 W. Distilled water (75°C) was circulated in the jacketed vessel for temperature control. The substrates were sonicated in a high grade titanium tip (TT13, diameter 13 mm) with a constant horn depth of 2 cm.

2.4.5. Ultrasonic bath-assisted esterification (UBAE)

The conditions of this reaction resembled those used by Zare et al. (15). The difference was that the distilled water surrounding the flask had a temperature of 75°C instead of 50°C. The distilled water was used for controlling the systematic temperature during the operation.
2.4.6. Structure of A-15 dry
SEM images of A-15 dry beads were observed before the operations (when they were fresh catalysts) and after operating with MAE, OAE, UBAE, UPAE, and MSAE methods.

2.4.7. Energy consumption
Power consumption was monitored according to method of Seidi Damyeh et al. (16).

2.5. Isoamyl acetate yield
The yield of isoamyl acetate was measured according to method of Zare et al. (15). Actual yield is obtained according to method of Ding et al. (17). Limited reagent is acetic acid.

2.6. Statistical analysis
All experiments were according to methods of Zare et al. (15).

3. Results and discussion
3.1. Optimization of MAE
3.1.1. Catalysts type
Figure 2(a) shows that the type of ion-exchange resin can affect the yield of isoamyl acetate. Even though the yields of all catalysts showed an increasing trend until the end of the reaction, the final yields of A-15 dry and A-16 wet were significantly higher than those of A-120 IR and especially of Novozyme 435. Also, the T50 value of different ion-exchange resins were arranged in order as A-15 dry (21 min) < A-16 wet (49 min) < A-120 IR (50 min) < Novozyme 435 (without t50). The lower T50 value of A-15 dry is due to its higher pore diameter with a higher BET (Brunauer, Emmett, and Teller) surface area and a higher total exchange capacity. Accordingly, it can be concluded that the active sites of A-15 dry by their inner surfaces are more accessible and readily available for participation in the esterification reaction (6, 10). Similarly, Singh et al. (6) evaluated the production of ethyl butyrate using A-15 dry and A-35. A previous report suggested that the ethyl butyrate yield of A-15 dry is higher than that of the A-35 due to its higher total exchange capacity, surface area, and pore volume (6). Novozyme 435 caused the lowest yield of direct esterification due to its inactivation, instigated by high acid concentrations. Accordingly, A-15 was found to be the best catalyst and was used in future experiments.

3.1.2. Catalyst concentration
The catalyst concentration affected the yield of isoamyl acetate (Figure 2(b)). For all concentrations of A-15 dry, the yield of isoamyl acetate showed an increasing trend during the reaction. Despite the differences between the amounts of final yield, obtained by 0.5%, 1%, and 2% A-15 dry, there were no significant differences among the final yields obtained by 2%, 4%, and 6% A-15 dry. The final yield of 2% A-15 dry was 26% higher than 0.5% A-15 dry because active catalytic sites were more numerous in the case of 2% A-15 dry (18). Furthermore, it seems that higher concentrations beyond 2% A-15 dry caused limitations on mass transfer (9). Therefore, 2% A-15 dry was selected as an optimum catalyst concentration.

3.1.3. Acetic acid:isoamyl alcohol mole ratio
Acetic acid:isoamyl alcohol mole ratio affected the yield of isoamyl acetate (Figure 2(c)). A higher alcohol ratio was shown to be able to drive forward the reaction more efficiently since a higher acid ratio generates a lower yield of isoamyl acetate. In most instances, when the actual esterification is concerned, the surplus occurrence of one component can make the reaction proceed well. Therefore, when the isoamyl alcohol (nucleophile) ratio occurs in excess, more ester is created by a shifted pattern of esterification.

The dielectric constant of isoamyl alcohol (15.6) is higher than the acetic acid (6.2). Therefore, heating up this polar molecule can selectively lead to a rapid formation of microzones with temperatures much higher than that of the reaction mixture. These high temperature microzones are called “hot spots” which can accelerate temperature-dependent chemical reactions such as esterification (19). In another study, Patil and Kulkarni evaluated different mole ratios of acetic acid:isoamyl alcohol (1:2, 1:3, 1:1, and 2:1) using A-15 dry in a batch reactor and reported that the equilibrium yield of 1:3 mol ratio was at least 40% higher than that of the 1:1 mol ratio. The solvent-free lipase esterification of isoamyl acetate has been reported previously using different mole ratios of acetic acid:isoamyl alcohol under conventional heating (20). The maximum yield was reached at a higher acid ratio (2:1). The current study showed that a higher isoamyl alcohol ratio in MAE led to a higher isoamyl acetate yield, but caused a lower yield of isoamyl acetate in the conventional method, which can be attributed to the different heating mechanisms in the two different heating methods. Therefore, an optimum condition involved a specific mole ratio of acetic acid:isoamyl alcohol (1:2) which was continued throughout the experiment.
Figure 2. Effect of (a) catalysts performance (mole ratio of 1:1, 4% (w/v); 100 rpm; 200 W), (b) catalyst concentration (mole ratio of 1:1, Amberlyst 15 dry; 100 rpm; 200 W), and (c) acetic acid:isoamyl alcohol mole ratio on isoamyl acetate (2% (w/v) Amberlyst 15 dry; 100 rpm; 200 W) yield of microwave-assisted solvent free esterification method.
3.1.4. Reusability of A-15 dry
Using A-15 dry several times can affect isoamyl acetate yield (Figure 3). There was a steady decrease in isoamyl acetate yield of A-15 dry after each time of usage. The highest isoamyl acetate yield was obtained after the first usage. Nonetheless, there were no significant differences among isoamyl acetate yields after the second, the third, and the fourth usages. This difference, however, can be explained by an initial leaching of A-15 dry after the first usage. The yield of isoamyl acetate was reduced by 30% after six times of being reused. This can be due to the combined effect of simultaneous processes, e.g. losses that are incurred as a result of reusing the material which leads to partial inactivation, the disconnection between the surface of the catalyst and the sulfonic acid groups, initial leaching, and the initiation of intra-particle diffusion resistance to solid–liquid mass transfer.

SEM images of A-15 dry beads before and after six times of MAE are shown in Figure 4. About 35% A-dry beads were broken down after six times of usage. Similarly, Oh et al. (21) reported that A-36 beads were completely broken down after three times of usage in producing 5-hydroxymethylfurfural (21).

3.2. Comparison of different esterification methods
3.2.1. Yield
Figure 5 shows the effect of different esterification methods on isoamyl acetate yield. The final yields of MAE, OAE, UBAE, UPAE, and MSAE methods were 99%, 91%, 88%, 69%, and 67%, respectively. Higher MAE yields can be related to the fact that MAE allows three ways of heat transfer to the reaction mixture. These three are, namely radiation, conduction, and convection. However, heat transfers only take place through conduction and convection when other esterification methods are used (22). Therefore, microwaves can heat the entire sample almost simultaneously and at a higher rate in comparison with other esterification methods. Radiation caused the formation of microzones with temperatures much higher than that of the reaction mixture (22).

Catalysts in MAE may possibly behave differently to some extent in comparison with other esterification methods. A-15 dry is a hygroscopic catalyst which adsorbs water during the reaction, and the catalyst almost always carries a trace of water as the water–wave interactions enable a rapid rate of heating (13). Accordingly, the activities of catalysts are improved by thermal and non-thermal effects which are characterized by different molecular mechanisms (23).

Yields of ultrasonic-assisted esterification methods (UBAE and UPAE) were lower than that of MAE. It seems that the creation of cavitation in ultrasonic systems and also the creation of turbulence by overhead stirrer can help uniform mixing, while at the same time they cause the depth-crack of the catalyst.

3.2.2. Catalyst structure
SEM images of A-15 dry beads were generated before esterification (i.e. when the catalysts were fresh) and after several repeats of esterification (Figure 6). Nonetheless, little cracks were observed in both MAE (Figure 6(b)) and MSAE (Figure 6(c)) in comparison with the fresh catalyst (Figure 6(a)), but MAE also caused the melting of A-15 dry beads.
Figure 6(d) confirms higher cracks and melting when the OAE is used, compared to the MAE. Two explanations can clarify the destruction of A-15 dry beads in OAE. First, heat is generated swiftly within the entirety of the sample because of the high local heat flux. This leads to an adequate occurrence of electrical conductivity, thereby influencing the catalyst as well (Fourier’s law). This phenomenon can be responsible for the depth-crack of the catalyst. The second reason is electrical conductivity between two electrodes in OAE, which leads to the melting of catalyst beads.

A-15 dry beads become completely destroyed at a point in UPAE and UBAE (Figure 6(e and f), respectively). Even though high-speed jets of liquid create turbulence in the reaction mixture, they also gradually destroy the catalyst beads and consequently reduce the yield of isoamyl acetate.

3.2.3. Cost, cleanliness and scale up

The T50 value and energy consumption of different esterification methods varied (Table 2). The T50 of MAE, OAE, UBAE, UPAE, and MSAE were 11, 13, 27, 54, and 104 min, respectively. This finding revealed that the lower T50 value found in MAE is not only due to its earlier onset of reaction, but also because of its higher reaction rate which is mainly due to its
efficient transfer of heat caused by selective heating. Energy consumption (kWh), specific energy consumption (kWh/g ester), CO$_2$ emission (g), and Specific CO$_2$ emission (g/g ester) of different esterification methods showed different trends in comparison to the values of T$_{50}$ and isooamyl acetate yield which were arranged in the order of MAE < OAE < UBAE < UPAE < MSAE. Therefore, MAE can be considered as an environmentally friendly method.

4. Conclusion

Extracting isoamyl acetate via MAE can be of significant importance due to the fact that the chemical compound is broadly applicable in the food industry as a common flavoring ester. This process was studied using different ion-exchange resins in solvent-free systems. The final yield obtained by the MAE method was substantially comparable to the final yields obtained by OAE, UBAE, UPAE, and MSAE methods. This difference can be attributed to the fact that heat transfer in MAE employs radiation in addition to conduction and convection. By the MAE method, a higher isoamyl alcohol (polar molecule) mole ratio led to a rapid formation of microzones in the presence of temperatures that exceed the temperature used for the actual reaction mixture. Therefore,
MAE caused a higher yield of isoamyl acetate. MAE not only reduced the specific CO₂ emission and the specific energy consumption, but also alleviated the destruction of A-15 dry and increased the yield of isoamyl acetate. There were also improvements in the reproducibility of the catalyst. All in all, MAE can be suggested as an environmentally-friendly method for the green synthesis of various flavoring esters.

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