

A sustainable pathway to convert volatile fatty acids coming from fermented food waste into bio-based solvents

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Keywords: Direct-esterification, Alkyl-esters, Bio-based solvents, Aluminium Chloride Hexahydrate

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Introduction

In this study, a new process for obtaining alkyl-esters of volatile fatty acids (VFAs) coming from fermentation of food waste was proposed by using aluminium chloride hexahydrate as a catalyst. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ not only was active in promoting the direct-esterification of acids and alcohol as conventional homogeneous catalysts (hydrochloric acid, sulphuric acid, etc.), but differently from them, it also induced a convenient separation of phases, where alkyl esters were primarily dissolved in the organic upper layer (>99%wt), well separated by the co-formed water. The resultant catalyst was dissolved into the aqueous phase (>97.8%wt), and therefore completely recoverable from the reactive mixture. The principal kinetics and thermodynamics parameters were determined, and reactive conditions were optimised to improve final conversion and repartition.

Materials and Methods

Direct-esterification of VFAs with ethanol using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as catalyst

The direct-esterification reaction of VFAs with ethanol was carried out in a glass reactor equipped with a silicone cap that allows sampling throughout the reaction. Acetic (AA), Propionic (PA), or Butyric (BA) acids were introduced into the reactor with ethanol, and placed into a thermostatic oil bath (343, 333, 323 and 313 K, respectively) and magnetically stirred (250 rpm). Then, an ethanolic solution of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was introduced via syringe into the reactor, to obtain a final molar ratio acid:ethanol:catalyst = 1:1:0.01. Samples were collected at 30, 60, 90, 120, 150, 180, 240 and 480 minutes and analysed for any residual acidity and ethyl ester. At the end of the esterification process, when a bi-phasic system was observed, the two distinguishable phases were recovered, weighed and analysed for residual acids, ethyl esters, ethanol, water, aluminium and chloride content.

Phase repartition in the esterification of AA with ethanol

The effect of catalyst amount on phase repartition was evaluated on a synthetic mixture with a known thermodynamic composition obtained by reacting an equimolar mixture of AA and ethanol (343 K, 8 h). In a glass reactor, 3.52 g of AA were placed with 2.7 g ethanol, 11.4 g of ethyl acetate (EA) and 2.34 g of water. The resulting solution was a homogenous system in which no phase separation was observed. Then, 0.45 g of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1% mol respect to starting AA) were added to form a bi-phasic system. The two phases were recovered, weighed and analysed. Finally, the effect of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ loaded (2, 3, 4 and 5%mol) on the phase separation was evaluated with the results that were compared using HCl, H_2SO_4 , and p-toluene-sulfonic acid in the same experimental conditions.

Analysis of results

Kinetics and thermodynamics of direct-esterification of VFAs and ethanol mediated by $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Pure AA, PA and BA were reacted with a stoichiometric amount of ethanol at different temperatures in presence of catalytic amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (1%mol by respect with starting acids). The direct-esterification was monitored along the time, by analysing residual acidity and the corresponding ethyl esters (Fig. 1).

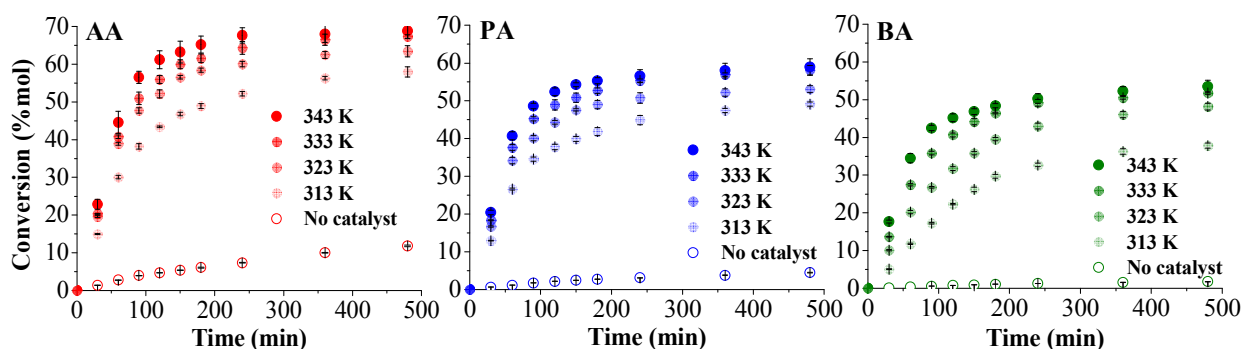


Fig 1. Kinetic profiles of direct esterification of Ethanol and Acetic, Propionic and Butyric acids.

Kinetic profiles in Fig. 1 suggest the following points: i) there is a positive effect of temperature on kinetics and thermodynamics of the reaction; the increase of temperature improves the rate of the reaction and the final

conversion to esters; ii) kinetics and thermodynamics of direct-esterification strongly depends on the acid used with the order of reactivity AA > PA > BA connected to the size of the alkyl tail, and iii) in absence of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, reaction did not occur even at 343 K after 8 h (final yields were 11.8, 4.8 and 1.7% for AA, PA and BA, respectively). Based on these experimental data, a more specific kinetic elaboration was carried out by applying second order model for homogeneous reaction (Table 1).

Table 1. k_1 and K_{eq} determined for acetic, propionic and butyric acids at 313, 323, 333 and 343 K.

| (K) | Acetic acid | | Propionic acid | | Butyric acid | |
|-----|--|----------|--|----------|--|----------|
| | k_1 ($\text{L mol}^{-1}\text{min}^{-1}$) | K_{eq} | k_1 ($\text{L mol}^{-1}\text{min}^{-1}$) | K_{eq} | k_1 ($\text{L mol}^{-1}\text{min}^{-1}$) | K_{eq} |
| 313 | $8.3 \cdot 10^{-4}$ | 1.91 | $7.4 \cdot 10^{-4}$ | 0.94 | $4.1 \cdot 10^{-4}$ | 0.44 |
| 323 | $1.2 \cdot 10^{-3}$ | 3.03 | $1.1 \cdot 10^{-3}$ | 1.28 | $6.6 \cdot 10^{-4}$ | 0.72 |
| 333 | $1.4 \cdot 10^{-3}$ | 4.27 | $1.3 \cdot 10^{-3}$ | 1.92 | 10^{-3} | 1.15 |
| 343 | $1.8 \cdot 10^{-3}$ | 4.91 | $1.6 \cdot 10^{-3}$ | 2.15 | $1.4 \cdot 10^{-3}$ | 1.32 |

From the data obtained in Table 1, it is possible to observe that K_{eq} is strongly dependent on the acid catalyst; at equilibrium, final AA conversion yields were higher than those obtained for PA and BA. For more specific information on kinetics and thermodynamics on direct-esterifications, Arrhenius and Van't Hoff equations were applied with the results that were collected in Table 2.

Table 2. E_a , ΔH^0 and ΔS^0 calculated for the reaction of direct-esterification between acetic, propionic and butyric acid with ethanol, under $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ catalysis.

| VFAs | E_a | ΔH^0 | ΔS^0 |
|----------------|------------------------------------|----------------------|-----------------------------------|
| | $\text{kJ K}^{-1} \text{mol}^{-1}$ | kJ mol^{-1} | $\text{J K}^{-1} \text{mol}^{-1}$ |
| Acetic Acid | 22.3 | 28.5 | 97.1 |
| Propionic Acid | 22.8 | 25.9 | 82.3 |
| Butyric Acid | 35.8 | 34.7 | 104.3 |

The E_a values of the catalyses increased following the order AA > PA > BA. In any case, the absolute values of these reactions suggested lower E_a values than those calculated for heterogeneous catalysts (over $30 \text{ kJ K}^{-1} \text{mol}^{-1}$), to confirm the higher efficiency of homogenous catalysis.

Effect of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ on phase repartition

A mixture of AA, EA, water and ethanol was prepared, simulating the final equilibrium composition obtained from the reaction of an equimolar mixture of AA and ethanol at 373 K. Such solution appeared to be perfectly homogeneous, even after the addition of conventional mineral acids at different catalyst to AA molar ratios (from 1 to 5%mol). On the contrary, when $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was added a clear separation of phases was observed (Fig. 2).

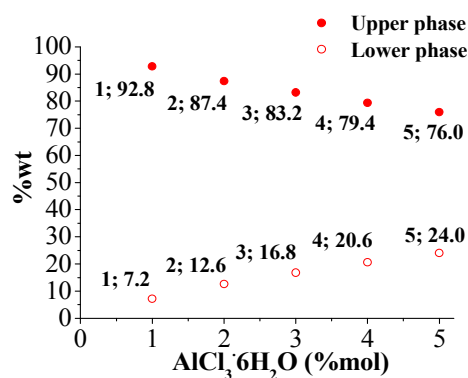


Fig. 2. Effect of different molar percentage of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the separation of phases.

Increasing the amount of catalyst (up to 5%mol), an increase of the water content in the lower phase was detected (from 7.2 to 92.8 %wt), with a concomitant purification and dewatering of EA present in the upper phase (>99%).

Conclusion

The use of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst in direct-esterification of VFAs with ethanol is a clean and simple process, competitive with current conventional routes of ethyl-ester production.

Acknowledgements

This work was supported by the REsources from URban Bio-waste[®] - RES URBIS (GA 7303499) project in the European Horizon2020 (Call CIRC-05-2016) program.