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Effect of catalytic conditions on the synthesis of new aconitate esters

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Green indicators

A B S T R A C T

Sugar cane is a crop which generates large amounts of biomass and a juice rich in high-value natural molecules. After extracting sugar from the juice, the recovering of various compounds such as organic acids contained in molasses could contribute to increase the competivity of the sugar industry. Therefore, according to the biorefinery approach, we propose to study the chemical conversion of one of these acids, the aconitic acid, by esterification reactions. A new series of aconitate esters have been synthesized by combining aconitic acid and alcohols from natural origin. The effects of experimental conditions have been investigated and have shown that the type of catalysis has a significant effect on the selectivity. Kinectics have thus been performed to determine the best conditions to synthetize enriched compositions in esters. Homogeneous catalysis generates the highest yield in triester. Heterogeneous catalysis (macroporous resins) is prefered for the production of monoesters while catalysis assisted by ionic liquid is adapted to prepare mainly diesters. Green indicators have been discussed according to the calculations performed. The resulting polyfunctional esters are totally biosourced molecules and have a great potential as bioproducts for different applications.

1. Introduction

There is an ever-increasing interest for the use of renewable resources for the production of bioproducts based on natural ingredients. The rising crude oil price due to its rarefaction incites to diversify the feedstocks towards renewable raw materials. There are different purposes to replace a petroleum based product by a biobased compound, according to the specifications of the products:

- a clean process of production which generates a lower environmental impact such as a gain in VOC emission,
- a low toxicity which makes them adapted to benign and green formulations,
- a high biodegradability which is necessary in case of contact with the environment at their end of life,
- innovative properties which make them attractive for users.

So, we intended to investigate the potential of aconitic acid (1,2,3-propentricarboxylic acid) as a raw material for the preparation of bioproducts. Aconitic acid is a tricarboxylic acid industrially produced by dehydration of citric acid. Aconitic acid can also be extracted from co-products generated by sugar industry.

The up-grading of the natural aconitic acid represents an opportunity to use an available feedstock and to increase the competiviness of sugar industry. This approach corresponds to the biorefinery concept which is being developed in numerous agroindustry chains in order to minimise the waste and diversify the outlets.

We propose to study the esterification of aconitic acid with natural alcohols such as isoamyl alcohol and lauryl alcohol. Isoamyl alcohol is one of the short alcohols present in fusel oils obtained in the pot residue after distillation of ethanol from fermented sugar.

This C5 alcohol represents between 60 and 75% of fusel oils, according to the origin of bioethanol (beet, wheat, etc.).

Lauryl alcohol (dodecanol) is obtained from lauric acid which is the main fatty acid present in coconut oil. It is used for the

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E-mail address: pascale.decaro@ensiacet.fr (P. de Caro).

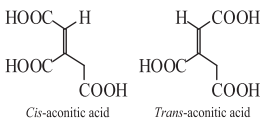

Fig. 1. The two isomers of aconitic acid.

preparation of surface active agents for cosmetic and health care industry.

The first objective consists in preparing esters which could have interesting properties to replace petroleum based products which are banned by regulations. Esters from natural organic acids are mentioned to be potential candidates. For example, citrate esters are used as plasticizers in formulation for plural component latex-foam (Olang et al., 2010) or for liquid coating compositions (Jonn et al., 2008). Glycerol esters are used as lubricant or surfactant in formulation for cleaning applications (Gross et al., 2008) and for engine lubricants (Patil et al., 2010; Seemeyer et al., 2008).

The second objective is to select a synthetic route which is compatible with the principles of green chemistry. The improvement of esterification methods to take into account the environmental and sanitary aspects is still a challenge in industry.

Moreover, the study of new experimental conditions is the opportunity to orientate the reaction towards a specific ester category.

Aconitic acid has two forms, *cis* and *trans* (Fig. 1). In the sugarcane, the *trans* isomer which is the most stable, is the dominant one.

Acid aconitic has thus three non-equivalent acid functions that is to say doted of a different reactivity. In particular, two acid functions take part to the delocalisation of the electron. Thus, the carbonyl site which is not conjugated should be the most reactive.

Esterification reactions from aconitic acid (AA) lead to three successive reactions to prepare monoesters, diesters and one triester (Fig. 2).

The synthesis of aconitate esters has been previously performed in batch or continuous stirred reactor with a homogeneous catalyst. For example, Bruins and Canapary (1956) have used sulfuric acid to synthesize tributyl aconitate with a high molar ratio alcohol:acid 12:1 at 175 °C. Roberts et al. (1954) have synthetised esters of aconitic acid using p-toluenesulfonic acid with a molar ratio 3.3:1 for 3.5 h by codistillating water with toluene with a yield of tri-isoamyl aconitate of 85.6%. Guthrie et al. (1976) have used acid halide to prepare methyl aconitate with a molar ratio of 65:1 for 3.5 h.

The equilibrium is usually shift continuously by adsorption on drying agents or by codistillation with "entrainers" such as benzene or toluene (Cockrem et al., 1993; Cox and Carruthers, 1936; Frappier et al., 2002; Weiberg and Stimpson, 1942).

The major drawbacks of homogeneous catalyst are the final neutralization of the homogeneous catalyst, and the extraction of reaction products by a volatile solvent. Moreover, these conditions require high temperatures, a heavy treatment and a large excess of alcohol.

Therefore, heterogeneous catalysis becomes more and more attractive for the chemical industry. For instance, zeolites and metal oxides, acid treated clays or cation-exchange resins (Choudhary et al., 2001; Ma et al., 1996) are used to perform clean esterifications.

Macroporous resins are mentioned as a performing catalyst for esterification. Thus, they constitute an alternative to homogeneous catalysts since they are non-corrosive. They can be easily removed from the reaction mixture and can be reused after the reaction.

Petrini et al. (1988) have synthetised monomethyl aconitate using Amberlyst 15 with a molar ratio of 100:1 for reagents, at room temperature for 10 h with a yield of 80% and a total selectivity. AG 50W-X4 resins were used by Gil et al. (2006) to prepare tributyl aconitate with an excess of 50% of alcohol at 140 °C for 1.5 h, to provide a final composition of 83% in triester.

A kinetic study was performed for the esterification of citric acid with ethanol catalyzed by Amberlyst 15 (Kolah et al., 2006) with a yield above 90%. Similar conditions were applied to the esterification of succinic acid with ethanol (Kolah et al., 2008).

Room temperature ionic liquids (RTILs) called "designer solvent" do not contribute to volatile organic compound emissions thanks to their low vapor pressure. They represent an alternative media which could be interesting for the esterification of a solid compound, since it acts both as solvent-catalyst and can intervene in the shift of equilibrium.

Cole et al. (2002) have reported the use of Bronsted acidic ionic liquid as a dual solvent-catalyst in esterification reaction. Another work by Zhu et al. (2003) has shown that the Bronsted ionic liquid 1-methylimidazolium tetrafluoroborate [hmim][BF_4] is also a suitable catalyst for the esterification of carboxylic acids (C2–C11) with a primary alcohol. Joseph et al. (2005) have shown that [bmim][PTSA] can catalyse the synthesis of benzyl acetate in good yield (100%). Fraga-Dubreuil et al. (2002) synthesize benzyl acetate using [bmim][HSO_4] with a yield of 95%. [mimps]$_3$[$PW_{12}O_{40}$] was used by Leng et al. (2009) to prepare tri-n-butyl citrate with an excess of alcohol (1:5) at 130 °C during 3 h to obtain a yield of 98% and a selectivity of 98%.

For an esterification, the choice of RTILs must take into account the separation between the esters and water formed during the reaction.

According to the state of the art, few studies on the esterification of aconitic acid were carried out and few data about yields and selectivity are available. Most of them deal with the syntheses of triesters at high temperature (above 140 °C) or in presence of sol-

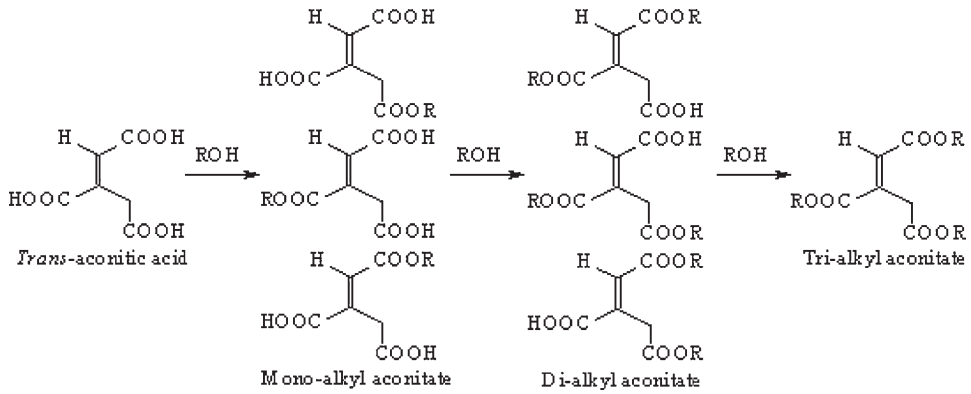

Fig. 2. Esterification of aconitic acid.

vent to get an azeotropic mixture. Exchanger ion resins are cited to be more adequate for the preparation of monoesters at room temperature with a high excess of alcohol.

We propose to carry out the synthesis of aconitate esters with a better control of selectivity by developing new experimental conditions for cleaner processes. The emphasis was placed to compare performances of a conventional homogeneous catalysis with two other catalyses: heterogeneous and ionic liquid.

2. Materials and methods

2.1. Materials

Trans-aconitic acid (98%), isoamyl alcohol (98%), sulfuric acid (95–98%), ionic liquid: 1-methylimidazolium hydrogensulfate [mim] [HSO_4] (Basionics® AC 39, BASF, ≥95%) were purchased from Sigma–Aldrich. Amberlyst® 15 (Fluka) was used in H^+ form without modification.

2.2. Esterification procedure

Esterification reactions were performed in a batch reactor (50 mL). For the conditions corresponding to homogeneous (H_2SO_4) and heterogenous catalyses (resins), a device to remove water by distillation was connected to the reactor. Mass percentages of catalyst are expressed relative to isoamyl alcohol weight.

2.2.1. Homogeneous catalysis (method 1)

Isoamyl alcohol (172.2 mmol) and aconitic acid (28.7 mmol) were mixed and heated under stirring until the solubilization of the solid aconitic acid, before 2.7 wt.% of sulfuric acid was added. The reaction was stirred at 100 °C during 540 min. At the end of the reaction, 20 mL of ethyl acetate was added to the reaction medium and the organic phase was washed four times with 10 mL of water. The organic phase was dried with 9 g of sodium sulphate. Ethyl acetate and isoamyl alcohol were removed in the same time by evaporation.

2.2.2. Heterogeneous catalysis (method 2)

Isoamyl alcohol (172.2 mmol) and aconitic acid (28.7 mmol) were mixed and heated under stirring until the solubilization of the solid aconitic acid, before 3 wt.% of cation exchange resin H^+ Amberlyst® 15 (or enzyme) was added. The reaction was stirred at 85 °C during 90 min. At the end of the reaction, the catalyst was separated through filtration and washed two times with 20 mL of ethyl acetate. Organic phase was then concentrated by solvent evaporation.

2.2.3. Catalysis by ionic liquid (method 3)

Isoamyl alcohol (86.1 mmol) and ionic liquid (9.50 g) were mixed and heated under stirring. When the mixture reached 100 °C, aconitic acid (28.7 mmol) was added and the medium was stirred during 540 min. At the end of the reaction, the medium was cooled at room temperature until the formation of two distinct phases. 10 mL of ethyl acetate was added and the organic phase was separated by settling. Ionic phase was washed with 20 mL of ethyl acetate. The organic phase was dried on sodium sulphate (6 g) and ethyl acetate was evaporated.

2.3. Characterization

2.3.1. High-performance liquid chromatography (HPLC)

Aconitic acid and the aconitate esters were identified with Dionex HPLC using a reversed phase C18 column (Omnisphere, 4.6 mm × 250 mm). The mobile phase is composed of water with 0.1% H_3PO_4 and CH_3CN (1.0 mL/min) according to the following gradient: 50% CH_3CN (t = 0–5 min) to 100% CH_3CN (t = 15–20 min) to 50% CH_3CN (t = 25–30 min).

The UV detection (Hewelett-Packard 1100) was performed at a wavelength of 210 nm. Aconitic acid and tri-isoamyl aconitate were identified and quantified by comparing HPLC retention time and peak area with their respective calibration standards. Mono and diesters were identified by HPLC–MS.

The relative percentages of compounds (aconitic acid and esters) were determined by the ratio between product peak area and the sum of compounds peak area. Aconitic acid was quantified through a calibration performed with a commercial standard (98%).

2.3.2. Nuclear magnetic resonance (NMR)

^1H and ^{13}C NMR spectra were collected on a Bruker Avance 300 spectrometer with a 5 mm BBFO ATMA probe. All spectra were acquired at 298.0 K using $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported as parts per million from tetramethylsilane with an absolute frequency 300.13 MHz.

^1H and ^{13}C NMR of *trans-aconitic acid* (AA) (DMSO-d_6). ^1H NMR: δ 6.92 (s, 1H, C=CH), and 3.95 ppm (s, 2H, CH_2). ^{13}C NMR: δ 171.76 (s, C=O), 167.84 (s, C=O), 167.84 (s, C=O), 140.60 (s, **C**=CH), 129.32 (s, C=**C**H), and 33.17 ppm (s, CH_2).

^1H and ^{13}C NMR of *mono-isoamyl aconitate* (MIA) ($CDCl_3$). ^1H NMR: δ 7.07 (m, 1H, C=CH), 4.13–4.18 (m, 2H, O–CH_2), 3.95 (m, 2H, CH_2), 1.71–1.62 (m, 1H, CH_2–C**H**–), 1.57–1.46 (m, 2H, C$\mathbf{H_2}$–CH–), and 0.95–0.90 ppm (m, 6H, CH_3). ^{13}C NMR: δ 170.87–170.38 (d, C=O), 169.80–169.58 (d, C=O), 165.19 (d, C=O), 141.99–140.95–138.93 (t, **C**=CH), 131.04–130.07 (t, C=**C**H), 64.08–63.96 (d, CH_2–O), 37.11 (s, O=C–**C**H_2), 33.07–32.86 (m, CH_2), 24.95–24.65 (m, CH) and 22.55–22.37 ppm (m, CH_3).

^1H and ^{13}C NMR of *di-isoamyl aconitate* (DIA) ($CDCl_3$). ^1H NMR: δ 7.04–6.96 (d, 1H, C=CH), 4.28–4.10 (m, 4H, O–CH_2), 3.95–3.94 (d, 2H, CH_2), 1.71–1.69 (m, 2H, CH_2–C**H**–), 1.60–1.50 (m, 4H, C$\mathbf{H_2}$–CH–), and 0.95–0.90 ppm (t, 12H, CH_3). ^{13}C NMR: δ 170.82 (s, C=O), 169.92 (d, C=O), 165.17 (d, C=O), 141.99–138.95 (d, **C**=CH), 130.97–128.22 (d, C=**C**H), 64.80–63.91 (d, CH_2–O), 37.14 (s, O=C–**C**H_2), 33.34–32.85 (d, CH_2), 25.02 (s, CH) and 22.39 ppm (d, CH_3).

^1H and ^{13}C NMR of *tri-isoamyl aconitate* (TIA) ($CDCl_3$). ^1H NMR: δ 6.92 (s, 1H, C=CH), 4.28–4.10 (m, 6H, O–CH_2), 3.96 (s, 2H, CH_2), 1.72–1.62 (m, 3H, CH_2–C**H**–), 1.60–1.50 (m, 6H, C$\mathbf{H_2}$–CH–), and 0.95–0.90 ppm (t, 18H, CH_3). ^{13}C NMR: δ 169.89 (s, C=O), 166.06 (s, C=O), 165.43 (s, C=O), 139.98 (s, **C**=CH), 129.06 (s, C=**C**H), 64.55–63.71 (d, CH_2–O), 37.15 (s, O=C–**C**H_2), 33.15 (s, CH_2), 25.02 (d, CH) and 22.40 ppm (d, CH_3).

3. Results and discussion

Three catalyses conditions have been selected: homogeneous catalyse (H_2SO_4) as the standard conditions, Amberlyst 15 as a cation exchanger and 1-methylimidazolium hydrogensulfate as an ionic liquid (Fig. 3).

With macroporous resins, the minimum alcohol/aconitic acid ratio which was possible to use is equal to 6. The liquid phase constituted by the alcohol must cover the solid phase (resin).

The amount of ionic liquid was determined as the minimum volume to ensure the solubilization of the aconitic acid. With ionic liquid, the starting medium was homogeneous and became biphasic during the formation of esters.

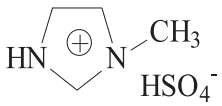

Fig. 3. 1-Methylimidazolium hydrogensulfate.

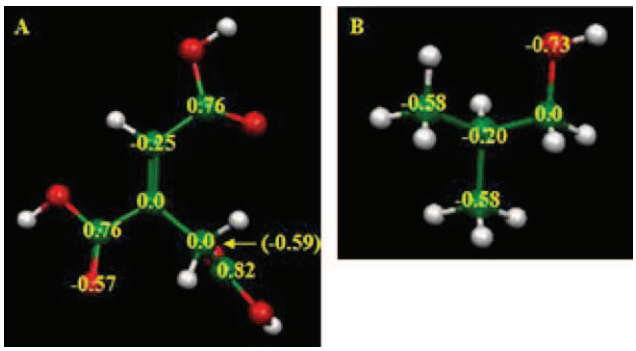

Fig. 4. Charges on the atoms (NBO population analysis). A: aconitic acid; B: isoamyl alcohol.

The effects of several experimental parameters have been studied in order to optimize the conversion of aconitic acid and to enrich the medium with one of the esters.

3.1. Quantum calculations

We have performed quantum calculations to investigate the reactivity of aconitic acid and isoamyl alcohol. We have first looked for the most stable conformations of both *cis* and *trans* isomers. The structures were optimised at the B3LYP/pVTZ and MP2/pVTZ level of theory using the Gaussian03 package (Frisch et al., 2004).

The *trans* isomer is more stable of 2.6 kcal/mol (MP2/pVTZ) than the *cis* isomer and is thus thermodynamically favoured. This is in agreement with the isomerisation of the *cis* to the *trans* isomer observed experimentally. The bond lengths are similar for the two *cis* and *trans* isomers. We estimated a molar volume of 120.5 cm^3/mol for the *trans* isomer, with an average radius of 4.49 Å and a molar volume of 106.0 cm^3/mol for the *cis* isomer, with an average radius of 4.33 Å.

In order to calculate the charges on the atoms for the aconitic acid and the isoamyl alcohol, we performed a NBO and Mulliken population analysis. The results are presented in Fig. 4.

The first step of the reaction of esterification is a protonation of the oxygen atom of the carbonyl function of the aconitic acid. It is followed by a nucleophilic addition of the alcohol on the carbon of the carbonyl function. The calculated charges on the three oxygen atoms of the aconitic acid molecule are similar and should exhibit a similar reactivity.

The calculated charges on the C atoms (Fig. 5) of the carbonyl functions show that C6 has a slightly more positive charge. This difference may explain the preferential reactivity of this site for the addition of the alcohol molecule. This data is in agreement with the experimental part since we have observed that the chemical shift

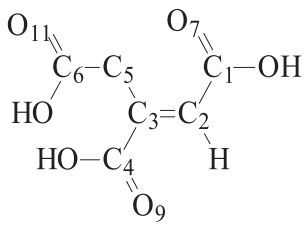

Fig. 5. *Trans*-aconitic acid.

of C6 on aconitic acid (172 ppm) has moved after esterification. The mono-isoamyl aconitate thus presents a chemical shift at 170 ppm.

The calculated charges on ethylenic carbon, C2 and C3 atoms show that C2 has a higher electronic density, meaning that in ^{13}C NMR, C3 is more unshielded than C2. It is thus possible to determine the following chemical shifts: δ_{C2} = 129 ppm and δ_{C3} = 140 ppm.

3.2. Effect of temperature

The effect of temperature from 85 to 120 °C on the esterification of aconitic acid with isoamyl alcohol was studied. Results are presented in Table 1. An increasing temperature does not improve the conversion of aconitic acid but acts positively on the yield of triester.

Whatever the catalyst, the proportion of triester in the medium is thus increased with temperature. We can note that heterogeneous catalysis is very sensitive to temperature since an increase from 85 °C to 100 °C, is enough to enhance the percentage of triester from 6 to 46%.

The diesters contents depend on the relative conversion rates of monoester into diesters and of diesters into the triester.

The temperature conditions which lead to the highest contents of triester (66%), diesters (59%) and monoesters (54%) will be kept for the following studies.

3.3. Effect of catalyst loading

The effects of the catalyst loading are presented in Table 2. For homogeneous catalysis, the catalyst loading varies from 1.7 to 3.7% wt and for heterogeneous catalysis between 3 and 7 wt.%.

It appears that catalyst loading has few effects on the conversion of aconitic acid. But, the yield of triester increases with catalyst loading for homogeneous catalysis leading to an enriched medium in triester. Moreover, it is not useful to increase the loading above 3% in heterogeneous catalyst to prepare monoesters.

We observe that the yields of diesters and triester are better when the ionic liquid is used as a cosolvent. In the latter case, the ionic liquid brings 12.5 times more milli-equivalents H^+ than

Table 1
Influence of temperature.

Catalysis	*T* (°C)	Acid conversion (%)	Yield of triester (%)*	Relative percentage of esters (%)		
				Monoesters	Diesters	Triester
	85	88.4	34.0	10	50	40
Homogeneous[a]	100	91.2	59.1	4	30	66
	120	87.3	65.2	3	26	71
	85	86.1	6.9	54	40	6
Heterogeneous[b]	100	86.6	43.3	8	46	46
	120	86.3	56.5	5	41	54
	85	88.1	7.4	38	52	10
Ionic liquid[c]	100	87.6	19.7	15	59	26
	120	89.3	34.1	5	51	44

Reaction conditions: 5 h, [a]molar ratio isoamyl alcohol/aconitic acid, 6:1, catalyst loading, 2.7 wt.%; [b]molar ratio isoamyl alcohol/aconitic acid, 6:1, catalyst loading, 5 wt.%; [c]molar ratio isoamyl alcohol/aconitic acid, 3:1, ionic liquid as co-solvent.

* Yield of triester has been determined by HPLC calibration.

Table 2
Influence of catalyst loading.

Catalysis	Catalyst loading (wt.%)	Acid conversion (%)	Yield of triester (%)	Relative percentage of esters (%)		
				Monoesters	Diesters	Triester
	1.7	90.3	47.1	6	41	53
Homogeneous[a]	2.7	91.2	59.1	4	30	66
	3.7	89.5	64.5	3	27	70
	3	87.0	3.7	59	36	5
Heterogeneous[b]	5	86.1	6.9	54	40	6
	7	88.5	5.3	53	40	7
Ionic liquid[c]	5	84.6	11.1	35	51	14
[d]	Cosolvent	87.6	19.7	15	59	26

Reaction conditions: 5 h, [a]molar ratio isoamyl alcohol/aconitic acid 6:1, 100 °C; [b]molar ratio 6:1, 85 °C; [c]molar ratio 6:1, 100 °C; [d]molar ratio 3:1, 100 °C.

it does in catalytic conditions, which enhances the conversion of monoesters into diesters and into triester.

In the absence of device to remove water, the use of a hydrophilic ionic liquid seems efficient to trap water and to shift the equilibrium. Furthermore, as the solubilization of aconitic acid is ensured by ionic liquid, it is possible to reduce the excess of alcohol to the ratio 3:1.

Eventually, for homogeneous catalysis, the conditions allowing to minimise the amount of acidic effluents and to get an enriched media in triester corresponds to a catalyst loading equal to 2.7%.

For heterogeneous catalysis, we observed that 3% of catalyst loading is enough to get an enriched medium in monoesters.

3.4. Kinetic studies

3.4.1. Free catalytic esterification

The reaction of aconitic acid with isoamyl alcohol was tested under free catalyst under the standard, 100 °C and a molar ratio "isoamyl alcohol:aconitic acid" of 6:1.

Fig. 6 represents the relative percentage of compounds during the reaction, corresponding to the self-catalysis capacity of the reaction.

Spontaneously, the reaction of esterification generates the formation of monoesters which are converted progressively into diesters and in more limited proportions into triester.

This experiment confirms that monoesters and then diesters are intermediates for the synthesis of the final triester.

Finally, the contribution of self-catalysis must be considered especially for low catalyst loadings under high temperatures.

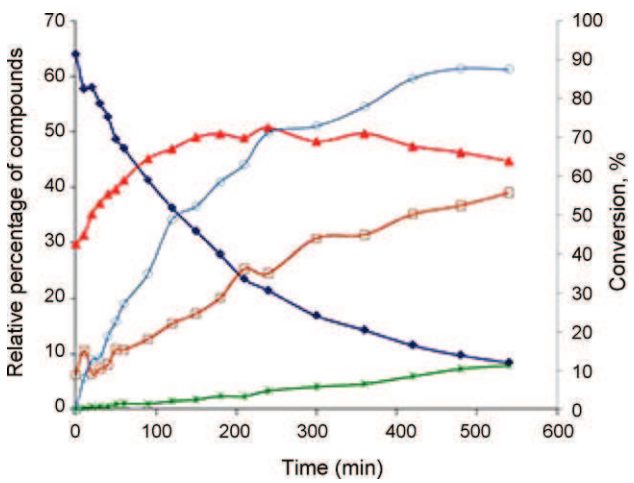

Fig. 6. Self-catalyzed esterification of aconitic acid: molar ratio isoamyl alcohol/aconitic acid, 6:1, 100 °C (♦: AA; ▲: MIA; □: DIA; ×: TIA; ○: conversion).

3.4.2. Kinetic profiles according to catalyst

The preliminary tests allowed to define the experimental conditions summarized in Table 3 to perform the kinetic studies.

Figs. 7–9 show the plots of the conversion of aconitic acid as limiting reactant. The relative percentages in the reaction media (aconitic acid, monoester MIA, diester DIA and triester TIA) are also represented.

It was found that the use of sulphuric acid leads to the maximum conversion close to 100% before 2 h.

The cation-exchange resin also provides a high conversion but with a slower kinetic: almost 100% of aconitic acid is converted after 4 h.

With the ionic liquid, a lower conversion close to 70% is observed, that is still acceptable.

We can note that the type of catalyst has an influence on the selectivity of reaction since the compositions of esters are different according to the conditions. Table 4 indicates the major esters present in the final reaction media; homogeneous catalyst mainly provides the triester whereas heterogeneous catalyst orientates the reaction towards the production of monoesters and diesters. The ionic liquid rather favours the formation of diesters.

As it is not possible to get a total selectivity for the monoesters and the diesters, we thought that it could be interesting to prepare compositions enriched with the desired ester. We have thus selected specific times of reaction corresponding to the highest content in esters (Table 4). Unreacted aconitic acid of conditions 2* and 3, was removed by extraction with water.

It is thus possible to prepare five enriched compositions with one of the esters. Methods 1 and 2 improved performances that were mentioned in previous works as we got almost complete conversion of acid and higher ester contents.

Moreover, the production of these mixtures avoids an expensive step to separate esters and their resulting properties may be adapted to some applications.

3.4.3. Effect of the hydrocarbon chain length

The previous conditions have been adapted to the synthesis of aconitate esters from dodecyl alcohol. Experimental conditions and results are presented in Table 5.

Dodecyl alcohol presents a good reactivity towards aconitic acid, leading to a high conversion of the acid into triester, under homogeneous catalyst (method 1′).

Table 3
Conditions for kinetic reaction.

Methods	Catalysis	T (°C)	Catalyst loading (wt.%)	Molar ratio isoamyl alcohol:aconitic acid
1	Homogeneous	100	2.7	6:1
2	Heterogeneous	85	3	6:1
3	Ionic liquid	100	Cosolvent	3:1

Table 4
Composition of esters in selected media.

Methods	Catalysis	Selected time (min)	Percentage of the major ester (%)	Acid conversion (%)
1[a]	Homogeneous	40	Diesters (57)	98
1		540	Triester (79)	99
2[a]	Heterogeneous	90	Monoesters (67)	73
2		540	Diesters (59)	98
3	Ionic liquid	540	Diesters (69)	64

[a] Derived from methods 1 or 2 by modifying the reaction time.

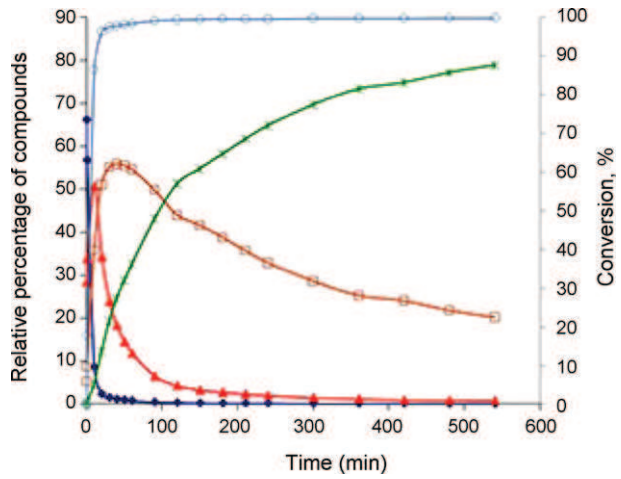

Fig. 7. Esterification of aconitic acid catalyzed by sulfuric acid, according to method 1 (♦: AA; ▲: MIA; □: DIA; ×: TIA; ○: conversion).

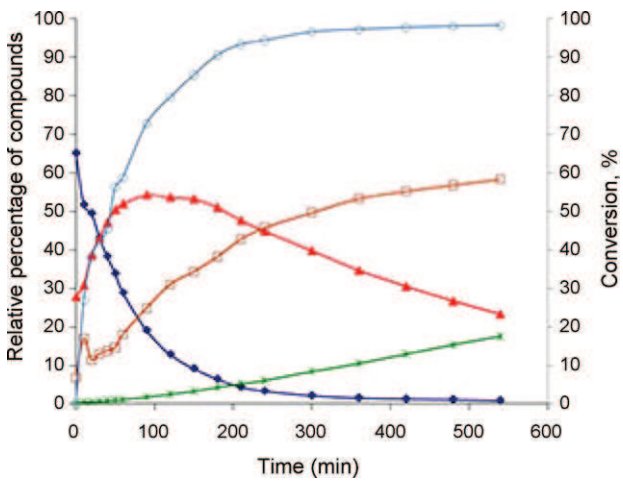

Fig. 8. Esterification of aconitic acid catalyzed by ion-exchange resin, according to method 2 (♦: AA; ▲: MIA; □: DIA; ×: TIA; ○: conversion).

For heterogeneous conditions, the conversion of aconitic acid is lower with dodecyl alcohol compared to isoamyl alcohol (methods 2 and 2′). This result can be explained by the limiting effect due to the more restricted accessibility of the catalytic sites by the long chain alcohol and to a lower alcohol:acid ratio.

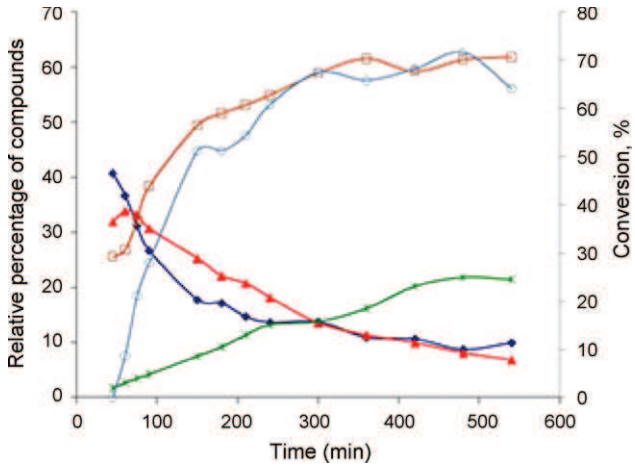

Fig. 9. Esterification of aconitic acid with ionic liquid, according to method 3 (♦: AA; ▲: MIA; □: DIA; ×: TIA; ○: conversion).

Therefore, the chain length effect is mainly observed in the presence of macroporous catalysis.

Moreover, the results confirm that macroporous catalytic sites also limit the conversion of monoesters and diesters into triester. In fact, macroporous resins represent efficient conditions to prepare preferentially monoesters and diesters with both alcohols.

The compositions in monoesters/diesters obtained with methods 2 and 2′ show that the temperature is a significant parameter to enhance the conversion of monoester into diester, as it was noted with Table 1.

Finally, heterogeneous catalysis offers performing conditions to reach a good selectivity towards mono/diesters but also let the possibility to obtain composition rich in triester by acting on the temperature.

3.5. Environmental factors

A convenient tool is proposed by Eissen and Metzger to compare alternative chemical syntheses regarding their potential environmental impact. The EATOS (Environmental Assessment Tool for Organic Synthesis) procedure (Eissen and Hungerbühler, 2003; Eissen and Metzger, 2002) allows to calculate environmental performances metrics when the systematic design of more sustainable processes is undertaken on a laboratory scale. Metrics which are considered are the following ones:

Table 5
Comparison between the reactivity of isoamyl alcohol and dodecyl alcohol (for 5 h).

Methods	Catalysis	Percentage of the major ester (%)	Aconitic conversion (%)	Temperature (°C)	Catalyst loading (%)	Molar ratio alcohol:acid
1	Homogenous	Tri-isoamyl aconitate (66)	91	100	2.7	6:1
1′		Tridodecyl aconitate (75)	96	100	2.7	3:1
2	Heterogeneous	Mono-/di-isoamyl aconitate (59/36)	87	85	3	6:1
2′		Mono-/di-dodecyl aconitate (36/56)	49	100	3	2:1

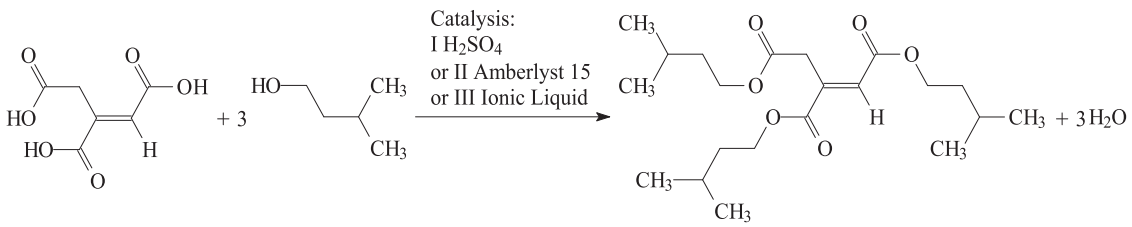

Fig. 10. Preparation of tri-isoamyl aconitate.

- The mass index, S^{-1}, which is the mass of all raw materials [kg] used for the synthesis, per mass unit of the purified product (raw materials, solvents, catalysts, auxiliaries, etc.).
- The environmental factor, E, which represents the mass of wastes [kg] per mass unit of the product.

For the determination of E and S^{-1}, the following materials have been integrated for the calculation of the amount of wastes:

- The non-reactant alcohol and acid according to the yield;
- The co-products such as water and other esters;
- The homogeneous catalyst (H_2SO_4);
- The amount of water necessary to remove the homogeneous catalyst;
- The amount of sodium sulphate to dry organic layer;
- A quarter of the macroporous resin and ionic liquid weight, since the tests have shown that they could be used four times without significant loss of performances;
- The extraction solvent.

These hypotheses allowed to compare the different routes to obtain the targeted product.

Calculations were carried out with two different purposes:

- Comparison of different syntheses of the triester;
- Comparison of syntheses for three different enriched media.

3.5.1. *Calculation of E-factor and S^{-1} for syntheses of triester*

The calculations deal with the synthesis of tri-isoamyl aconitate according to the methods I, II and III which have been adapted from methods 1, 2 and 3 (Fig. 10 and Table 6).

Fig. 11 shows a quantitative assessment of methods I, II and III.

The protocol II is the most effective procedure with regard to its mass efficiency (S^{-1} = 10.3 kg kg^{-1}), and to its environmental factor (E = 9.3 kg kg^{-1}). The effectiveness of method II is due to an easy treatment step (recovering of catalyst, low amount of auxillaries, no sewage). Moreover, we know that the yield of triester can still be improved by rising the temperature.

We can confirm that the weak point of the method I is the production of sewage. Method III is penalized by several factors: the lower conversion in triester, the use of an extraction solvent and the amount of ionic liquid.

Table 6
Data used for the calculation of green units for the syntheses of tri-isoamyl aconitate for a reaction time of 300 min.

Conditions	Methods		
	I	II	III
Temperature	100	120	120
Catalyst loading (%)	3.7	5	Cosolvent
Acid conversion (%)	89.5	86.3	89.3
Yield of triester (%)	64.5	56.5	34.1

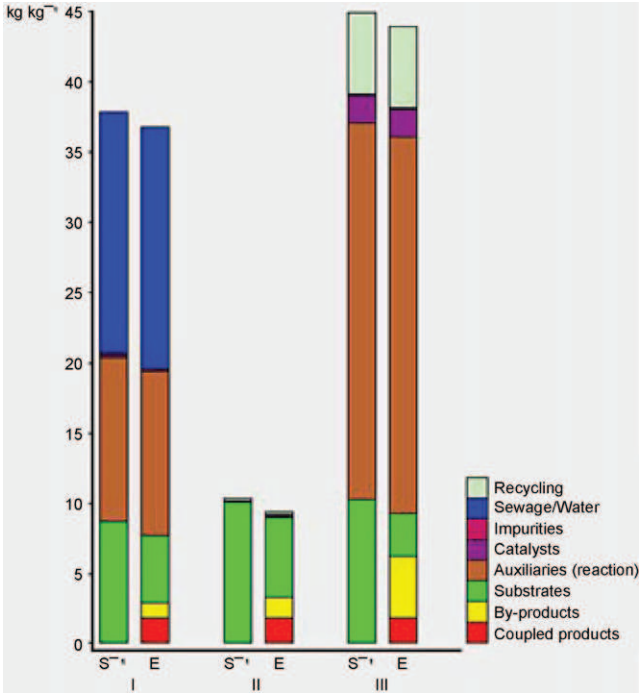

Fig. 11. Calculation of mass index S^{-1} and environmental factor E (software EATOS) for the tri-isoamyl aconitate synthesis – methods I (H_2SO_4), II (Amberlyst 15) and III (Ionic liquid).

3.5.2. *Calculation of E and S^{-1} for synthesis of enriched media*

The calculations concern the syntheses of the three enriched media, with the conditions presented in Table 7.

Fig. 12 shows the comparison of mass index S^{-1} and E-factor for the methods 1, 2 and 3.

The production of monoester with method 2 leads to the lowest mass efficiency (S^{-1} = 18.5 kg kg^{-1}) and the lowest environmental factor (E = 17.5 kg kg^{-1}) due to the advantages described for heterogeneous catalyst.

For method 3, we can thus identify two limiting factors, the yield and the amount of auxiliaries. By modifying the characteristics of ionic liquid, we might affect positively the mass efficiency and the environmental factor. The present results show the use of an ionic liquid can be justified when a specific selectivity is targeted.

Table 7
Data used for the calculation of green units for the synthesis of enriched media according to the described protocols.

Conditions	Methods		
	1	2	3
Temperature (°C)	100	85	100
Catalyst loading (%)	2.7	3	Cosolvent
Reaction time (min)	540	90	540
Acid conversion (%)	99	73	64
Yield of major ester (%)	Triester (78)	Monoesters (49)	Diesters (44)

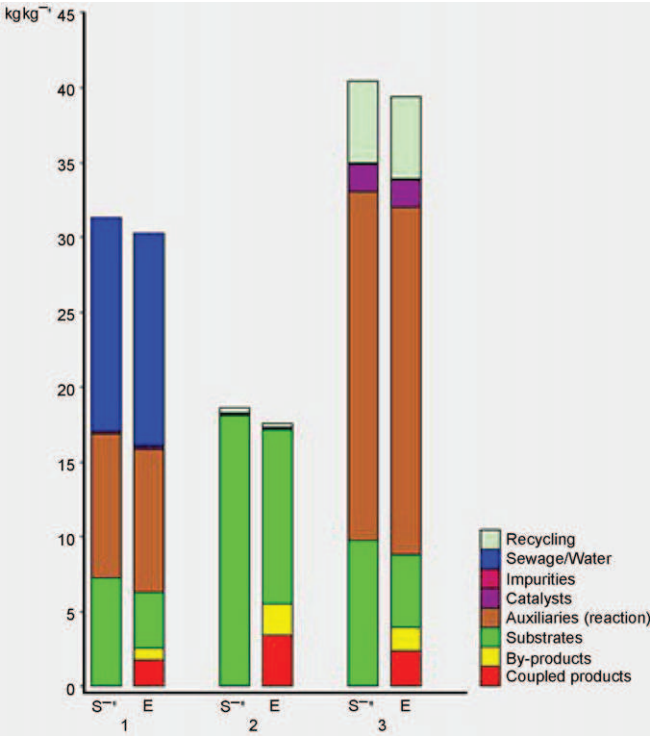

Fig. 12. Calculations of mass index S^{-1} and environmental factor E (software EATOS) for the preparation of enriched compositions – methods 1 (H_2SO_4), 2 (Amberlyst 15) and 3 (Ionic liquid).

These data should be taken into consideration when a scale-up is planed.

4. Conclusion

This study shows the potentialities of a co-product of the sugarcane industry as raw material to prepare several esters.

New conditions have been studied to synthesize aconitic esters in a stirred batch reactor and to orientate the reaction towards an ester category (monoesters, diesters or triester).

Quantum calculations have given insight in the reactivity of the three sites and have confirmed the site which is preferentially esterified.

In the experimental part, the effects of parameters have been studied to prepare enriched compositions avoiding a further step of purification and leading to improved yields for specific esters.

Moreover, the preparation of esters with different hydrocarbon chains allows to modulate the physico-chemical properties of the molecules to meet several specifications.

For the production of triesters with long or short chains, homogeneous catalysis leads to the best selectivity, but heterogeneous catalyst represents the best conditions to meet green chemistry criteria.

For the production of enriched media, high conversions are obtained to produce compositions with major esters contents above 65%. These enriched compositions have variable hydrophilic properties according to the number of esterified sites, which modifies the polar head.

Among the three enriched compositions, the calculated green indicators (mass index and environmental factor) were the best for the heterogeneous conditions. Despite the lack of benefits concerning green indicators, conditions assisted by an ionic liquid are performing to shift the equilibrium without the cost of a distillation.

The features of resin macroporous sites foster the production of monoesters and diesters, by limiting the conversion of diesters into triester. In this case, we have shown that an increasing triester proportion can be reached by acting on temperature.

Finally, macroporous resins still remain the best way to improve conventional methods into more ecofriendly routes. Moreover, such conditions offer the opportunity to act on the selectivity and thus to prepare new bioproducts of great interest.

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References

Bruins, P.F., Canapary, R.C., 1956. Esterification of acids. US Patent 2,766,273.
Choudhary, V.R., Mantri, K., Jana, S.K., 2001. Selective esterification of tert-butanol by acetic acid anhydride over clay supported $InCl_3$, $GaCl_3$ $FeCl_3$ and $InCl_2$ catalysts. Catal. Commun. 2, 57–61.
Cockrem, M., Milner, C., Douglas, J.P., 1993. Récupération des esters de lactate et de l'acide lactique dans un bouillon de fermentation. WO 9300440.
Cole, A.C., Jensen, J.L., Ntai, I., Tran, K.L.T., Weaver, K.J., Forbes, D.C., Davis, J.H., 2002. Novel brönsted acidic ionic liquids and their use as dual solvent-catalysts. J. Am. Chem. Soc. 124, 5962–5963.
Cox, H.L., Carruthers, T.F., 1936. Hydroxy carboxylic acid esters. US Patent 2,046,150.
Eissen, M., Hungerbühler, K., 2003. Mass efficiency as metric for the effectiveness of catalysts. Green Chem. 5, G25–G27.
Eissen, M., Metzger, J.O., 2002. Environmental performance metrics for daily use in synthetic chemistry. Chem. Eur. J. 8, 3580–3585.
Fraga-Dubreuil, J., Bourahla, K., Rahmouni, M., Bazureau, J.P., Hamelin, J., 2002. Catalysed esterifications in room temperature ionic liquids with acidic counteranion as recyclable reaction media. Catal. Commun. 3, 185–190.
Frappier, E.P., Davis, J.E., Grendze, M., Scriven, E.F.V., Wyeth, J.T., Kuen-Wai, C., 2002. Process for producing citrate esters. US Patent 6,403,825.
Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., 2004. Gaussian 03, Revision E.01. Gaussian, Inc., Wallingford, CT.
Gil, N., Saska, M., Negulescu, I., 2006. Evaluation of the effects of biobased plasticizers on the thermal and mechanical properties of poly(vinyl chloride). J. Appl. Polym. Sci. 102, 1366–1373.
Gross, S.F., Barabash, M.J., Hessel, J.F., 2008. Graffiti remover, paint stripper, degreaser. US Patent 7,449,437.
Guthrie, R.W., Hamilton, J.G., Kierstead, R.W., Miller, O.N., Sullivan, A.C., 1976. Citric acid derivatives. US Patent 3,810,931.
Jonn, J.Y., McCrum, B., Su, W., Warren, T., Badejo, I.T., 2008. Liquid coating compositions. US Patent 7,318,937.
Joseph, T., Sahoo, S., Halligudi, S.B., 2005. Brönsted acidic ionic liquids: a green, efficient and reusable catalyst system and reaction medium for Fischer esterification. J. Mol. Catal. A: Chem. 234, 107–110.
Kolah, A.K., Asthana, N.S., Vu, D.T., Lira, C.T., Miller, D.J., 2006. Reaction kinetics of the catalytic esterification of citric acid with ethanol. Ind. Eng. Chem. Res. 46, 3180–3187.
Kolah, A.K., Asthana, N.S., Vu, D.T., Lira, C.T., Miller, D.J., 2008. Reaction kinetics for the heterogeneously catalyzed esterification of succinic acid with ethanol. Ind. Eng. Chem. Res. 47, 5313–5317.
Leng, Y., Wang, J., Zhu, D., Ren, X., Ge, H., Shen, L., 2009. Heteropolyanion-based ionic liquids: reaction-induced self-separation catalysts for esterification. Angew. Chem. Int. Ed. 48, 168–171.
Ma, Y., Wang, Q.L., Yan, H., Ji, X., Qiu, Q., 1996. Zeolite-catalyzed esterification. I. Synthesis of acetates, benzoates and phthalates. Appl. Catal. A: Gen. 139, 51–57.
Olang, F.N., O'leary, R.J., Korwin-Edson, M., Quinn, R.E., 2010. Formulation method for plural component latex-foam. US Patent 20,100,189,908.
Patil, A.O., Wu, M.M.-S., Ho, S.C.H., 2010. Lubricant composition containing glycerol tri-esters. US Patent 20,100,216,678.
Petrini, M., Ballini, R., Marcantoni, E., Rosini, G., 1988. Amberlyst 15: a practical, mild and selective catalyst for methyl esterification of carboxylic acids. Synth. Commun. 18, 847–853.
Roberts, E.J., Martin, L.F., Magne, F.C., Mod, R.R., 1954. Aconitic and tricarballylic acid ester as vinyl plasticizers. Rubber World, 801–804.
Seemeyer, S., Morrison, E.D., Scharrenbach, S., Caussin de Schneck, C., Rich, P., Court, C., 2008. Conveyor lubricants including emulsion of a lipophilic compound and an emulsifier and/or an anionic surfactant and methods employing them. US Patent 20,080,176,778.
Weiberg, S.M., Stimpson, E.G., 1942. Preparation of lactic acid. US Patent 2,290,926.
Zhu, H.-P., Yang, F., Tang, J., He, M.-Y., 2003. Bronsted acidic ionic liquid 1-methylimidazolium tetrafluoroborate: a green catalyst and recyclable medium for esterification. Green Chem. 5, 38–39.