Esterification of Lactic Acid by Catalytic Extractive Reaction: An Efficient Way to Produce a Biosolvent Composition

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Abstract A biosolvent composition containing ethyl lactate and biodiesel was directly obtained by catalytic extractive esterification of lactic acid. Since the esterification of organic acids with alcohols is a thermodynamically limited reaction, the methodology consists in conducting the esterification and the ester extraction simultaneously thereby shifting the equilibrium towards more esters. The acid catalyzed esterification was performed in a biphasic solvent system composed of (i) a reactive polar phase which contains the esterification constituents, lactic acid, ethanol and an acid catalyst (ii) an extractive solvent selective of the ester, fatty acid methyl ester (biodiesel). This solvents system increases the ethyl lactate yield of more than 30 %. During the reaction progress, the selective solvent, fatty acid methyl ester, is progressively blended with ethyl lactate providing a mixture of esters, which can be directly used as an efficient composition of biosolvents without further purification. The solid acidic potassium salt of 12-phosphotungstic acid, K_{2.5}H_{0.5}PW₁₂O₄₀, was shown to be more efficient than the conventional esterification catalysts, H₂SO₄ or Amberlyst 15. K_{2.5}H_{0.5}PW₁₂O₄₀ gives a yield in ethyl lactate higher than 80 mol% after 2 h of reaction in the biphasic solvent system, using a molar ratio ethanol/lactic acid of 3.3 only. Moreover, K₂ ₅H₀ ₅PW₁₂O₄₀

N. Q. Bui · N. Essayem (⊠) Institut de Recherche sur la Catalyse et l'environnement de Lyon, CNRS, Lyon1, 2 Avenue Albert Einstein, 69626 Villeurbanne, France e-mail: nadine.essayem@ircelyon.univ-lyon1.fr shows a remarkable higher activity per protonic sites (factor 30) and is recyclable at least two times without apparent loss of activity. These excellent properties were ascribed to its low density of strong Brønsted acid sites and its adequate hydrophobicity which would make this acid more water tolerant than the conventional esterification catalysts, H_2SO_4 or Amberlyst 15.

Keywords Ethyl lactate · Biosolvent · Extractive reaction · Esterification · Solid acid catalyst

1 Introduction

Solvents represent an important class of chemicals. They are used in many industries for their abilities to dissolve, dilute or remove other compounds without causing chemical changes. Conventional solvents, obtained from fossil carbons are usually volatile organic compounds. Many of them are hazardous to human health and the environment in general. Nowadays, new environmental regulations have forced the industry to find solutions to reduce their emission and waste released into the environment. The ideal solution consists in the replacement of conventional solvents by new alternative environmentally friendly solvents, which would be non volatile, non toxic to human and the environment. Importantly, it would provide effective performances and be economically viable and moreover obtained from renewable feedstock. Most of the biosolvents, issued from natural resources, addressed the previous criteria. The major classes of biosolvents are esters of natural organic acids produced by fermentation of carbohydrates, fatty acid esters, bioethanol, terpenic compounds, isosorbide or glycerol derivatives. These biosolvents are incorporated into different compositions for cleaning

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applications, pesticides, printing inks, paints, varnish or bituminous binders.

Ethyl lactate and esters of fatty acids are biosolvents which can be used alone or in mixture [1, 2]. Their mixture provides effective solvency for a broad range of applications. Their high boiling point, their biodegradability and non-toxicity make this class of biosolvents of high interest. Currently, lactic acid manufacture is based on carbohydrate fermentation. The major problem of this technology is the salts formation because the fermentation is efficient at neutral pH, which requires the neutralization of the media. Thereby, salts of lactic acid are produced instead of lactic acid. Hence, the main drawback of this technology is the lactic acid separation and purification, which is hardly crystallized or distilled [3]. Note that recent developments report its formation via a thermochemical way from lignocellulosic resources [4]. In other respects, the production of ethyl lactate of high purity, in high yield, is not an easy task for two main reasons: first, due to the versatility of lactic acid, second because of the thermodynamic equilibrium of the esterification reaction. Lactic acid is a hydroxy-carboxylic acid with a hydroxyl group born on the C2 carbon. Under the esterification conditions, this functional group is at the origin of the secondary reactions such as the self esterification reaction of lactic acid or transesterification reactions between ethyl lactate and any hydroxy-compounds present in the media producing heavy oligomers (Schemes 2, 3). To overcome the limitations due to the thermodynamic equilibrium, more or less complex technologies were reported. One can mention the use of an excess amount of alcohol and the continuous removal of the ethanol–water azeotrope, i.e. by reactive distillation [5, 6]. Note that the ethanol recycling is problematic too and requires a further dehydration step. The use of catalytic membranes was also reported to shift the reaction equilibrium [7, 8]. Earlier patents already reported the application of reactive extraction to shift the esterification equilibrium and promote the yield in the ester product. One can distinguish two approaches which were applied to upgrade mixtures of organic acids of low volatility into mixtures of esters of higher volatility which can be separated by distillation. The older one reports the use of water miscible alcohol and of a water immiscible extractive solvent [9]. The acid and the alcohol remain in the aqueous phase while the esters are extracted in the non-aqueous phase. The preferred solvents were conventional volatile ones, such as alkanes or aromatics which can be separated by distillation and reused. A more recent approach reported the preparation of esters from acids miscible in water and water immiscible alcohols in the presence of an aprotic solvent [10].

Recent articles report the use of biphasic solvents systems, not to shift an equilibrium but to prevent secondary reactions due to the over-reactivity of peculiar reactants and products. This approach is efficient for the synthesis of HMF, a versatile product which can be easily involved in successive reactions leading to polymers [11]. By a continuous extraction of the target product, its yield can be significantly improved.

The concept of extractive esterification applied for ethyl lactate preparation would present two advantages: the shift of the esterification reaction equilibrium and the limitation of secondary reactions due to the functionalities of lactic acid.

As regard to the catalytic aspect of the esterification, homogeneous mineral acids, such as sulfuric acid, are known to promote efficiently the esterification of various carboxylic acids [9, 10]. Nevertheless, the use of homogeneous acid catalysts presents drawbacks such as the hard catalyst recovery, the production of acidic waste liquids, and the inescapable corrosion of the equipment. The use of solid acids is an alternative. Sulfonated acidic resins are reported to be one of the most efficient solid acid catalysts for esterification reactions [12]. Although efficient, the resins remain expensive catalysts which can be hardly regenerated due to their limited thermal stability. The heterogeneous acidic potassium salt of 12-phosphotungstic acid (K_{2.5}H_{0.5}PW₁₂O₄₀) was previously reported as strong Brønsted solid acid of high potential for petrochemical applications owing to its strong acid strength, close to that of the parent acid $H_3PW_{12}O_{40}$ [13]. Moreover, the acidic potassium salt has a BET surface area higher than 100 m² g⁻¹, more than ten time that of $H_3PW_{12}O_{40}$ and is insoluble in polar media by contrast to the bulk acid [14]. The heterogeneous catalysts are non-corrosive, easy to separate from the reaction mixture, and can be used repeatedly over a prolonged period without any difficulty in handling and storing.

In the present work, to overcome these shortcomings of the esterification of lactic acid, a heterogeneous heteropolyacid and other reference catalysts were evaluated in a biphasic solvent system consisting of a polar reactive phase, containing the esterification constituents lactic acid/ ethanol/acid catalysts and an extractive phase, fatty acid methyl ester, in which the ethyl lactate has a greater solubility than in the reactive phase. This situation would permit to shift and to reach more rapidly the esterification equilibrium. In other respect, fatty acid methyl ester was also selected as regards to the solvent properties of mixtures of fatty acid methyl ester and ethyl lactate. Hence, the addition of fatty acid methyl ester in the esterification reaction would not only increase the yield of the esterification reaction due to the continuous extraction of ethyl lactate in the biodiesel, but would produce a biosolvent composition in one step.

2 Experimental

2.1 Materials and Catalysts

Lactic acid, ethanol (99.7 wt%) and 12-phosphotungstic acid ($H_3PW_{12}O_{40}$ ·21 H_2O) were purchased from Sigma Aldrich. Amberlyst 15 resin was obtained from Rohm & Hass Co.

The acidic potassium salt of 12-phosphotungstic acid, $K_{2.5}H_{0.5}PW_{12}O_{40}$ (KPW) was prepared according to the literature procedure [16, 17] by adding dropwise the required amount of a saturated aqueous solution of KCl to an aqueous solution of $H_3PW_{12}O_{40}$ (0.1 M) under stirring. The precipitate obtained was filtrated, washed with distilled water and then dried at 70 °C for 10 h and then at 120 °C for 5 h.

2.2 Catalysts Characterizations

The Infrared spectrum of the heteropolyacid sample was recorded on a Brucker FTIR spectrometer with catalyst sample diluted in KBr disk, within the 400–4,000 cm⁻¹ wavenumbers range.

The X-ray diffraction pattern of the heteropolyacid sample was recorded with a Bruker D5005 diffractometer with the Cu $K_{\alpha 1+\alpha 2}$ ($\lambda = 1.54184$ Å).

Nitrogen adsorption/desorption isotherms were recorded at liquid nitrogen temperature with an equipment supplied by Micromeritics (ASAP 2020). Before analysis, $K_{2.5}H_{0.5}PW_{12}O_{40}$ was vacuum treated at 200 °C for 2 h. The specific surface area was calculated using the BET method in the range of relative pressure from 0.03 to 0.2. The BET surface area of $K_{2.5}H_{0.5}PW_{12}O_{40}$ equals 150 m² g⁻¹, an expected value for acidic alkaline salts of $H_3PW_{12}O_{40}$ prepared by precipitation using saturated solutions of precursors [16, 17].

Calorimetry of NH_3 adsorption The acid properties were measured by NH_3 adsorption at 80 °C, using a *TianCalvet* calorimeter coupled with a volumetric equipment. The samples of $K_{2.5}H_{0.5}PW_{12}O_{40}$ or Amberlyst 15 (0.1 g) were evacuated at 100 °C for 1 h under secondary vacuum. Then, the pre-treated samples were placed into the calorimeter up to the stabilization of the temperature (one night), then contacted with small doses of gas up to equilibrium and the differential enthalpy of adsorption was recorded together with the amount of adsorbed NH_3 .

2.3 Esterification of Lactic Acid

The synthesis of ethyl lactate was carried out in Pyrex flask equipped with a condenser and under argon atmosphere.

The reaction solution was obtained by mixing 66.7 g of ethanol with 39.1 g of lactic acid (molar ratio of EtOH/acid lactic = 3.3). 0.33 g of 96 % H_2SO_4 (6.46 mmol of H^+) catalysts was added to the mixture solution or 1.4 g of solid acid catalysts, $K_{2.5}H_{0.5}PW_{12}O_{40}$ (0.235 mmol of H^+) or Amberlyst 15 (6.6 mmol of H^+). The solid catalysts were dehydrated before use; for one night in an oven at 110 °C. The reaction mixture is stirred by means of a magnetic stirrer and heated at 80 °C. The yield of ethyl lactate was determined all along the reaction progress by regular GC analysis.

To perform the reaction in a biphasic liquid media, 24 g of methyl ester of rapeseed oil were added.

3 Results and Discussion

3.1 Catalyst Characterizations

The XRD pattern of KPW catalyst confirms that the potassium salt has the expected cubic phase, in agreement with previous studies.

The FTIR spectrum indicate also that the Keggin structure is retained in the KPW catalyst. The FTIR spectrum of KPW catalyst (shown in Fig. 1) exhibits the characteristic vibration bands of the Keggin anion (Scheme 4). In the range 1,100–600 cm⁻¹, KPW catalyst presents strong bands at 1,080 and 986 cm⁻¹, which are characteristic of P–O_a and W–O_d vibrations, respectively. The peaks at 891 and 808 cm⁻¹ are ascribed to W-O_b-W and W-Oc-W bridges vibrations, respectively (Fig. 1).

The calorimetric curves recorded on KPW present a short plateau compared to that measured on the Amberlyst A15 (Fig. 2). Note that, for the latter case, the experiment



Fig. 1 FTIR spectrum of fresh and used KPW catalyst

was stopped before the saturation of all the acid sites; when the experiment was stopped, only 25 % of the expected total amount of H^+ (4.7 mmol g^{-1} according to Rohm & Hass Co.) was probed. For the KPW sample, the amount of sites probed with ammonia equals 0.168 mmol g^{-1} , a value in close agreement with the expected one considering the stoichiometry of the catalyst: K_{2.5}H_{0.5}PW₁₂O₄₀. Indeed, for the parent acid H₃PW₁₂O₄₀, the amount of titrated acid sites, probed by calorimetry of NH₃ adsorption, achieved 0.850 mmol g^{-1} . This value is five times higher to that obtained on K_{2.5}H_{0.5}PW₁₂O₄₀ [18] and corresponds to 0.6 protons per P atom instead of 0.5. Both samples present initially a few amount of sites of very high strength, then a plateau is observed for both samples. The differential heat of NH₃ adsorption at half NH₃ coverage was respectively of 190 and 135 kJ mol⁻¹ for KPW and Amberlyst A15. These results clearly demonstrate the higher acid strength of the KPW sample compared to the Amberlyst A15.



Fig. 2 Calorimetric curves of $\rm NH_3$ adsorption on KPW and Amberlyst 15



Fig. 3 Esterification of lactic acid with ethanol in mono-phasic solvent medium. Influence of acid catalyst addition. Conditions: m EtOH = 66.7 g, m lactic acid = 39.1 g, mH₂SO₄ (96 %) = 0.33 g (6.46 mmol H+), m A15 = 1.4 g (6.6 mmol H⁺), m KPW = 1.4 g (0.235 mmol H⁺), T = 80 °C (reflux)

3.2 Esterification Reaction

3.2.1 Homogeneous Versus Heterogeneous Acid Catalysts in Monophasic Solvent Media

The result of esterification of lactic acid using different catalysts is presented in Fig. 3 together with that obtained in absence of catalyst. Without catalyst addition, the yield in lactate increased linearly during the first 2 h, then the rate of esterification reaction slowed down to give an yield in ethyl lactate of 30 % after 6 h of reaction. The addition of an acid catalyst, homogeneous or heterogeneous, i.e. H₂SO₄, Amberlyst 15 or KPW, increased significantly the initial rate of esterification (Fig. 3; Table 1), and the ethyl lactate yield after 6 h of reaction is far above the value achieved in the absence of catalyst. The highest initial rate in ethyl lactate formation is obtained with the homogeneous mineral acid H₂SO₄, 0.45 mol h^{-1} , more than two times the values obtained with the heterogeneous acid catalysts. After 6 h of reaction, in the presence of H₂SO₄ or Amberlyst 15, the curves representing the yield in ethyl lactate with time, show a quasi plateau with a value in ethyl lactate yield of 50 %. With KPW, after 6 h a reaction, the yield in ethyl lactate still increases slowly, indicating that the thermodynamic equilibrium is not reached, the ethyl lactate achieved 60 % after 6 h. This also indicates that part of its superficial acid sites is still active for ethyl lactate formation. Note that, for this set of experiments, the weight amount of Amberlyst 15, was chosen in order to adjust the protons amount to that of H₂SO₄. The higher initial rate of ethyl lactate formation observed with H₂SO₄ could be explained by the more accessible protonic sites compared to the heterogeneous catalyst and/or to the highest acidity of H₂SO₄, but any ranking in terms of acid strength between homogeneous and heterogeneous catalysts is always questionable. In other respects, the amount of KPW was equivalent to that of the resins, but one can remark that the protonic densities of the two heterogeneous catalysts are different: 0.168 mmol H^+ g⁻¹ for KPW and 4.7 mmol H^+ g⁻¹ for Amberlyst 15. The initial rates of ethyl lactate formation per acid sites (see Table 1), evidenced that the value measured on KPW is more than ten time that of H₂SO₄ or Amberlyts 15. The higher activity per acid sites of KPW compared to Amberlyst 15 can logically be explained by its highest acid strength as shown by calorimetry of NH_3 adsorption (see Section 3.1). More hardly explained, is the highest yield in ethyl lactate achieved over KPW after 6 h of reaction. A priori, the value of a (quasi)plateau depends on the thermodynamic equilibrium and/or on the poisoning of the acid sites. An alternative explanation could be the occurrence the side reactions such as the ethyl lactate self-transesterification producing heavy products (Scheme 3). It is reasonable to think that a few amount of this by-product could remain strongly adsorbed on the superficial acid sites and inhibit the solid acid activity. In addition, this consecutive secondary

 Table 1
 Initial rate of ethyl

 lactate formation. Influence of
 the nature of the catalysts and of

 the biphasic medium composed
 of the reactive phase (lactic

 acid/ethanol/catalyst) and the
 extractive solvent selective of

 ethyl lactate (Biodiesel)
 of

Reaction liquid media	Catalysts	Initial rate of ethyl lactate formation (mol h^{-1})	Initial rate of ethyl lactate formation per acid sites [mol (mol H^+ h) ⁻¹]
	Without	0.06	_
	H_2SO_4	0.45	70
Mono-phasic	Amberlyst 15	0.16	24
	KPW	0.18	766
	H_2SO_4	0.59	91
Bi-phasic	Amberlyst 15	0.42	64
	KPW	0.63	2,680



Fig. 4 Esterification of lactic acid with ethanol in the presence of different acid catalysts. Comparison between the bi-phasic and the mono-phasic solvent system. Conditions: m EtOH = 66.7 g, m lactic acid = 39.1 g, mH₂SO₄ (96 %) = 0.33 g (6.46 mmol H⁺), m A15 = 1.4 g (6.6 mmol H⁺), m KPW = 1.4 g (0.235 mmol H⁺), T = 80 °C (reflux)

reaction might be favored by the high protonic density combined to the absence of steric hindrance over Amberlyst 15. However, this explanation does not hold true for the homogeneous sulfuric acid. Therefore, to rationalize the higher ethyl lactate yield over KPW as compared to A15 and H₂SO₄, distinct water tolerance appears as a more likely explanation. Since the main difference between the two solid acid catalysts is their protonic density, one can propose that KPW has certainly the more hydrophobic surface which might limit its deactivation by water adsorption during the course of reaction. KPW would be more tolerant to the competitive adsorption of water or solvation of the proton by the water produced by the esterification reaction. KPW should permit to reach more rapidly the thermodynamic equilibrium compared to the two other catalysts. This can rationalize the higher lactate yield obtained on KPW after 6 h of the reaction.

3.2.2 Esterification of Lactic Acid Carried Out in Bi-phasic Solvent System

Figure 4 shows the evolution of the yield of esterification with the course of reaction, in the absence or presence of methyl ester of fatty acid as selective extractive solvent of



Scheme 1 Extractive catalytic reaction concept: application to ethyl lactate formation



Scheme 2 Self-esterification of lactic acid

the ethyl lactate. Performing the reaction in a bi-phasic liquid system leads to remarkable results: the yield in ethyl lactate was significantly increased. After 6 h of reaction, for H_2SO_4 and Amberlyst 15, the yield in ethyl lactate achieve 80 % while this value is even overreached for KPW after 2 h of reaction. In the biphasic system, the initial rates of reaction are strongly increased, by three fold in the case of the heterogeneous acid catalysts. The initial rate measured in the presence of H_2SO_4 is less modified in the presence of the extractive phase.

Hence, these results demonstrate that the esterification of lactic acid in a bi-phasic solvent system, containing an Od

Scheme 3 Selftransesterification of ethyl







Scheme 4 Keggin structure

extractive solvent selective of the ethyl lactate is a simple way to shift the equilibrium of esterification leading to high yield in ethyl lactate. This methodology is certainly operative for most of the carboxylic acids derived from natural sources such as succinic, itaconic, aconitic acids and others.

In the peculiar case of lactic acid, the presence of biodiesel not only increased the yield of the esterification reaction, but also provided in one reaction step, an efficient biosolvent composition, made of ethyl lactate and methyl ethyl esters of fatty acid (biodiesel) (Scheme 1).

3.2.3 Catalyst Recycling

The recycling investigations were done with the most efficient catalyst, KPW. After a first esterification reaction of 420 min, the solid catalyst was separated by filtration, washed with ethanol, dried at 100 °C for 3 h and then reused with fresh reaction mixture under identical conditions as the first cycle. The recycle procedure was repeated two times. The results of esterification recycles are shown in Fig. 5. There were no significant differences in the yield of the esterification reaction between each cycle performed over the KPW catalysts, showing that KPW catalyst can be reused in the esterification reaction of lactic acid in a biphasic solvent system. The excellent recyclability of KPW can be explained by the catalyst stability in the reaction medium. Indeed, the FTIR spectrum of KPW recovered after the first use didn't show any detectable modification

Fig. 5 Esterification of lactic acid with ethanol catalyzed by KPW. Recycling study. Conditions: m EtOH = 66.7 g, m lactic acid = 39.1 g, m KPW = 1.4 g (0.235 mmol H⁺) T = 80 °C (reflux)

of the vibrations bands of Keggin anions in the range $500-1,200 \text{ cm}^{-1}$.

4 Conclusion

The results presented in this paper demonstrate that biosolvent compositions can be prepared in one step by esterification of lactic acid with ethanol with excellent yield in the presence of non volatile solvent based on fatty acid esters, a solvent selective of ethyl lactate. This is a successful application of the concept of catalytic extractive reaction. In addition, $K_{2.5}H_{0.5}PW_{12}O_{40}$ is shown to be a more efficient catalyst than the conventional esterification catalysts, H₂SO₄ and Amberlyst 15. Its efficiency is ascribed to its strong acid strength associated to a low protonic density which is proposed to insure an adequate superficial hydrophobicity which makes this catalyst resistance towards water poisoning. This strong Brønsted acid catalyst is environmentally friendly, non-toxic, reusable and in addition, much more cheaper than its more famous homologue the acidic cesium salts Cs_{2.5}H_{0.5}PW₁₂O₄₀. The present procedure represents a clean, practical, and simple method to prepare biosolvents composition in one step [15].

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