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High yield of ethyl valerate from the esterification of renewable valeric acid catalyzed by amino acid ionic liquids†

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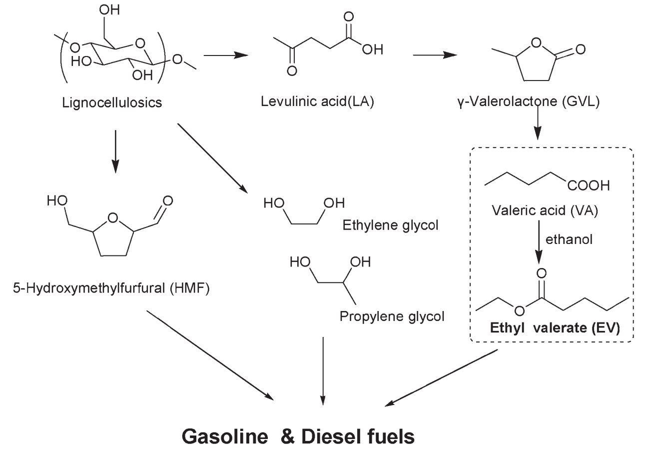
Ethyl valerate (EV) as a promising fuel additive was produced by esterification of valeric acid with ethanol over Brønsted acidic amino acid ionic liquids. Hammett method and density functional theory (DFT) calculations were preformed to evaluate the acidities of the catalysts. The composition of catalyst, reaction temperature, reaction time, molar ratio of reactants, amount of catalyst, and recycling ability of the catalyst were investigated. Proline bisulfate ($ProHSO_4$) ionic liquid has the highest catalytic activity and the best recyclability under the optimized esterification conditions. A high conversion of valeric acid (>99.9%) was obtained for 7 h at 80 °C, with 100% selectivity of EV. The density, viscosity, melting point, boiling point, elemental analysis and heat of combustion of the EV product were measured. The density of EV is 0.896 g cm^{-3}. The viscosity of EV was 1.7 cP at room temperature. The heating values of EV are 4158.1 kJ mol^{-1} and 31.9 kJ g^{-1}. EV obtained from esterification has higher energy density than methanol, ethanol, γ-valerolactone, and valeric acid, which illustrates that EV is a promising biofuel candidate.

Introduction

The depletion of fossil fuels, environmental issues, and future energy requirements have propelled biomass as the most possible alternative resource to petroleum for fuels and chemicals. Starch based plants as renewable energy-storage biomass have been converted into biofuels in recent years.[1] However, the large-scale supply of starch based plants as the feedstock for fuels has resulted in direct competition with food. Cellulosic materials, a sort of cheap and abundant renewable feedstock, can serve as a sustainable source of carbon for the fuel and chemical industries. From lignocellulose, several important platform molecules including 5-hydroxymethylfurfural (HMF), levulinic acid (LA), γ-valerolactone (GVL), valeric acid (VA) and some important chemicals like 1,2-alkanediols have been obtained (Scheme 1).[2] GVL was considered as an important feedstock for its potential application in the sustainable utilization of energy and has been widely investigated since 2008.[3] VA is the key component in the hydrogenated product of GVL. This acid itself has 31% oxygen content, which is still too high to be a good biofuel candidate. Dumesic *et al.* described a series of conversion routes of cellulose and got LA, GVL, VA, a mixture of C_9 and C_{18} olefins and a mixture of alkanes stepwise.[3e]

Ethyl valerate (EV) is the product of the esterification of VA and ethanol, and was considered as a possible second generation biofuel (Scheme 1).[4] An experimental and kinetic modeling study for the combustion characteristics of EV was carried out.[4c] The acceptable energy density and more appropriate polarity of EV make it suitable for gasoline applications. Furthermore, the material safety data sheet (MSDS) shows that EV is a compound with low hazardousness and it is mild irritant. The acceptable low polarity of EV makes it less sensitive to elastomer swell or water pickup than ethanol. 10–20 vol% of EV splash-blended in regular gasoline



Scheme 1 Schematic strategy of ''valeric biofuels''.

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still meets the research and motor octane number (RON and MON) specification for European gasoline (EN 228). Road trials using a 15% blend of EV in regular gasoline were carried out with 10 vehicles and a total of about 250 000 km of driving.

Esterification is an important industrial process for ester productions in chemical and pharmaceutical industries, which has also attracted much fundamental academic interest. In esterification, reactive acid derivatives or coupling agents are often required to shift the equilibrium toward the desired ester in high yield. Dehydrating agents such as surfactants, zeolite, $scCO_2$, and fluorous solvents[5] have been investigated to remove water immediately from the reaction system. However, homogeneous processes using inorganic acids or organic acids[6] as catalysts have the disadvantages of corrosiveness, high susceptibility to water, difficulty in catalyst recovery, and deterioration of the side reactions, while heterogeneous esterification catalyzed by supported metal oxide, zeolites, heteropolyacids, or resins[5c,7] is also problematic with the removal of adsorbed products and rapid deactivation as well as restricted acidic sites of the catalysts. Furthermore, lipase enzymes were also used to catalyse esterification, while their high costs and tough purification procedures render the enzymes economically unattractive.[8] Therefore, an ideal greener approach would be a biphase esterification employing an environment-friendly catalyst without any additional dehydrating agent. Such a system could be auto-phase-separation even in the presence of carboxylic acid, alcohol and water. Some acidic ionic liquids have acted as Brønsted acids in biphase esterification,[9] with auto-phase-separation after the esterification reaction. That is, because the Brønsted acidic ionic liquids could mix well with carboxylic acids and short-chain alcohols but are immiscible with esters, the system was a monophasic solution at the beginning of the esterification reaction, but ended in a biphasic mixture. They were more selective to the desired esters accordingly.

In 2005, Kou *et al.* reported the "green" amino acid ionic liquids ([AA]X and [AAE]X)[10] and their intrinsic Brønsted acidity. Compared with previous Brønsted acidic ionic liquids,[9] L-amino acids derived from natural materials were chosen as precursors. Protic amino acid ionic liquids [AA]X can be easily obtained by one-step protonation reactions without any byproduct or complicated post-processing. In addition, they are low cost and can be produced in significant quantities.[10] Herein, three [AA]X amino acid ionic liquids based on bisulfate anion were prepared. Their acidities were studied by the Hammett method and theoretical calculation. These amino acid ionic liquids were used as acidic catalysts for the esterification of VA with ethanol to obtain EV. The esterification reaction parameters including composition of catalyst, reaction time, reaction temperature, molar ratio of reactants, amount of catalyst as well as recycling ability were investigated. The fuel performances of EV products were also evaluated.

Experimental

Chemicals and instruments

All chemicals of analytical grade were obtained commercially and used as received. Solvents were dried by standard procedures. Infrared spectra (IR) were recorded by using KBr plates on a Nicolet NEXUS 670 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz nuclear magnetic resonance spectrometer with d_6-DMSO as locking solvent unless otherwise stated. ^{1}H and ^{13}C chemical shifts were reported in ppm relative to TMS. The products obtained in each experiment were analyzed using a GC9790II equipped with an AT SE-54 column (30 m × 0.25 mm × 0.25 μm) and FID detector. The ester yield was quantified by GC using cyclohexane as internal standard. The density of EV was measured at 25 °C on a Micromeritics Accupyc 1330 gas pycnometer. Elemental analysis of EV was performed on a CARLO ERBA 1106 Elemental Analyzer. The viscosity was measured with a NDJ-1B-1 viscometer at room temperature.

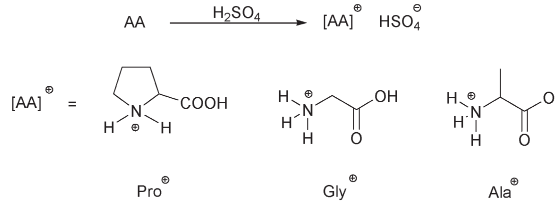
Synthesis of the catalysts

The amino acid ionic liquids were synthesized similar to the literature procedure[10] by direct protonation reactions of the corresponding amino acid precursors with dilute sulfuric acid. The ratio of amino acid and sulfuric acid must be kept to 1 : 1 in mole to obtain bisulfate ionic liquids. The preparation is one-step protonation reaction in water without any byproduct or complicated post-processing, which is an atom-economic reaction (Scheme 2). Thus the preparation of the amino acid ionic liquids is highly efficient and low cost.

Proline bisulfate ($ProHSO_4$). To a 50 mL round flask, proline (1.151 g, 10 mmol) was dissolved in 40 mL water with stirring. An equal molar ratio of sulfuric acid (3.0 mol L^{-1} aqueous solution) was dropped into the flask and kept stirring for 1 h at room temperature. The mixture was concentrated and evaporated under vacuum to obtain a colorless transparent liquid in high yield (yield 99%).

^{1}H NMR, δ (ppm): 4.27 (m, 1H), 3.21 (m, 2H), 2.27 (m, 1H), 1.93 (m, 3H); ^{13}C NMR, δ (ppm): 170.33, 58.82, 45.46, 27.78, 23.01. IR (KBr, cm^{-1}): ν = 3172, 1739, 1584, 1420, 1335, 1140, 1053, 875, 659, 577.

Glycine bisulfate ($GlyHSO_4$). The same procedure was followed as that described above for $ProHSO_4$. Glycine (751 mg, 10 mmol) and an equal ratio of sulfuric acid (3.0 mol L^{-1} aqueous solution) were reacted for 1 h to obtain a white solid (yield 99%).



Scheme 2 The preparation of the amino acid ionic liquids $ProHSO_4$, $GlyHSO_4$, and $AlaHSO_4$.

^{1}H NMR, δ (ppm): 3.66 (s, 2H, CH_2); ^{13}C NMR, δ (ppm): 169.19, 40.17. IR (KBr, cm^{-1}): ν = 3473, 3225, 2362, 1750, 1606, 1510, 1433, 1175, 1048, 866, 583, 476.

Alanine bisulfate ($AlaHSO_4$). The same procedure was followed as that described above for $ProHSO_4$. Alanine (891 g, 10 mmol) and an equal ratio of sulfuric acid (3.0 mol L^{-1} aqueous solution) were reacted for 1 h to obtain a colorless transparent liquid (yield 99%).

^{1}H NMR, δ (ppm): 3.95 (m, 1H, CH), 1.40 (d, 3H, CH_3); ^{13}C NMR, δ (ppm): 171.46, 47.87, 15.70. IR (KBr, cm^{-1}): ν = 3281, 1748, 1609, 1511, 1386, 1112, 871, 611, 516.

Hammett acidity determination

Hammett acidity function study of the ionic liquids was performed on a HITACHI Model U-4100 UV/Vis spectrometer. Samples were measured in sealed 1 mm quartz cuvettes (Helma). Absorbance values, A, of indicator based on the ionic liquids in methanol and ethanol were recorded between 350 and 400 nm in steps of 0.1 nm. The dye *p*-nitroaniline (Fluka, $\geqslant$99%) was used as an indicator and molecular probe for the determination of acidity, H_0, with 7.5×10^{-5} mol L^{-1}. The concentration of ionic liquid was 5.0×10^{-2} mol L^{-1}. An appropriate amount of solution was placed into vials which were sealed for determination.

General procedure for EV production

In a typical esterification procedure, appropriate amounts of VA, ethanol and ionic liquids were placed in a 25 mL round bottom flask. The reaction was refluxed under the desired temperature in an oil bath equipped with a thermostat. After reaction, the reaction mixture formed two liquid phases. The product layer was directly separated and detected by GC to provide conversion and selectivity data. Conversions were calculated from the amount of EV/the amount of VA in moles. The experiments were repeated to control the error less than ±1%. Each data set was repeated at least three times. The separated ionic liquid layer was treated at 100 °C under vacuum to remove water and reused immediately (see Fig. 1).

Bomb calorimetry

The calorimetric measurement was performed using a Parr 6725 bomb calorimeter (static jacket) equipped with a Parr 207 A oxygen bomb for the combustion of EV products. EV products were carefully dropped on an analytical grade benzoic acid pellet, which was subsequently burned in a 3.05 MPa atmosphere of pure oxygen. The pellet (~100 mg) was loaded in a platinum pan and a Parr 45C10 alloy fuse wire was used for ignition. The experimental heat of combustion was obtained from the average of three separate measurements with standard deviations calculated as a measure of experimental uncertainty. The bomb was examined for no evidence of unburned carbon after each run. In all measurements, the calorimeter was calibrated by the combustion of certified benzoic acid in an oxygen atmosphere at the same pressure of 3.05 MPa, combined with a correction for burned wire (1400 cal cm^{-1}).

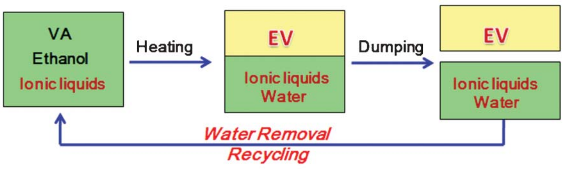


Fig. 1 The esterification for EV catalyzed by amino acid ionic liquids.

Results and discussion

The acidity of amino acid ionic liquids

The acidity determination by the Hammett method. The efficiency of esterification is closely associated with the acidity of the catalysts. For nonaqueous Brønsted acids, the acidity could be studied using electrochemical windows or Hammett acidity function.[12] Herein, the amino acid ionic liquids with labile protons exhibit Brønsted super acidity. Their acidity could not be determined using a pH meter. The Hammett acidity function method given by Gilbert *et al.*[12d] was used to evaluate the acidity of the amino acid ionic liquids. Samples in ethanol and methanol solution were measured by UV/Vis spectroscopy. The Hammett function (H_0) values of ionic liquids and sulfuric acid are summarized in Table 1. The Hammett acidity function (H_0) can be expressed by the equation: $H_0 = pK_a(In) + \log([In]/[InH^+])$. $pK_a(In)$ is the pK_a value of the *p*-nitroaniline indicator solution. [In] and [InH$^+$] are the molar concentrations of the protonated and unprotonated forms of *p*-nitroaniline indicator, respectively. In ethanol system, a solution of 0.05 mol L^{-1} sulfuric acid gave a H_0 value of 1.20. Amino acid ionic liquid $ProHSO_4$ gave a H_0 value of 2.74. $AlaHSO_4$ gave a similar H_0 value of 2.78. However, the solubility of $GlyHSO_4$ in ethanol solution was very limited, and 0.05 mol L^{-1} solution was not able to be obtained. Thus, the value of $GlyHSO_4$ was not comparable with the values of $ProHSO_4$ and $AlaHSO_4$. Methanol as a good solvent for all of the three amino acid ionic liquids was selected. In methanol system, a solution of 0.05 mol L^{-1} sulfuric acid gave a H_0 value of 1.00. Amino acid ionic liquid $ProHSO_4$ gave a H_0 value of 1.76. $GlyHSO_4$ gave the same H_0 value of 1.76 as that of $ProHSO_4$. $AlaHSO_4$ gave a H_0 value of 1.82, which was a little higher. The values of the three amino

Table 1 Hammett function values of various ionic liquids[a]

Acid	Absorbance[b]	[In] (%)[c]	[InH$^+$] (%)[d]	H_0[e]
none	1.20/1.13	100/100	0/0	—/—
H_2SO_4	0.74/0.63	61.7/50.8	38.3/49.1	1.20/1.00
$ProHSO_4$	1.18/1.06	98.3/85.5	1.7/14.5	2.74/1.76
$GlyHSO_4$	—/1.06	—/85.5	—/14.5	—/1.76
$AlaHSO_4$	1.18/1.08	98.4/87.1	1.6/12.9	2.78/1.82
$[MIM][CH_3SO_3]$[f]	1.12	99.1	0.9	3.03
$[NMP][CH_3SO_3]$[f]	0.99	87.6	12.4	1.84

[a] The Hammett function values were obtained in ethanol/methanol solution. [b] Determination conditions (25 °C): $c(In) = 7.5 \times 10^{-4}$ mol L^{-1}, $c(H_2SO_4)$ = 0.05 mol L^{-1}, c(ionic liquids) = 0.05 mol L^{-1}. [c] The molar concentration of the *p*-nitroaniline indicator. [d] The molar concentration of the protonated *p*-nitroaniline. [e] $H_0 = pK_a(In) + \log([In]/[InH^+])$, $pK_a(In) = 0.99$. [f] See ref. 11.

acid ionic liquids are all higher than that of sulfuric acid, which means their acidities are a little weaker than that of sulfuric acid. The acid strengths are similar to those of common Brønsted acidic ionic liquids like [NMP][HSO_4], and much stronger than [MIM][CH_3SO_3], which gave a H_0 value of 3.03.

Density functional theory (DFT) calculations of the acidity. On further investigation of the acidity of the amino acid ionic liquids, the acid dissociation constants (pK_a) of the amino acid ionic liquids were accurately calculated using the Gaussian(R) 09 program.[13] The protonated amino acid ionic liquids and deprotonated amino acid ionic liquids were optimized in the gas phase using the popular Becke three-parameter hybrid functional Lee–Yang–Parr (B3LYP) analyses up to the 6-311+G** basis set,[14] and $G(A^-_{gas})$ and $G(AH_{gas})$ were obtained accordingly. Then the PCM solvation model developed by Tomasi and co-workers[15] was used to calculate the solvation free energies of amino acid ionic liquids and deprotonated amino acid ionic liquids in ethanol.

The definition of pK_a is

$$pK_a = -\log K_a \tag{1}$$

and in gas phase standard state

so, $$\Delta G^\circ = 2.303RT \log K_a \tag{2}$$

$$pK_a = \Delta G^\circ/2.303RT \tag{3}$$

From the thermodynamic cycle, we get

$$pK_a = \Delta G_{aq}/2.303RT \tag{4}$$

$$\Delta G_{aq} = G_{aq}(H^+) + G_{aq}(A^-) - G_{aq}(AH) \tag{5}$$

So, in the standard state of 1 mol L^{-1} and room temperature,

$$\Delta G^*_{aq} = G^*_{aq}(H^+) + G^*_{aq}(A^-) - G^*_{aq}(AH) \tag{6}$$

It is necessary to add 1.89 kcal mol^{-1} ($RT\ln(1/R_gT)$) to convert the calculated gas phase standard free energy, G°_{gas}, from its standard state of 1 atm gas phase/1 mol L^{-1} solution to G^*_{gas} with a standard state of 1 mol L^{-1} gas/1 mol L^{-1} solution phase. The values of $G(H^+_{gas})$ and $\Delta G_s(H^+)$ are derived from literature as −6.28 kcal mol^{-1} and −265.9 kcal mol^{-1} respectively.[16]

$$G^*_{aq} = G^*_{gas} + \Delta G^*_{sol} = (G^\circ_{gas} + 1.89) + \Delta G^*_{sol} \tag{7}$$

Combining these values and the equations, the pK_a values using the thermodynamic cycle (Scheme 3) were finally obtained using eqn (8).

$$pK_a = [G^\circ(A^-_{gas}) + G^\circ(AH_{gas}) + \Delta G^*_s(A) - \Delta G^*_s(AH) - 270.29]/2.303RT \tag{8}$$

$$\begin{tikzcd}
AH_{gas} \arrow[r, "\Delta G_{gas}"] & A^-_{gas} \arrow[d, "\Delta G^*_s(A^-)"] & + & H^+_{gas} \arrow[d, "\Delta G^*_s(H^+)"] \\
AH_{aq} \arrow[u, "-\Delta G^*_s(AH)"] \arrow[r, "\Delta G_{aq}"] & A^-_{aq} & + & H^+_{aq}
\end{tikzcd}$$

Scheme 3 Thermodynamic cycle used in the calculation of the pK_a of the amino acid ionic liquids.

The results are listed in Table 2. We can see that the theoretical pK_a values of the three amino acid ionic liquids are all less than 0. The theoretical pK_a value of $ProHSO_4$−H was the lowest (−2.0) among the three amino acid ionic liquids, while the pK_a value of $GlyHSO_4$−H was the highest (−1.8). According to the definition of the pK_a value, the H^+ in $ProHSO_4$ was the easiest one to dissociate, and the acidity of $ProHSO_4$ was the strongest accordingly.

Esterification to produce EV

The composition of catalysts. As a comparison, no EV could be detected from the reaction of VA and ethanol at 25 °C in the absence of acidic catalyst (Table 3, entry 1). Concentrated sulfuric acid (98%) was also used in the esterification for comparison where less than 1% EV was detected at room temperature (entry 2), and only about 67.0% of EV was found even at 80 °C (entry 4). As a comparison, the esterification results of VA and ethanol by lipase enzyme are listed in Table 3. The lipase process needs up to 9 days to reach 97.8% esterification. Amino acid ionic liquids show better catalytic reactivity than H_2SO_4 at both room temperature and 80 °C (entries 3, 5–7). Their efficiencies are also much higher than

Table 2 Theoretical gas-phase data of amino acid ionic liquids and their pK_as in ethanol[a]

	G_{gas}(a.u)	G_s(a.u)	ΔG^*_s(kcal mol^{-1})	pK_a
$GlyHSO_4$−H	−984.809054	−984.938394	−81.162079	−1.8
$AlaHSO_4$−H	−1024.112701	−1024.26728	−97.001046	−1.9
$ProHSO_4$−H	−1101.51296	−1101.70059	−117.74023	−2.0

[a] The protonated amino acid ionic liquids and deprotonated amino acid ionic liquids were optimized in the gas phase at B3LYP/6-311++G(d,p).

Table 3 The esterification to produce EV over different catalysts[a]

Entry	Catalyst	T/°C	Conversion (%)[b]	Selectivity (%)[b]
1	Blank	25	0	—
2	H_2SO_4[c]	25	<1	—
3	$ProHSO_4$	25	62.4	100
4	H_2SO_4[c]	80	67.0	88
5	$ProHSO_4$	80	>99.9	100
6	$GlyHSO_4$	80	84.7	100
7	$AlaHSO_4$	80	87.1	100
8	Lipase[d]	37	97.8	—

[a] *Reaction conditions*: catalyst: 50 mol%, based on VA, VA/ethanol (molar ratio) = 1, 7 h. [b] Conversion and selectivity of EV determined by GC analysis. [c] Concentrated sulfuric acid (98%). [d] pH 7.2, 150 rpm, 9 days, ref. 8.

that of lipase.[8] Their reaction mechanisms are difference. The sulfuric acid system is a typical homogenous catalysis reaction. After reaction, the catalyst, the unreacted reactants, the byproduct water and the product EV were all in the same liquid phase. However, the amino acid ionic liquid system is a biphasic catalysis reaction. For example, in the $ProHSO_4$ system, the reactants (VA and ethanol) and the catalyst were miscible in a single phase before reaction, which was a homogenous reaction at the beginning. Because of the poor solubility of EV in the ionic liquid system, as the reaction proceeded, a biphasic system formed. Since the reactants VA and ethanol have good solubility in $ProHSO_4$, even though the conversion of VA was not 100%, the unreacted reactants may stay in the ionic liquid layer. Moreover, water is also miscible with $ProHSO_4$, and as a byproduct stayed in the ionic liquid layer. In the esterification process, $ProHSO_4$ acts not only as a catalyst but also as a water absorbent. Thus the equilibrium of the esterification reaction was shifted automatically to the product side, without any simultaneous water removal. As a result, $ProHSO_4$ would facilitate the phase separation of the product from the reactants and the byproduct during the esterification, which favours the conversion of VA to achieve high yield of EV. EV was concentrated into the upper layer by auto-phase separation, and the reversible reaction of the ester was restrained.

Compared with the $AlaHSO_4$ and $GlyHSO_4$ systems, the $ProHSO_4$ system gave the highest conversion of VA, more than 99.9%. The EV yield in the $ProHSO_4$ system is also more than 99.9%. The reason may be the effect of the different strengths of acidity of the three amino acid ionic liquids. In ethanol, $ProHSO_4$ has a stronger Brønsted super acidity than the other two amino acid ionic liquids, based on the experimental and theoretical evaluation of Brønsted acidity above.

The reaction time. The effect of the reaction time on the esterification was determined using 50 mol% of $ProHSO_4$ with 1 : 1 (molar ratio) VA/ethanol at room temperature. The results of the esterification at different reaction times are shown in Fig. 2. The conversion of VA increased from 15.0% to 62.4% with the extension of reaction time from 1 h to 7 h. During this procedure, the selectivity of EV remained at 100%. After 7 h, the conversion of VA did not clearly increase along with the longer reaction time. When the time was extended to 24 h, the conversion remained steady at 63.8%. Therefore, the ideal reaction time of the esterification for EV production was selected as 7 h.

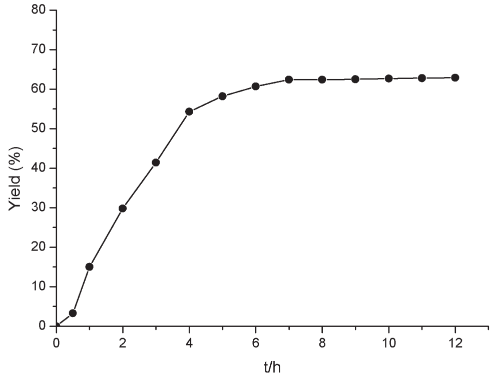


Fig. 2 The esterification to produce EV after different reaction times at room temperature (reaction conditions: catalyst = $ProHSO_4$ (50 mol%, based on VA), VA/ethanol (molar ratio) = 1; conversion and selectivity of EV determined by GC analysis).

The reaction temperature. Higher temperature will increase the speed to reach the equilibrium of a reaction. The effect of the reaction temperature on the esterification is shown in Table 4. EV was obtained from the esterification of VA with ethanol over $ProHSO_4$ ionic liquid from room temperature to 80 °C after 7 h. The high reaction temperature promotes the efficiency of the esterification significantly. The yield of EV increased gradually from 62.4% (entry 9) to more than 99.9% (entry 14) as the temperature increased from 25 °C to 80 °C. At 80 °C, the conversion of VA was up to >99.9% with 100% selectivity of EV (entry 14).

The amount of catalyst. The yields of EV from the esterification over various amounts of $ProHSO_4$ are summarized in Table 5. The yield increased upon the increasing the amount of catalyst from 2% to 50% (based on the mol of VA). An increase in the amount of catalyst clearly increases the number of acid sites available. On the other hand, because the ionic liquids are also water absorbent, the amount of catalyst was associated with the water produced. More $ProHSO_4$ catalyst results in easier auto-phase-separation, which effectively moves the reaction equilibrium toward EV. For 1 : 1 mole ratio of VA/ethanol, more than 99.9% EV was obtained when 50 mol% $ProHSO_4$ was used (entry 19).

The molar ratio of the reactants. The high ethanol/acid molar ratio is favorable for normal acid catalyzed esterifica-

Table 4 The esterification for EV production at different temperatures[a]

Entry	$T/^\circ C$	Conversion (%)[b]	Selectivity (%)[b]
9	25	62.4	100
10	40	72.6	100
12	50	82.9	100
13	60	88.9	100
14	70	95.9	100
14	80	>99.9	100

[a] *Reaction conditions*: catalyst = $ProHSO_4$ (50 mol%, based on VA), VA/ethanol (molar ratio) = 1 : 1, 7 h. [b] Conversion and selectivity of EV determined by GC analysis.

Table 5 The esterification for EV production over different amounts of catalyst[a]

Entry	mol%	Conversion (%)[b]	Selectivity (%)[b]
15	2	72.1	100
16	5	79.8	100
17	10	81.3	100
18	20	83.2	100
19	50	>99.9	100

[a] *Reaction conditions*: catalyst = $ProHSO_4$, VA/ethanol (molar ratio) = 1, 80 °C, 7 h. [b] Conversion and selectivity of EV determined by GC analysis.

Table 6 The esterification for EV production over different molar ratios of ethanol/VA[a]

Entry	Molar ratio	Conversion (%)[b]	Selectivity (%)[b]	Status after reaction
20	1 : 1	>99.9	100	Two phases
21	2 : 1	79.8	100	Two phases
22	3 : 1	58.1	100	Single phase
23	4 : 1	67.2	100	Single phase
24	5 : 1	76.0	100	Single phase
25	6 : 1	84.7	100	Single phase
26	7 : 1	88.1	100	Single phase
27	8 : 1	91.5	100	Single phase
28	9 : 1	94.6	100	Single phase

[a] *Reaction conditions*: catalyst = $ProHSO_4$, 80 °C, 7 h, molar ratio = ethanol/VA. [b] Conversion and selectivity of EV determined by GC analysis.

tion. The effect of the ethanol/VA molar ratio on the esterification reaction was studied in the range of 1 : 1–9 : 1 (Table 6). The reaction was carried out at 80 °C for 7 h. Finally, the EV yield dramatically decreases from >99.9% to 58.1% upon increasing the ethanol/VA molar ratio from 1 : 1 to 3 : 1 (entries 20–22). When ethanol/VA was 3 : 1, auto-phase-separation did not occur like biphasic catalysis. The reaction became a homogeneous process again. Even when ethanol/VA increased from 3 : 1 to 9 : 1, the EV yield increased gradually to 94.6% (entry 28), but EV still can not be separated automatically after the reaction. The result reveals that for homogeneous esterification, the increase of ethanol would shift the reaction equilibrium toward the product. However, for ionic liquid involved biphasic esterification, excess ethanol may not help the production of EV but block the occurrence of auto-phase-separation, leading to low ester yield.

The recycling ability of catalyst. We further explore the recycling ability of the $ProHSO_4$ catalyst for EV production. The recycling reaction was performed under the optimized reaction conditions above. The esterification of VA with ethanol was carried out on 1 : 1 mole ratio of VA/ethanol using 50 mol% $ProHSO_4$ at 80 °C for 7 h. $ProHSO_4$ was easily isolated from the product and then reused by simple removal of water under vacuum by heating at 100 °C for 2 h. The recovered catalyst exhibited similar catalytic activity to that of the original (Fig. 3). A consistent EV yield of higher than 95% with 100% selectivity was obtained in each cycle. No obvious activity loss of $ProHSO_4$ was found even after five cycles. Compared with the traditional organic solvents and inorganic acid catalysts, the easy recycling performance of the amino acid ionic liquid catalysts is also attractive from environmental protection and economic aspects.

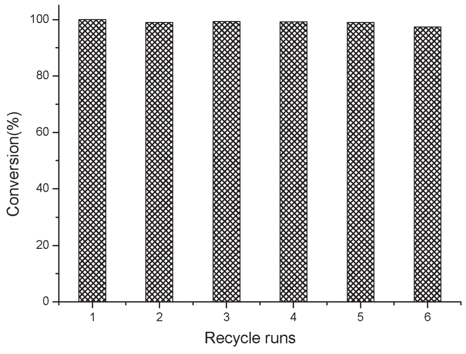


Fig. 3 Reaction recycling of the esterification for EV production over $ProHSO_4$ catalyst.

The fuel performances of EV

In most cases, the ester products of the esterification were pure EV. Because the amino acid ionic liquid can help to separate the product from the reactants and the byproduct, impurities would stay in the ionic liquid layer. Therefore, the esterification procedure catalyzed by amino acid ionic liquid is an efficient route to obtain high quality EV products.

The fuel performances of EV are important parameters for fuel applications. Our products from the esterification were evaluated and the measured properties are listed in Table 7. The colorless transparent liquid samples were taken from the esterification at 80 °C for 7 h catalyzed by 50 mol% $ProHSO_4$. The density of EV product was 0.897 g mL^{-1}. The viscosity of EV was 1.7 cP at room temperature, as determined using a rotational viscometer. Thus, the product has good fluidity. The low viscosity EV is suitable to be transported and utilized as a fuel component. The melting point of EV was found at −91 °C, measured by differential scanning calorimetry (DSC) analysis. The boiling point of EV is 146 °C as recorded by the thermometer in the atmospheric distillation set. No impurity was found in the distillation flask after EV was distilled to the receiving flask.

The heating value of the EV product was obtained by two different methods. The heating value was calculated using the following formula proposed by Friedl *et al.* in 2005:[17]

$$\text{HHV}\ (\text{kJ g}^{-1}) = (3.55\text{C}^2 - 232\text{C} - 2230\text{H} + 51.2\text{C} \times \text{H} + 131\text{N} + 20\,600)/1000 \quad (9)$$

The calculated elemental analysis for EV ($C_7H_{14}O_2$, 130.18) is C 64.58%, H 10.84%, and O 24.58%. The theoretical calculated heating value of EV according to eqn (9) was 4177.8 kJ mol^{-1} and 32.2 kJ g^{-1}. From elemental analysis, our EV product without any post-processing was found to consist of C 64.13%, H 11.28%, and O 24.59%. The result confirms that the EV product obtained from the $ProHSO_4$-catalyzed esterification under optimal conditions is pure. Using the data obtained from the element analysis and eqn (9), the calculated heating value of EV is 4192.4 kJ mol^{-1} and 32.2 kJ g^{-1}, which is very close to the theoretical heating value of EV.

Meanwhile, we obtained the heating value from the measured constant-volume combustion energy of EV using a Parr 6725 bomb calorimeter. The mean constant-volume combustion energy ($\Delta_c U$) of EV could be directly obtained by three combustion experiments of EV in the bomb calorimeter, and was found to be 4152.0 kJ mol^{-1}. Then the standard molar enthalpy of combustion ($\Delta_c H^\circ$) of EV could be obtained by using the expression: $\Delta_c H^\circ = \Delta_c U + \Delta nRT$ ($\Delta n = \sum n_i$ (products, g) $- \sum n_i$ (reactants, g); $\sum n_i$ is the total molar amount of gases

Table 7 Physical properties of methanol, ethanol, GVL, VA and EV

	Methanol (CH_4O)[4b]	Ethanol (C_2H_6O)[4b]	GVL ($C_5H_8O_2$)[4b]	VA ($C_5H_{10}O_2$)[4b]	EV ($C_7H_{14}O_2$)
Molecular weight (g mol^{-1})	32.04	46.07	100.12	102.13	130.18
Density (g cm^{-3})	0.79	0.79	1.05	0.94	0.90
Melting point (°C)	−97.8	−114.3	−31	−34.5	−91
Boiling point (°C)	64.8	78.4	207–208	185	146.1
Flashing point (°C)	11	12	96	95	38
Carbon content (%)	37.48	52.14	59.98	58.80	64.58
Hydrogen content (%)	12.59	13.13	8.05	9.87	10.84
Oxygen content (%)	49.93	34.73	31.96	31.33	24.58
Solubility in water (%)	soluble	soluble	soluble	soluble	insoluble
Heating value (kJ mol^{-1})	415.7	1102.3	2625.7	2751.0	4158.1
Heating value (kJ g^{-1})	12.8[a]	23.9[a]	26.3[a]	26.9[a]	31.9

[a] Heating value was calculated using the following formula: HHV (kJ g^{-1}) = $(3.55C^2 - 232C - 2230H + 51.2C \times H + 131N + 20\,600)/1000$.[17]

in the products or reactants),[18] which gave values of 4158.1 kJ mol^{-1} and 31.9 kJ g^{-1}.

The heating value of EV obtained by elemental analysis data is in good agreement with that from the experimental heat of combustion. By using eqn (9), the heating values of methanol, ethanol, GVL, and VA were calculated to be 12.8 kJ g^{-1}, 23.9 kJ g^{-1},26.3 kJ g^{-1} and 26.9 kJ g^{-1} respectively. Compared with the heating values of methanol, ethanol, GVL, and VA, the heating value of our EV product is the highest one among the five molecules (Table 7). The esterification products may be sufficiently pure to be directly used as fuel additive. With the low melting point, relatively high boiling point, low viscosity and high heating value, EV is a promising high energy density fuel additive, better than the commercial ethanol fuel additive.

Conclusions

High yield of EV as a promising fuel additive was obtained by the esterification of VA and ethanol over several amino acid ionic liquids. The composition of catalysts, reaction time, reaction temperature, molar ratio of reactants, catalyst amount, and its recycling ability were investigated. The amino acid ionic liquids exhibited moderate Brønsted acidity. The experimental results have shown $ProHSO_4$ to be more active than the other ionic liquids in the esterification reaction. A conversion of more than 99.9% has been obtained with 100% selectivity of EV under the optimized reaction conditions. Hammett method and density functional theory (DFT) calculations were studied for a better understanding of the acidities of the catalysts, and the calculated results are in good agreement with the experimental results. The physical properties including density, viscosity, elemental analysis, melting and boiling points were measured. The heating value of EV was evaluated by two methods, and the concordant results illustrated that EV has higher energy density than methanol, ethanol, GVL, and VA. EV obtained from esterification is a promising fuel additive.

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