Remarkable effects of deep eutectic solvents on the esterification of lactic acid with ethanol over Amberlyst-15

Ayşe Ezgi Ünlü[†], Azime Arıkaya[‡], Aybike Altundağ, and Serpil Takaç

Ankara University, Faculty of Engineering, Department of Chemical Engineering, 06100, Ankara, Turkey

Abstract−Deep eutectic solvents (DESs) are widely used in numerous reactions both as a solvent and a catalyst. In this study, different types of DESs were investigated as a supplementary component for Amberlyst-15 to enhance its catalytic activity in the esterification reaction of lactic acid with ethanol. The effects of the following parameters such as DES type, choline chloride : glycerol (ChCl-Gly) (1 : 2) amount, molar ratio of reactants, temperature and agitation rate on the initial rate of reaction and yield of ethyl lactate were investigated. According to the results, DESs alone did not have any catalytic effect on the esterification; however, DESs together with Amberlyst-15 provided a significant increase in the initial rate of reaction and yield. The activation energy of the reaction decreased significantly with the combined use of Amberlyst-15 and ChCl-Gly (1 : 2). Internal and external mass transfer limitations were found to be negligible under optimum reaction conditions.

Keywords: Ethyl Lactate, Esterification, Amberlyst-15, Deep Eutectic Solvent

INTRODUCTION

Deep eutectic solvents (DESs) are an important class of green solvents that are used in a broad range of technological research fields, such as synthesis, extraction, electrochemistry, and metal processing, accompanying numerous advantages [1-6]. In several types of reactions, DESs are shown to act as catalyst as well [7-14]. They differ from ionic liquids in terms of easy preparation techniques and low cost. Additionally, DESs are biodegradable and non-toxic. They are eutectic mixtures that have two or more components of which one of them being hydrogen bond donor and one of them being hydrogen bond acceptor.

Ethyl lactate (EL) is a well-known monobasic ester and a biodegradable green molecule that is mainly used in pharmaceutical preparations [15], food additives [16] and fragrances [17]. It is also used as a solvent for cellulose acetate, nitrocellulose and cellulose ethers [18] or as a co-solvent for the synthesis of aryl aldimines [19].

Ethyl lactate is synthesized by the esterification reaction of lactic acid (LA) with ethanol (EtOH) until equilibrium is reached. However, esterification reactions are quite slow and many days are required to attain equilibrium in the absence of a catalyst [20]. Therefore, strongly acidic homogeneous (sulfuric acid, hydrochloric acid) or heterogeneous catalysts should be used to perform the synthesis. The processes generally involve distillation steps and also separation units for the recovery of EL with high purity [16]. The main disadvantages of these types of processes are the requirement of a high volume reactor, high energy demanding separation processes, low level of conversion due to the chemical equilibrium and the utilization of strongly acidic homogeneous catalysts [21]. Consequently, these processes are a potential threat to the environment.

To eliminate these negative, unrequired effects, researchers have presented different strategies such as enzymatic esterification of LA [22-25], chemical esterification of LA using reactive distillation [16,26,27] or membrane-based water separation systems [16,17,28, 29] either with homogeneous or heterogeneous acidic catalysts. However, considering the harmful effects of homogeneous acid catalysts on the environment researchers have preferred to use Amberlyst-15 as a heterogeneous catalyst.

Amberlyst-15 is a sulfonic acid ion exchange resin that is environmentally benign, highly selective and powerful catalyst for esterification reactions [30]. It has also been used in the esterification reaction of LA with EtOH in many studies. Tanaka et al. [17] used Amberlyst-15 in a hybrid system using zeolite T membranes for synthesis of EL. They reported that almost complete conversion of LA could be achieved in eight hours. The system also prevented the formation of LA polymers even at high concentrations of LA. Asthana et al. [26] studied the synthesis of EL in a continuous system containing reactive separation column filled with Amberlyst-15. Significantly high conversion of LA could be achieved in the process and the yield of EL was reported as 85%. On the other hand, Delgado et al. [28] used a batch reactor with Amberlyst-15 and a hydrophilic membrane. The authors reported that thermodynamic yield could be exceeded by the removal of water from the esterification medium.

Apart from these reports that used hybrid systems, which targeted to exceed thermodynamic equilibrium of the reaction, our study focused mainly on the enhancement of the performance of the catalyst Amberlyst-15. With this aim, we performed the esterification reaction of LA with EtOH in the presence of different types of DESs. We investigated the parameters such as the amount of DES, molar

[†]To whom correspondence should be addressed.
E-mail: Ezgi.Unlu@eng.ankara.edu.tr
[‡]Present address: İzmir Institute of Technology, Department of Chemical Engineering, 35430, İzmir, Turkey

ratio of reactants, temperature and agitation rate on production of EL. The results were discussed over the change of catalytic activity of Amberlyst-15 with DES.

MATERIALS AND METHODS

1. Materials

Lactic acid (27714), glycerol (G5516) and acetonitrile (1.000.302) were purchased from Sigma. Ethylene glycol (1.009.49), D-fructose (104.007), maltose (1.05911), D-xylose (1.0868901), urea (1.084.871.000), hexane (1.04391), dichloromethane (1.06050), sulfuric acid (1.00713) acetone (1.000.13) and diethyl ether (1.00926) were obtained from Merck. The other chemicals used were Amberlyst-15 (Fluka 6423), D-glucose (Applichem, A3666), D-sucrose (Applichem, A2211), EtOH (Isolab, 9.200.262) and o-phosphoric acid (Riedel de Haen, 4107).

2. Preparation of DESs

Choline chloride (ChCl)-based DESs were prepared by mixing appropriate amounts of choline chloride (ChCl) and following hydrogen bond donors; glucose (Glu), ethylene glycol (EG), glycerol (Gly), urea (U), maltose (Mal), xylose (Xyl), fructose (Fru) and sucrose (Suc). The mixture was heated to 80 °C for 1-2 h until a clear liquid was formed. Choline chloride was dried under vacuum over silica gel in a desiccator prior to use.

3. Physical Properties of DESs

The pH was measured using pH-meter (Sartorius PP25), viscosity was determined using a viscometer (Fungilab Viscometer), the conductivity was measured using Radiometer Ion Check 65, and the density was measured by a pycnometer.

4. Esterification of Lactic Acid

Lactic acid concentration (C_{Ao}=1 M), ethanol concentration (C_{Bo}=15 M), total reaction volume (5 ml) and agitation rate (200 rpm) were kept constant in all reactions, except for the '2. The effect of molar ratio' part. DES was added in required amounts into the reaction mixture. Catalyst loading was 3 wt%. The yield of EL was calculated from Eq. (1):

$$\text{Yield, \%} = \frac{\text{EL concentration}}{\text{Maximum theoretical EL concentration}} \times 100 \quad (1)$$

To investigate the effect of the molar ratio of the reactants on the reaction yield, appropriate amounts of EtOH and LA were added in the reaction medium. Total reaction volume (5 ml) and catalyst loading (3 wt%) were kept constant and molar ratios of 0.5, 1, 5 and 15 for EtOH/LA were tested. The experiments were conducted with and without 5% (v/v) ChCl-Gly (1:2).

5. HPLC Analysis

LA and EL analyses were performed by HPLC (Waters Alliance 2695) using XTerra RP 18 column (4.6 mm×150 mm×5 μm Waters) at 40 °C and 210 nm. Eluent flow rate was 0.6 ml/min and the composition was 20% A (acetonitrile:water (70:30% (v/v)) and 80% B (o-phosphoric acid:water (0.1:99.9% (v/v)). The injection volume was 10 μl. LA and EL concentrations were found by using calibration curves prepared by standard samples. The coefficients of variation were 0.28% and 0.66% for LA and EL, respectively. Each analysis was conducted at least in duplicate.

6. Determination of the Acid Capacity and Accessibility of Sulfonic Acid Groups of Amberlyst-15

Amberlyst-15 beads were treated with 5% DES (ChCl-Gly (1:2)) in EtOH at 50 °C for 2 h and then filtered and dried at 45 °C for 5 h (DES-treated Amberlyst-15). For comparison, Amberlyst-15 beads were dried at 45 °C for 5 h (untreated Amberlyst-15). Acidbase titrations were conducted to determine acid capacity of DES-treated and untreated Amberlyst-15 beads according to the method described by Dijs et al. [31], using 200 mM KOH and 0.1 M KCl solutions. The accessibility of the sulfonic acid groups in Amberlyst-15 was determined by following the change in the pH of the media containing DES-treated and untreated beads in water mixed with 33 mM KCl solution [31].

7. Reusability of Amberlyst-15

The following strategies were used to test the reusability of the DES-treated Amberlyst-15. For the Methods 1-4, the common steps of the procedures were as follows: the filtration of Amberlyst-15 from the reaction medium and drying the catalyst at 65 °C overnight. Method 1: Amberlyst-15 was washed with hexane (10 ml× 4) Method 2: Amberlyst-15 was washed with dichloromethane (10 ml×4) Method 3: Amberlyst-15 was washed with acetone (10 ml×4), at 50 °C. Method 4: Water and EtOH were used sequentially (10 ml×4, each) for washing at 50 °C and acetone was used in the last step (10 ml×1). Method 5: Acid treatment procedure consisted of mixing Amberlyst-15 in sulfuric acid solution for 5 h, washing thoroughly with water till all sulfate ions were removed and washing with methanol (10 ml×2) as suggested by Sampath

Table 1. The properties of deep eutectic solvents

| DES type	Density, g·cm⁻³	Viscosity, mPa·s	pH	Freezing point, K	Conductivity, μS·cm⁻¹
ChCl-Gly (1:2)	1.181* (25 °C), 1.180 (25 °C) [38]	351* (25 °C), 259 [39]	3.91* (25 °C)	N/A	1189* (25 °C), 1300 (25 °C) [40]
ChCl-Glu (1:1)	1.298 (25 °C) [41]	9037.10 [41]	6.73 [41]	304.15 [41]	440 (81 °C) [35]
ChCl-Mal (1:1)	1.441* (23 °C)	N/A	3.15* (25 °C)	N/A	520* (25 °C)
ChCl-Xyl (1:1)	1.250 (30 °C) [42]	887 (30 °C) [42]	4.38* (25 °C)	N/A	1092 (30 °C) [42]
ChCl-EG (1:2)	1.120 (25 °C) [43]	37 (25 °C) [43]	3.96* (25 °C)	207.15 [43]	7960* (24 °C), 7610 (20 °C) [43]
ChCl-Suc (1:1)	1.350 (23 °C) [44]	79590 [45]	3.78* (25 °C)	N/A	1683* (25 °C)
ChCl-Fru (1:1)	1.337 (25 °C) [46]	14702.7 (25 °C) [46]	4.00* (25 °C)	253.15 [46]	493* (51 °C)
ChCl-U (1:2)	1.250 (25 °C) [43]	750 (25 °C) [43]	10.21* (25 °C)	261.15 [43]	859* (25 °C)

*Measured in our laboratory

N/A: not available
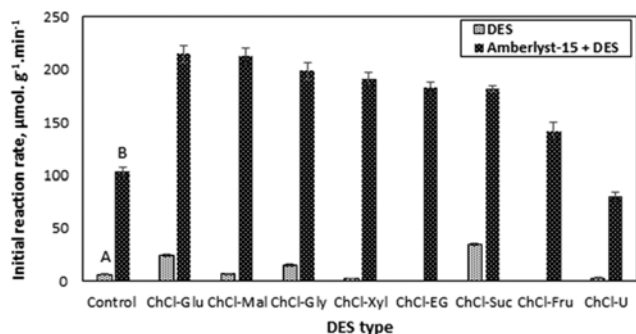
Fig. 1. The initial rates of reaction of lactic acid esterification with EtOH in the presence of different types of DESs (15 : 1 molar ratio of EtOH to lactic acid, DES: 5% (v/v), Amberlyst-15: 3 wt%, N=200 rpm, T=50 °C, t=2 h, Control A: Lactic acid+ EtOH, Control B: Lactic acid+EtOH+Amberlyst-15 (no DES)).
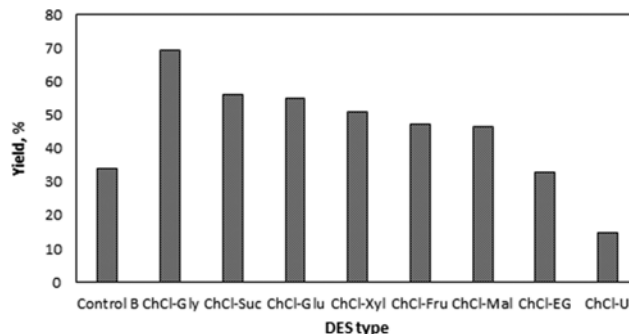

Fig. 2. Yield of ethyl lactate in the presence of different types of DESs (15 : 1 molar ratio of EtOH to lactic acid, Amberlyst-15: 3 wt%, DES: 5% (v/v), N=200 rpm, T=50 °C, t=2 h, Control B: Lactic acid+EtOH+Amberlyst-15 (no DES)).

and Kannan [32].

RESULTS AND DISCUSSION

1. The Effect of DES Type

The effect of DESs on the esterification of LA with EtOH was investigated by using the following solvents: ChCl-Gly (1 : 2) [33], ChCl-Glu (1 : 1) [33], ChCl-Fru (1 : 1) [33], ChCl-Mal (1 : 1) [34], ChCl-Xyl (1 : 1) [35], ChCl-EG [36] (1 : 2), ChCl-U (1 : 2) [37] and ChCl-Suc (1 : 1) [33]. Some of the properties of the solvents are summarized in Table 1.

The reaction was carried out both in the presence and absence of Amberlyst-15 acidic resin catalyst. The esterification reaction was also carried out by using EtOH instead of DES, as a control reaction. The results are shown in Fig. 1.

The esterification reaction of LA with EtOH is a self-catalyzed reaction due to the acidic character of LA. A minimal initial rate of reaction (6.18 ± 0.3 $\mu mol \cdot g^{-1} \cdot min^{-1}$) was observed when EtOH was brought in contact with LA (Control A in Fig. 1). On the other hand, when different types of DESs were introduced in the reaction medium, without Amberlyst-15, an increase in the initial rate of reactions was observed for ChCl-Suc, ChCl-Glu, ChCl-Gly, and ChCl-Mal. Among these, ChCl-Suc provided the highest initial rate of reaction as 35 ± 1.1 $\mu mol \cdot g^{-1} \cdot min^{-1}$ (Fig. 1), indicating that the catalytic effect of DES was considerably low. The catalytic effect of some DESs on the esterification reactions was also reported in the literature. Especially, Brønsted type and Lewis type DESs possessed high catalytic activity on the reaction between lauric acid and methanol [11], palmitic acid and methanol [47], acetic acid and 2-ethyl hexanol [48], glycerol and oleic acid [49], and also on the esterification reaction of formic acid and acetic acid with alcohols [50].

Following the investigation of catalytic effect of DESs alone on the reaction, the effect of DESs together with Amberlyst-15 was tested on the synthesis of EL. The results showed that almost all DESs had an impressive effect on the initial rate of reaction (Fig. 1). The highest rate was obtained with ChCl-Glu as 214.68 ± 8.3 $\mu mol \cdot g^{-1} \cdot min^{-1}$ followed by ChCl-Mal (212.68 ± 8.9 $\mu mol \cdot g^{-1} \cdot min^{-1}$) and ChCl-Gly ($198.54\pm8.0$ $\mu mol \cdot g^{-1} \cdot min^{-1}$), in order. When these

results were compared with the reaction performed with only Amberlyst-15 (Control B, Fig. 1), 1.4 to 2.1-fold increase in the reaction rates was found to be provided with the addition of DESs into the reaction medium.

As a result of the comparison of the initial rates of reactions of DESs alone and DESs together with Amberlyst-15 containing esterification reactions, one can conclude that DES solely has a negligible catalytic effect on the LA esterification.

Fig. 2 shows the effect of different types of DESs on the yield of EL, which was in consistent with that on the reaction rate. The stimulating effect of ChCl-Gly on the catalytic activity of Amberlyst-15 provided the highest yield of EL as 69.3% after 2 h of reaction, followed by ChCl-Glu and ChCl-Suc (Fig. 2).

Despite the high yield of EL and high initial rate of reaction they provided (Figs. 1 and 2), DESs prepared with glucose and maltose were quite viscous at room temperature and accordingly complicated the experimental procedures. Nevertheless, ChCl-Gly was quite fluidic and provided comparable reaction rates with ChCl-Glu and ChCl-Mal. Moreover, glycerol is a polyol that is a by-product with a large amount in biodiesel production. Consequently, ChCl-Gly (1 : 2) was preferred for further investigations.

In the present study, the enhancement in both the initial rate of reaction and the yield of EL due to the utilization of DES together with Amberlyst-15 were clearly determined. In the literature, the enhancement effect of DES on different types of Amberlyst catalyzed reactions was also reported, such as 5-(ethoxymethyl) furfural synthesis from carbohydrates [51], dehydration of pinacol [52] and esterification of oleic acid with methanol [53].

One of the possibilities of this increase could be the enhancement of the acid capacity and the accessibility of the sulfonic groups on the resin after exposure to DES. Therefore, we determined the acid capacity of the resin by acid-base titration and the accessibility of the active groups by following the change in pH due to the proton exchange ($AH+K^+ \leftrightarrow AK+H^+$). According to the results, the acid capacity of untreated Amberlyst-15 was found to be 4.7 $mmol \cdot g^{-1}$, which is compatible with that reported in the literature [31,54]. On the other hand, the acid capacity of DES-treated Amberlyst-15 was found to be 2.1 $mmol \cdot g^{-1}$, showing a significant decrease. This decrease in the acid capacity was also supported by the change in pH with time (Fig. 3), which corresponds to a lower
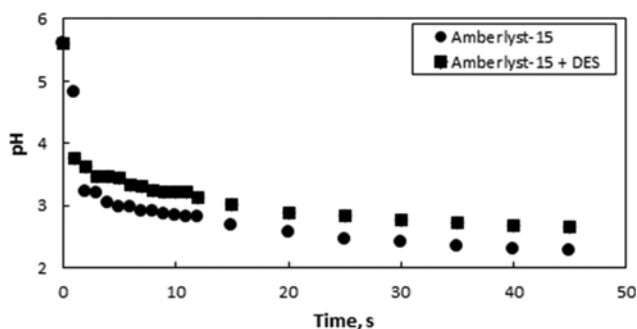
Fig. 3. The change in pH with time showing the accessibility of the active groups (DES: 5% (v/v) ChCl-Gly in EtOH).

accessibility of the sulfonic acid groups in the catalyst. Therefore, it can be concluded that the increase in the reaction rate and yield was not related to the acid capacity of Amberlyst-15.

It is very well documented in the literature that when DES is present in a reaction medium, the most significant phenomenon is the occurrence of hydrogen bonding between reaction components and DES resulting in an enhancement in the favor of synthesis [9,55-58]. Similarly, we propose an interaction between the active groups of the catalyst and ChCl-Gly due to hydrogen bonds, leading to increase in the initial rate of reaction and yield, independent of the acid capacity of Amberlyst-15. Zhang et al. [54] reported a similar result related to the reduction of the acidity of the catalyst while an induction in the activity. They studied the change in acid strength of polystyrene sulfonic acid resins, mainly caused by the formation and breakage of hydrogen bond interactions among neighboring sulfonic acid groups. The authors reported an increase in the catalytic activity of the modified Amberlyst-15 by hollow silica nanospheres (~2-fold increase in the conversion in an esterification reaction), while nearly one fifth decrease in the acidity. It was proposed that this could be due to the self-assembly of the sulfonic acid groups of Amberlyst-15, by the confined nano-space that caused a restriction of the free movement of sulfonic acid groups. This phenomenon was proposed to lead to an enhancement of hydrogen bond interactions with high local concentrations of the active groups. Herein, we also propose a similar hydrogen bond interaction among the adjacent sulfonic groups provided by ChCl-Gly during the esterification of LA with EtOH. As a hydrogen bond donor, glycerol has multiple hydroxyl groups that we think to facilitate the interaction with the ionic resin and also favor the synthesis of EL more than the other hydrogen bond donors. Additionally, ChCl-Gly was reported to be an effective solvent for esterification and transesterification reactions [59,60].

In a two-phase esterification reaction system that aimed at the production of biodiesel using methanol and oleic acid, Pan et al. [53] studied three different molar ratios of ChCl-Gly (1:1-1:3) with Amberlyst-15 and Amberlyst-BD20. They reported that ChCl-Gly (1:3) behaved as an assistant catalyst in the reaction together with the acidic resins and also played an important role in the reducing of the water content in both phases, favoring the synthesis. Although the present study involves only homogeneous liquid phase for all tested reaction media, the absorption of the by-product water by DES content is very likely during the synthe-
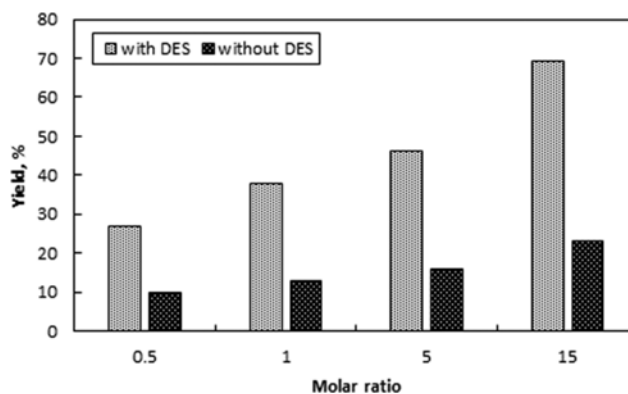

Fig. 4. The change in EL yield with molar ratio of EtOH : LA (Amberlyst-15: 3 wt%, ChCl-Gly: 5% (v/v), N=200 rpm, T=50 °C, t=2 h).

sis of EL.

On the other hand, in a recent work, which combines the experimental observations with quantum mechanical molecular dynamics simulations, Stefanovic et al. [61] proposed that the extent of hydrogen bond donor self-interaction yielded different hydrogen bond networks in ChCl-based DESs. Therefore, the lowest reaction rate determined in our study by the use of urea as hydrogen bond donor in DES could be a consequence of a strong hydrogen bond network in ChCl-U, which did not lead to any considerable interaction with sulfonic groups in the resin. However, hydroxyl-based DESs provided higher reaction rates due to weaker Cl- intercalation in DES.

2. The Effect of Molar Ratio

The effect of molar ratio of the reactants on EL yield was investigated in a wide range of EtOH : LA (Fig. 4). The results showed that ChCl-Gly had a stimulating effect on the catalytic activity of Amberlyst-15 at stoichiometric, lower and higher molar ratios of EtOH : LA. As the molar ratio increased, EL yield increased and reached 69.3% and 23.0% at the ratio of 15 with and without DES, respectively. In our experiments, high molar ratio was preferred to proceed the reaction forward.
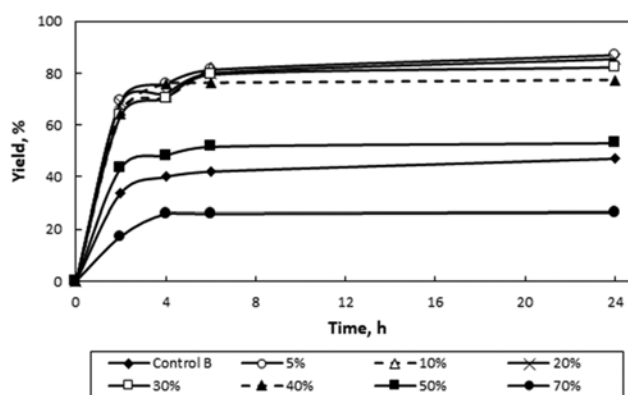

Fig. 5. Time course of ethyl lactate yield for different ChCl-Gly amounts in the presence of Amberlyst-15 (15 : 1 molar ratio of EtOH to lactic acid, Amberlyst-15: 3 wt %, N=200 rpm, T=50 °C, t=24 h, Control B: EtOH instead of DES).

3. The Effect of ChCl-Gly Amount

The effect of the amount of ChCl-Gly in the reaction medium on the esterification of LA catalyzed by Amberlyst-15 was investigated in the range of 5-70% (v/v), and the results are presented in Fig. 5. For all the reactions that contained DES, the yield of EL increased significantly in 2 h and then the increasing trend slowed and reached a nearly constant value after 6 h. On the other hand, the yield increased with the increasing amount of ChCl-Gly till 20% (v/v), while decreased considerably with increasing amount of DES. Particularly at 70% DES (v/v), a clear reduction was detected when compared with control. The decrease in the yield of EL at high DES amounts could possibly be due to the occupation of pores of the catalyst by DES and also excess hydrogen bonding of DES with sulfonic acid groups in Amberlyst-15. In the literature, the unfavorable effect of high amount of DES (70% and 90% (v/v)) on the polymerization yield of catechin was also reported [62]. Additionally, mass transfer limitations could have occurred at the range of 70-90% (v/v) due to the high viscosity of ChCl-Gly.

According to the results, the highest EL yields were obtained with 5 and 10% (v/v) ChCl-Gly as 87.2% and 86.3%, respectively, after 24 h of reaction. Consequently, further investigations were conducted using 5% (v/v) ChCl-Gly.

4. The Effect of Mass Transfer Limitations

The esterification reaction of LA was performed at different agitation rates to investigate the effect of external mass transfer limitations. The initial rates of reaction were found to be almost constant at 150 and 200 rpm; therefore, no external mass transfer limitation was detected throughout the experiments conducted using 5% ChCl-Gly (Fig. 6).

The level of internal mass transfer resistance, represented by observable Thiele modulus, Φ, was calculated using Eq. (2) which is valid for spherical particles [63]:

$$\Phi = \frac{r_0}{D_E C_{S0}} \left(\frac{R_P}{3} \right)^2 \tag{2}$$

The equation includes the initial rate of reaction (r_0; mol·L^{-1}·s), the effective diffusivity coefficient (D_E; cm^2·s^{-1}), the initial concentration of the substrate (C_{S0}; mol·L^{-1}) and the radius of the particle (R_P; cm).

The effective diffusivity coefficient was calculated from Eq. (3) that contains substrate diffusivity coefficient in liquid (D_s; cm^2·s^{-1}), porosity (ε_p) and tortuosity factor of the particle (τ) and the hindrance factor (σ) [64]. The values of ε_p, τ and R_p were used as 0.32, 3 [65] and 0.015 cm [66], respectively. The hindrance factor (σ) was neglected based on the assumption that the radius of catalyst pore was much greater than the solute molecule [67].

$$D_E = D_S \frac{\varepsilon_p}{\tau} \sigma \tag{3}$$

The substrate diffusivity coefficient in liquid (D_s; cm^2·s^{-1}) was estimated using the Scheibel equation (Eq.(4)) [68].

$$D_S = \frac{kT}{\mu V_S^{0.33}} \tag{4}$$

In this equation μ is the viscosity of the reaction medium (cp). It was estimated using the kinematic viscosity of the reaction medium that was calculated by the Refutas equation ASTM D7152 [69,70] as 0.77 cp and together with the density of the reaction mixture, calculated as 0.82 g·cm^{-3}. On the other hand, k is the equation constant (17.5×10^{-8}) [68], T is the reaction temperature (323.15 K), and V_S is the molar volume of substrate (for EtOH 60.30 cm^3; for LA 76.87 cm^3 [71,72].

As a result of the calculations, the substrate diffusivity coefficient and the effective diffusivity coefficient were found to be 1.97×10^{-5} cm^2·s^{-1} and 2.11×10^{-6} cm^2·s^{-1} for EtOH and 1.82×10^{-5} cm^2·s^{-1} and 1.94×10^{-6} cm^2·s^{-1} for LA, respectively. Under the reaction conditions, the observable Thiele modulus values were calculated as $\Phi = 7.93 \times 10^{-5}$ for EtOH (15 M) and $\Phi = 1.28 \times 10^{-3}$ for LA (1 M) indicating the negligible internal diffusion limitation, according to Weisz's criterion ($\Phi < 0.3$) [73].

5. The Effect of Temperature

The effect of temperature on the initial rate of esterification reaction with EtOH was investigated between 40-60 °C (Fig 7). The highest reaction rates at 60 °C were reached as 86.01±3.9 µmol·g^{-1}·min^{-1} with Amberlyst-15 and as 214.4±4.04 µmol·g^{-1}·min^{-1} with Amberlyst-15 together with 5% ChCl-Gly. The initial rate of reaction increased with increasing temperature, as expected.
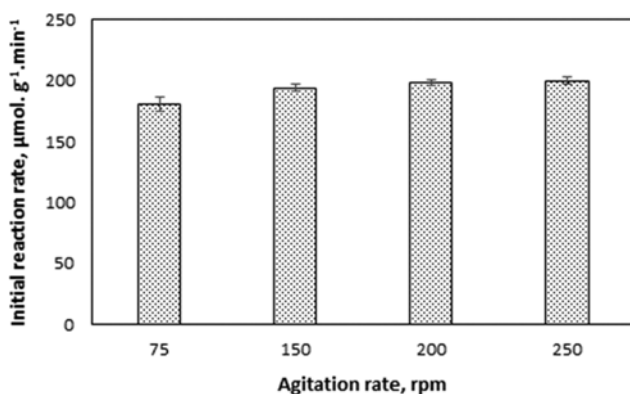

Fig. 6. The effect of agitation rate on the initial rate of the reaction (15 : 1 molar ratio of EtOH to lactic acid, ChCl-Gly: 5% (v/v), Amberlyst-15: 3 wt%, T=50 °C, t=2 h).
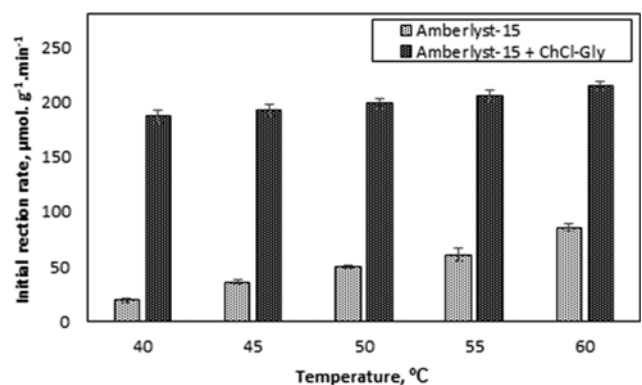

Fig. 7. The effect of temperature on the initial rate of reaction of lactic acid esterification with EtOH (15 : 1 molar ratio of EtOH to lactic acid, Amberlyst-15: 3 wt%, ChCl-Gly: 5% (v/v), N=200 rpm, t=2 h).

The activation energy of the esterification reaction of LA with EtOH under catalysis of Amberlyst-15 was determined as 60.87 kj/mol (R^2=0.97). This value is consistent with the other studies, reporting 62.5 kj/mol [74] and 51.58 kj/mol [75]. On the other hand, when ChCl-Gly was used together with Amberlyst-15, the activation energy was found to be 5.95 kj/mol (R^2=0.97), which is almost ten-fold less than the non-DES esterification. ChCl-Gly was discovered to have a considerable decreasing effect on the activation energy.

Such low activation energy values were also reported previously for esterification reactions of palm fatty acid with methanol using sulfuric acid and methane sulfonic acid (0.05%) as 6.528 kcal/mol and 3.785 kcal/mol, respectively [76].

On the other hand, Roman et al. [77] used an ionic liquid, 1-methylimidazolium hydrogen sulfate, as a catalyst in the esterification reaction of oleic acid with methanol. The activation energy of the reaction was found to be 6.8 kj·mol^{-1}, which was much lower than the values reported in the literature. Therefore, the authors presented the low activation energy as one of the advantages of the use of ionic liquid in the reaction. Additionally, they reported that the use of ionic liquid affected the significance of temperature considerably.

6. Reusability of DES-treated Amberlyst-15 and Recovery and Reusability of the Reaction Components

Amberlyst-15 is reported to be a reusable catalyst after different washing procedures [78-80]. In this study, commonly used solvents were tested for the reusability of Amberlyst-15 such as hexane, acetone, dichloromethane and EtOH-water. However, despite the use of various strategies (*Methods 1-4*) (Fig. 8), insufficient yields were obtained after the second cycle of the catalyst. The highest relative yield obtained in the second cycle was only 63% by using *Method 4*. Therefore, catalyst aging was likely to occur during the reaction. Considering this low yield in the second cycle and also our findings on the decrease of the acidity of Amberlyst-15 ('*1. The effect of DES type*'), a requirement of the regeneration of the catalyst appeared. Acid treatment was performed by using sulfuric acid (*Method 5*) for the regeneration and a significant enhancement on EL yield was achieved in the second cycle as 98% (*Method 5*). This showed that the regeneration of the catalyst was crucial after the esterification reaction with DES-treated Amberlyst-15.
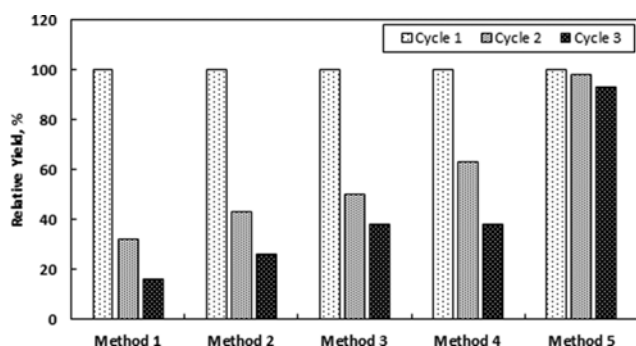

Fig. 8. Reusability experiments using different methods (15 : 1 molar ratio of EtOH to lactic acid, Amberlyst-15: 3 wt%, ChCl-Gly: 5% (v/v), N=200 rpm, t=2 h).

On the other hand, the separation of the product from the reaction medium was performed in sequential steps. First, the removal of EtOH from the medium was necessary due to the highly miscible nature of EtOH with numerous extraction solvents that complicated the recovery of the reactants. Therefore, EtOH was removed by vacuum evaporation and hexane was added to the remaining phase to extract EL from the mixture containing DES, LA and EL. EL was thoroughly extracted with hexane (5×10 ml) and later on was recovered by vacuum evaporation. The remaining phase containing LA and DES was recycled in two different ways. First, it was used as a new reaction medium, since it already contained one of the reactants and DES. After addition of required amount of EtOH and Amberlyst-15, the esterification reaction could be performed again with the recycling of the unreacted components. Second, LA was extracted by diethyl ether (5×10 ml) easily due to the advantage of immiscible nature of ChCl-Gly with the solvent. Consequently, all of the reaction components could be recycled, which is an advantage for the presented esterification reaction of LA.

CONCLUSIONS

The scientific novelty of this study is the utilization of DESs together with Amberlyst-15 in the esterification reaction of LA with EtOH, resulting in a significant decrease in the activation energy causing a significant increase in the initial rate of reaction and yield. It was shown that even at low amounts, DES had an impressive effect on Amberlyst-15 that resulted in nearly two-fold increase in both the initial rate of reaction and EL yield. A 69.3% yield of EL was obtained when Amberlyst-15 was used together with ChCl-Gly, while the yield was only 33.8% in the presence of Amberlyst-15 only. DES led to a significant decrease in the activation energy when used together with Amberlyst-15, resulting in 5.95 kj/mol. On the other hand, this study also presents that, when used alone, DESs, tested in this study, do not have a significant catalytic effect on the esterification reaction of LA. The maximum initial reaction rate obtained with ChCl-Suc was only 35 µmol·g^{-1}·min^{-1}, which is one-fourth of the lowest rate achieved (141.81 µmol·g^{-1}·min^{-1}) in the presence of Amberlyst-15 and ChCl-Fru.

In terms of recyclability, the reuse of the raffinate phase, after the removal of EtOH and extraction of EL, as a new reaction medium with the addition of the other reactant and catalyst, provided significant advantage to the process. Additionally, the reactants and the product EL were shown to be easily recovered by conventional extraction and evaporation methods. However, the regeneration procedure of Amberlyst-15 needs to be improved to increase the cyclability number.

To our knowledge, this is the first study to present the impressive effect of DES on Amberlyst-15 on the esterification reaction of LA with EtOH. These findings may also present a point of view for the researchers to activate other catalysts as well.

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