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Acidic Deep Eutectic Solvents as Green and Reusable Catalyst for Emulsifier Synthesis

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Abstract

Emulsifiers known as mono- and diglycerides (MDG) are produced when fatty acids are esterified with glycerol (glycerolysis of fatty acids) with the use of an acid catalyst. This work is the first to use non-toxic deep eutectic solvents (DES) as a green catalyst for palmitic acid glycerolysis. The effect of various reaction temperatures and catalyst loadings on the catalyst activity of acidic DES (mixtures of betaine hydrochloride and citric/propionic acid), and reusability test of the catalyst were studied. The reaction takes place at a palmitic acid to glycerol molar ratio of 1:6 at a stirring speed of 300 rpm, reaction temperatures of 120-180 °C, and catalyst loadings of 1-5 wt.% (based on palmitic acid). Conversion of palmitic acid tends to increase with the increasing in reaction temperature and catalyst loading. The highest reaction conversion reaching 90.3% and produce the monoglycerides emulsifier as much as 72.8%. In addition, this catalyst is also very effective for reuse.

Keywords

deep eutectic solvents, glycerolysis, mono- and diglycerides, palmitic acid

1 Introduction

Non-ionic surfactants called mono- and diglycerides (MDG) are frequently employed as emulsifiers in a variety of food products [1]. Glycerolysis of fatty acids, which is the direct esterification of glycerol with fatty acid can be used to create MDG [2]. Prior research has reported the esterification of glycerol with fatty acid with a variety of heterogeneous catalysts [3–7]. Furthermore, Konwaret al. [8] reported that a mesoporous carbon catalyst ($ACSO_3H$) has high selectivity of monoglycerides (MGs) product on the esterification of fatty acids (lauric and oleic).

The use of an acidic homogeneous catalyst such as sulfuric acid, p-toluene sulfonic acid, and methane sulfonic acid for the glycerolysis of free fatty acids is reported by Maquirriain et al. [9]. Deep eutectic solvents (DESs) that were formed by mixturs of allyl triphenyl-phosphonium bromide and p-toluene-sulfonic acid monohydrate were used as a catalyst in the esterification of fatty acid with glycerol to reduce the free fatty acids in low grade oil [10], and glycerolysis of free fatty acids in vegetable oil deodorizer distillate [11].

DESs are eutectic mixture of a quaternary ammonium salt (such as choline chloride, betaine monohydrate, betaine hydrochloride) as a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) (such as organic acids, poliols, sugars, alcohols). DESs are attractive because of the differences of HBD type in the DES affect their properties such as total interaction energy and molecular interactions [12, 13], density and viscosity [14], and solubility [15, 16]. In the reaction of converting cellulose into gluconic acid using DES, $FeCl_3 \cdot 6H_2O$/ethylene glycol DES can dissolve cellulose quickly, leading to a change from a heterogeneous to a homogeneous reaction [17].

Our previous study revealed that betaine hydrochloride-organic acid DES and choline chloride-sorbitol DES have good catalytic activity in the glycerolysis of stearic acid [18]. In addition, the kinetic study of the glycerolysis of stearic acid has also been presented by Zahrina et al. [19]. In the glycerolysis of fatty acids, the presence of an acid catalyst can increase the protonation of the fatty acids carbonyl group towards the nucleophilic attack of glycerol [10]. Palmitic acid can interact with the DES molecules [20], so using acidic DES in the glycerolysis of fatty acids can function as both a catalyst and a solvent, similarly to the conversion of cellulose to gluconic acid as reported by Liu et al. [17].

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The type of fatty acids affects the catalytic activity of a catalyst [21]. Therefore, acidic DESs consisting of betaine hydrochloride and citric/propionic acid were applied as catalysts in the emulsifier synthesis via glycerolysis of palmitic acid in this work. Catalytic activities of betaine hydrochloride–citric/propionic DESs were determined at various reaction conditions such as reaction temperatures, and catalyst loadings. The catalytic activity of the acidic DESs was confirmed by reaction conversion and infrared spectrum of product at different reaction conditions, also reusability test.

2 Experimental

2.1 Material

Glycerol (purity 99.5%), commercial palmitic acid (purity 99%), propionic acid (purity 99%), and citric acid (purity 99.5%) were purchased from Merck. Analytical grade ethanol, potassium hydroxide, oxalic acid and phenolphthalein indicator were purchased from Merck. Betaine hydrochloride (purity greater than 99%) was purchased from Sigma Aldrich.

2.2 Acidic DES preparation

Water and betaine hydrochloride were mixed at a molar ratio of 1:12 until a homogenous solution was achieved. Next, a beaker glass with a stirring bar was filled with the solution and HBD (propionic acid/citric acid) at a 1:2 molar ratio of betaine hydrochloride to acid. The mixture was stirred (150 rpm) at 80 °C heated for 90 min at ambient pressure. After stirring is completed, the mixture is cooled.

2.3 Physico-chemical properties of acidic DES

The viscosity of acidic DESs was measured at room temperature using a U-tube reverse type Cannon-Fenske Viscometer in a water-bath with controlled temperature 30 °C. The densities of the samples were measured using a calibrated liquid densitometer at room temperature. The pH of DESs was measured by a pH meter Hanna HI 98107. The FTIR spectra of the pure components (betaine hydrochloride, propionic acid, citric acid), and acidic betaine hydrochloride-based DESs at room temperature were recorded with a Perkin Elmer UATR instrumentin the range 4000 to 500 cm^{-1}.

2.4 Glycerolysis of palmitic acid

Glycerolysis of palmitic acid was carried out in a 250 mL laboratory scale agitated batch-reactor using a magnetic stirrer at a speed of 300 rpm. The reactor was heated and its temperature was measured with a thermocouple. The reaction was performed under atmospheric pressure for a reaction time 180 min. During the reaction, nitrogen was purged through the reactor (flow rate was set to 80 mL min^{-1}). Water vapor was removed from the reactor through a condenser during the reaction. The time taken to reach equilibrium was estimated by sampling the reaction mixture until a few consecutive samples produced essentially the same result of the analysis. It was determined that 180 min were sufficient to reach equilibrium.

Each experimental run was carried out at a molar ratio of palmitic acid to glycerol 1:6, catalyst loadings 1, 3, 5 wt.% (based on palmitic acid), and at different reaction temperatures (120 °C, 150 °C and 180 °C). Each experimental run was repeated twice.

The reaction mixture consisted of two layers, namely the upper layer which contains unreacted palmitic acid and MDG, while the lower layer contains unreacted glycerol and DES catalyst. After the reaction, the mixture was separated by centrifugation (Centrifuge DLAB DM 0412). Then the mixture was left still for at least 60 min.

2.5 Determination of palmitic acid conversion

Palmitic acid conversion was determined by analyzing the levels of unreacted palmitic acid in the upper layer. Because there is a possibility that DES is carried to the upper layer and DES is acidic, it will affect the analysis results. Therefore DES must be removed in the upper layer. The trace of DES in the upper layer was washed out with warm water until the pH was neutral. Then, the sample was dried under vacuum. The palmitic acid content in the upper layer was analyzed by the titration method [11].

2.6 GCMS and FTIR analysis of glycerolysis product

The composition of the glycerolysis product was analyzed by gas chromatography coupled with mass spectrometry (GCMS) (Shimadzu QP2010 using RTX-5 MS columns with dimensions of 30 × 0.25 mm × 0.25 μm and AOC-20i auto-injector). Samples were diluted 20 times with hexane and injected into the columns at injection temperature 250 °C. The FTIR spectra of the upper layer and the lower layer at room temperature were recorded with a Perkin Elmer UATR in the frequency range of 4000 to 500 cm^{-1}.

2.7 Catalyst reusability

The solubility of the DES in glycerol is greater than the solubility of the catalyst in palmitic acid, so it can be assumed that all the DES catalysts are in the lower layer [10]. The mass of glycerol after the reaction decreases, therefore pure glycerol was added to cover the shortage of glycerol for the next run. Then, this mixture was reacted with pure palmitic acid. The process was repeated three times. The reusability of the catalyst was tested at a molar ratio of palmitic acid to glycerol of 1:6, catalyst loading 5 wt.% and reaction temperature of 180 °C using betaine hydrochloride–propionic acid DES as catalyst.

3 Results and discussion

3.1 Physico-chemical properties of acidic DES

The physical properties of acidic DES are presented in Table 1. The density of betaine hydrochloride–citric acid DES is higher than that of the betaine hydrochloride–propionic acid DES as citric acid has a higher number of hydroxyl groups and a longer chain than propionic acid. The density of DES is influenced by the type of HBD. The density of DES increases with increasing the number of hydroxyl groups or the length of the HBD chain [22]. The density of the DES decreases due to the existence of holes and vacancies within the liquid DES [23]. Also DES with lower density has less stability [24], therefore the DES activity as a catalyst in the reaction increases due to reduced steric hindrance when interacting with the reactants.

The chain length in HBD affects viscosity. Longer alkyl chains increase the molecular dimensions of HBD, thereby hindering the free movement of HBD [25]. The viscosity of betaine hydrochloride–citric acid DES is higher than that of the betaine hydrochloride–propionic acid DES. Lower DES viscosity is also often associated with a hydrogen bond network between HBA and HBD, which causes an increase in free volume [26].

The pH of betaine hydrochloride–citric acid DES is higher than that of the betaine hydrochloride–propionic acid DES. The chemical nature of the HBD has a strong effect on the acidic or basic strength of the DES [24]. The relationship between the physical properties of acidic DES (density, viscosity, and pH) and their catalytic activity in the glycerolysis of palmitic acid is presented in Section 3.2.

DES can form through the hydrogen bonding between the HBA and the HBD compounds. Previous studies revealed that hydrogen bonding in the eutectic mixture can be claimed if the infrared spectral band of the hydroxyl group is shifted to lower frequency [12, 27]. The strength of the intermolecular interactions in the acidic DES is confirmed in this work by analyzing the infrared spectra of the starting components (betaine hydrochloride as HBA, also citric acid and propionic acid as HBD) and the resulting eutectic mixture.

Table 1 Physical properties of the acidic DES

HBD	Molar ratio of HBA:HBD	Density (g mL^{-1})	Viscosity (Pa s)	pH
Citric acid	1:2	1.340	$1.850 \cdot 10^{-3}$	0.74
Propionic acid	1:2	1.096	$0.718 \cdot 10^{-3}$	0.44

The infrared spectra of betaine hydrochloride, citric acid, propionic acid, and acidic DES are shown in Fig. 1. The peak of hydroxyl group is shifted to lower wavenumber in the betaine hydrochloride–citric acid DES (Fig. 1(c)) than the citric acid (Fig. 1(b)). The band of hydroxyl group of betaine hydrochloride–glycerol–propionic acid mixture is shifted to the lowest wavenumber. In this context, the strength of molecular interactions between the betaine hydrochloride and the propionic acid is lower than between the betaine hydrochloride and the citric acid. The extent of H-bonds in the betaine monohydrate–polyol eutectic mixtures related to the strength of molecular interactions was confirmed by infrared spectroscopy and total interaction energy [13]. Section 3.2 will discuss how the strength of the interactions between the molecules in the acidic DES affects their ability to catalyze reactions.

3.2 Catalytic activity of acidic DES

In this work, the catalytic activity of acidic DES on the glycerolysis of palmitic acid was evaluated. Therefore, the effect of acidic DES loading, reaction temperature, and HBD type on the palmitic acid conversion were investigated. Also, the change in the structure of compounds in the upper layer and the lower layer, due to variations in reaction temperatures, was also investigated with infrared spectroscopy.

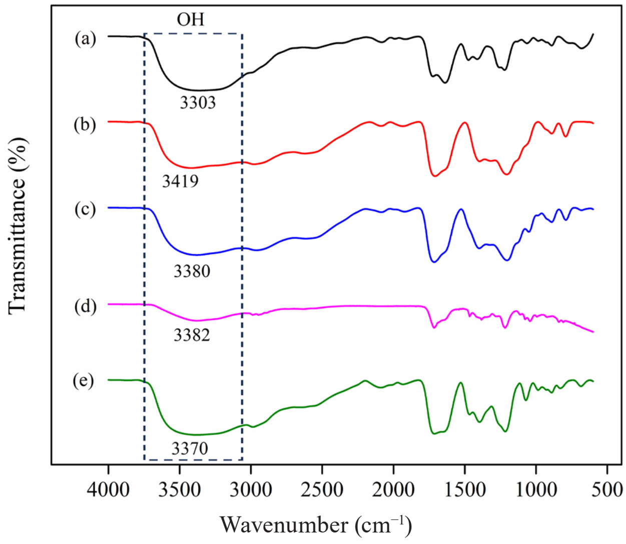
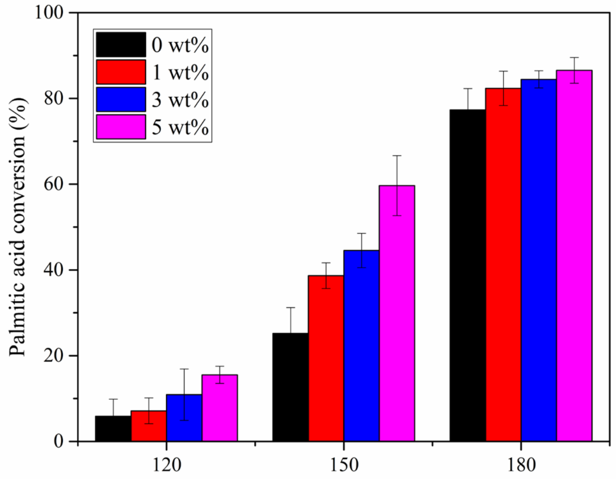


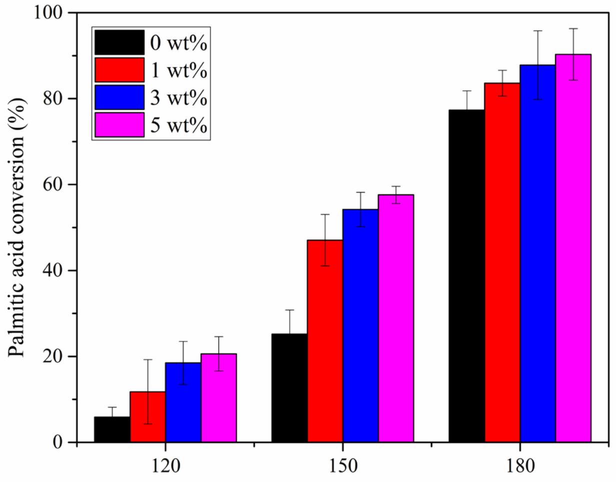
Fig. 1 Infrared spectra of (a) betaine hydrochloride, (b) citric acid, (c) betaine hydrochloride–citric acid DES, (d) propionic acid, (e) betaine hydrochloride–propionic acid DES

3.2.1 Effect of reaction temperature

The influence of reaction temperature on the glycerolysis of palmitic acid reaction using betaine hydrochloride–acid DES as catalyst can be observed in Fig. 2. The highest palmitic acid conversion (90.3%) was obtained at the highest temperature (180 °C) using 5 wt.% betaine hydrochloride–propionic acid DES catalyst and 86.5% using betaine hydrochloride–citric acid DES. As can be seen, the conversion of palmitic acid tends to increase with the increasing reaction temperature. Increasing temperature results in higher kinetic energy of glycerol and palmitic acid thereby increasing the adsorption to the active sites and increasing the effective interactions between the reactant molecules [5]. In addition, the increase in reaction temperature enhances the miscibility of the reactants, thus the reaction rate and conversion also increase [27]. Similar trend was observed in the synthesis of glycidol and glycerol carbonate from glycerol and dimethyl carbonate using DES as a catalyst [28], the synthesis of ethyl levulinate by levulinic acid esterification with ethanol using DES from the mixture of choline chloride and p-toluene sulfonic acid [27], and in the methanolysis of polycarbonate to valuable product bisphenol-A using choline chloride-based DES as catalyst [29].



(a)



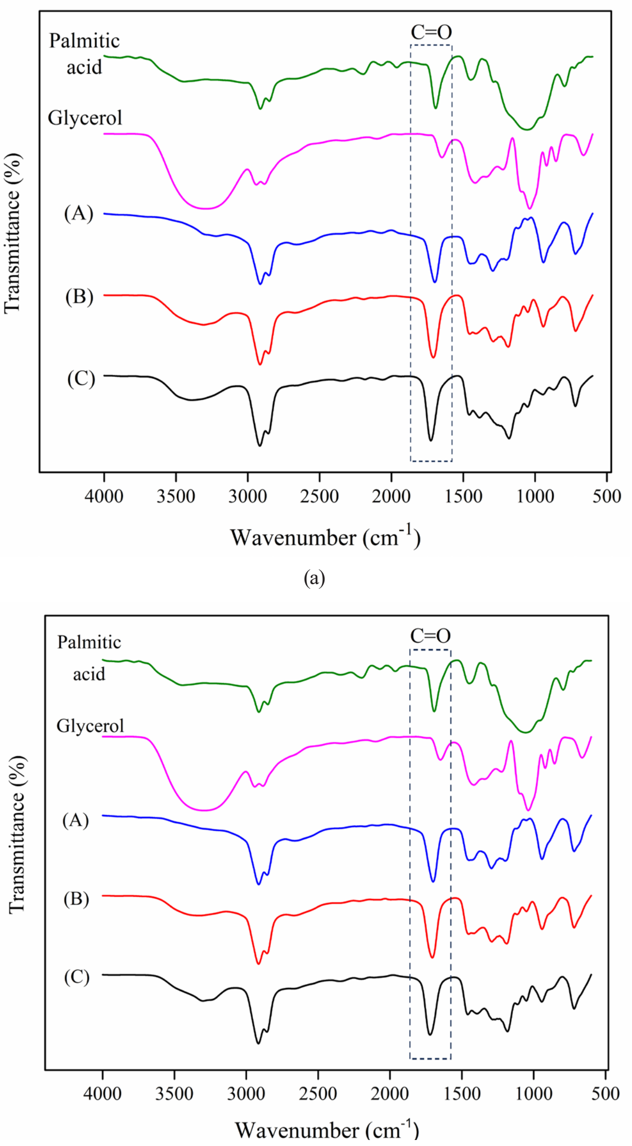
(b)

Fig. 2 Palmitic acid conversion in the glycerolysis of palmitic acid using catalyst (a) betaine hydrochloride–citric acid DES, and (b) betaine hydrochloride-propionic acid DES

In the glycerolysis of palmitic acid without catalyst, a color change occurred at 180 °C. The increase in reaction temperature causes a change in the color of the product (upper layer) from white crystals at 120 °C to a yellow solid emulsion at 180 °C using betaine hydrochloride–propionic acid DES. Increasing the reaction temperature also causes a color change in the lower layer (mixture of glycerol and DES) from clear at 120 °C to brown at 180 °C. The use of betaine hydrochloride–citric acid DES catalyst shows a darker color than betaine hydrochloride–propionic acid DES at the same temperature. Maquirriain et al. [9] reported that the reaction mixture became very dark depending upon the catalyst concentration, the reaction temperature, and the molar ratio of free fatty acid to glycerol. The dark color of the reaction mixture is due to secondary reactions that occur at high temperatures and/or in the presence of acids. At high temperature the acid catalysts accelerate the decomposition of glycerol to acrolein.

The infrared spectra of the glycerolysis products (upper layer) at different reaction temperatures are presented in Fig. 3. The glycerolysis of palmitic acid produces ester groups. The stretching of the C = O carbonyl group is a useful region of the spectrum for identifying MG, diglyceride (DG) and triglyceride (TG) compounds at 1650-1730 cm^{-1} [30]. In the infrared spectra of the glycerolysis products using betaine hydrochloride–citric acid DES catalyst, the ester group appears with higher intensity as the reaction temperature increases, and a similar trend is observed in the case of betaine hydrochloride–propionic acid DES. This indicates that the increase in temperature causes higher ester production.

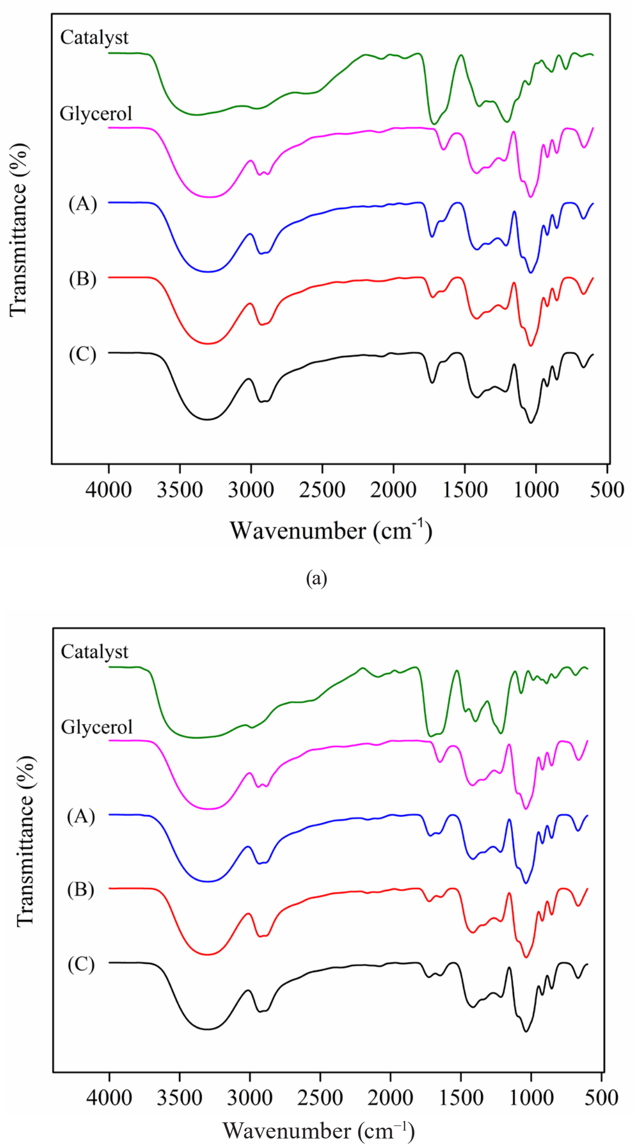
The infrared spectra of the lower layer at different reaction temperatures is presented in Fig. 4. Increasing the reaction temperature does not change the structure of glycerol and DES. Therefore, the unreacted glycerol and DES can be recycled for reuse.



(a)

(b)

Fig. 3 Infrared spectra of glycerolysis product (upper layer) at 5 wt.% catalyst loading and reaction temperatures (A) 120 °C, (B) 150 °C, (C) 180 °C using (a) betaine hydrochloride–citric acid DES catalyst and (b) betaine hydrochloride–propionic acid DES catalyst



(a)

(b)

Fig. 4 Infrared spectra of lower layer at 5 wt.% catalyst loading and reaction temperatures (A) 120 °C, (B) 150 °C, (C) 180 °C using (a) hydrochloride–citric acid DES catalysts and (b) hydrochloride–propionic acid DES catalyst

3.2.2 Effect of catalyst loading

The addition of a catalyst to the palmitic acid glycerolysis reaction increases the palmitic acid conversion as shown in Fig. 2. The glycerolysis of palmitic acid without using a catalyst produces a lower reaction conversion. The increase of catalyst loading to 1, 3, and 5 wt.% raised the palmitic acid conversion at 120 °C. A similar trend was also observed at 150 °C and 180 °C. The highest reaction conversion, 90.3% was obtained at 180 °C by adding 5% betaine hydrochloride–propionic acid DES catalyst. The increase in catalyst loading increases the acidity of the reaction mixture. During the glycerolysis reaction, nucleophilic acyl substitution occurs which is catalyzed by acids. Glycerol is not strong enough nucleophile to attack the carbonyl group of fatty acids. The acid catalysts increase the protonation of the carbonyl group towards nucleophilic attack, therefore the catalytic activity also increases [10].

Williamson et al. [10] reported that the conversion of oleic acid tended to increase with increasing catalyst loading using phosphonium-based DES as a catalyst in the esterification reaction of oleic acid with glycerol. In the glycerolysis of free fatty acid in vegetable oil deodorizer distillate, the conversion of free fatty acid also increases if the use of phosphonium-based DES catalyst loading increases [11].

The esterification of glycerine with free fatty acids using sulfuric acid, p-toluene sulfonic acid, and methane sulfonic acids as catalysts shows that an increase in catalyst concentration causes an increase in the reaction rate [9].

During the glycerolysis of palmitic acid, an increase of the acidic DES catalyst loading causes a darker color change in the upper and lower layers. It also occurs with sulfuric acid, p-toluene sulfonic acid, and methane sulfonic acid catalysts. The secondary reactions are associated withe the change of colour. The p-toluene sulfonic acid catalyst promotes the highest formation of by-products. The increase in catalyst concentration is also related to the concentration of by-products [9].

In the reaction of converting cellulose to gluconic acid using the $FeCl_3 \cdot 6H_2O$–ethylene glycol DES catalyst, the conversion also increases with the increasing concentration of the catalyst. Cellulose dissolves quickly in $FeCl_3 \cdot 6H_2O$–ethylene glycol, causing a shift from heterogeneous to homogeneous reactions. The dissolved cellulose is hydrolyzed into glucose due to the acidity of DES, and subsequently, glucose is oxidized into gluconic acid using the oxidative power of the solvent. $FeCl_3$ is partially reduced to $FeCl_2$, which can be reoxidized to $FeCl_3$, thus fully restoring the oxidative capacity of the solvent [17].

3.2.3 Effect of HBD type

In Fig. 2, the conversion of palmitic acid using betaine hydrochloride–propionic acid DES catalyst (90.3%) was higher than in the case of using betaine hydrochloride–citric acid DES (86.5%). This is due to the lower viscosity, density, and pH of the betaine hydrochloride–propionic acid DES compared to betaine hydrochloride–citric acid DES (Table 1). A longer alkyl chain in HBD will increase its molecular dimensions, thereby hindering the free movement of HBD [25]. Therefore, the DES with lower viscosity can increase the diffusion coefficient thereby increasing the penetration of DES to the glycerol and palmitic acid. Therefore that they easily bind to each other, consequently the rate of reaction also increases. In this work, DES with lower pH (betaine hydrochloride–propionic acid DES) resulted in the higher the conversion of palmitic acid. Similar trend was found in the synthesis of ethyl levulinate by levulinic acid esterification using choline chloride based-DES as catalyst [27].

In the glycerolysis using DES catalyst, competition occurs between the HBD of DES and the reactants to interact with the chloride ions from betaine hydrochloride. Citric acid and propionic acid have a simple structure, but the −OH branches of citric acid are close to each other, in contrast to propionic acid which only has one −OH branch. The chloride ion in betaine hydrochloride is large, it has obstacles to bind freely with all the −OH groups in citric acid. Therefore the that betaine hydrochloride–citric acid DES has a tight conformation and has higher strength in the intermolecular interactions (see infrared spectra in Section 3.1). The higher stability makes it difficult for the active groups of reactants to interact. Therefore, it takes a higher energy to access the reactants and form hydrogen bonds with chloride anions. In the betaine hydrochloride–propionic acid DES, the HBD cluster is only locked in a certain position so that it can rotate freely. In addition, lower DES viscosity and density are often associated with a hydrogen bond network between the betaine hydrochloride and the acid which causes an increase in the free volume. Thus the chloride ions in the betaine hydrochloride–propionic acid DES interact more easily with the reactants. Therefore, the conversion using betaine hydrochloride–propionic acid DES is higher than in betaine hydrochloride–citric acid DES.

The comparison of the performance of various catalysts in the glycerolysis of fatty acids is shown in Table 2. Under the same conditions the conversion of the glycerolysis of palmitic acid using the betaine hydrochloride – propionic acid DES catalyst is lower than the conversion of the glycerolysis of stearic acid using the choline chloride – sorbitol DES and methanesulfonic acid catalyst.

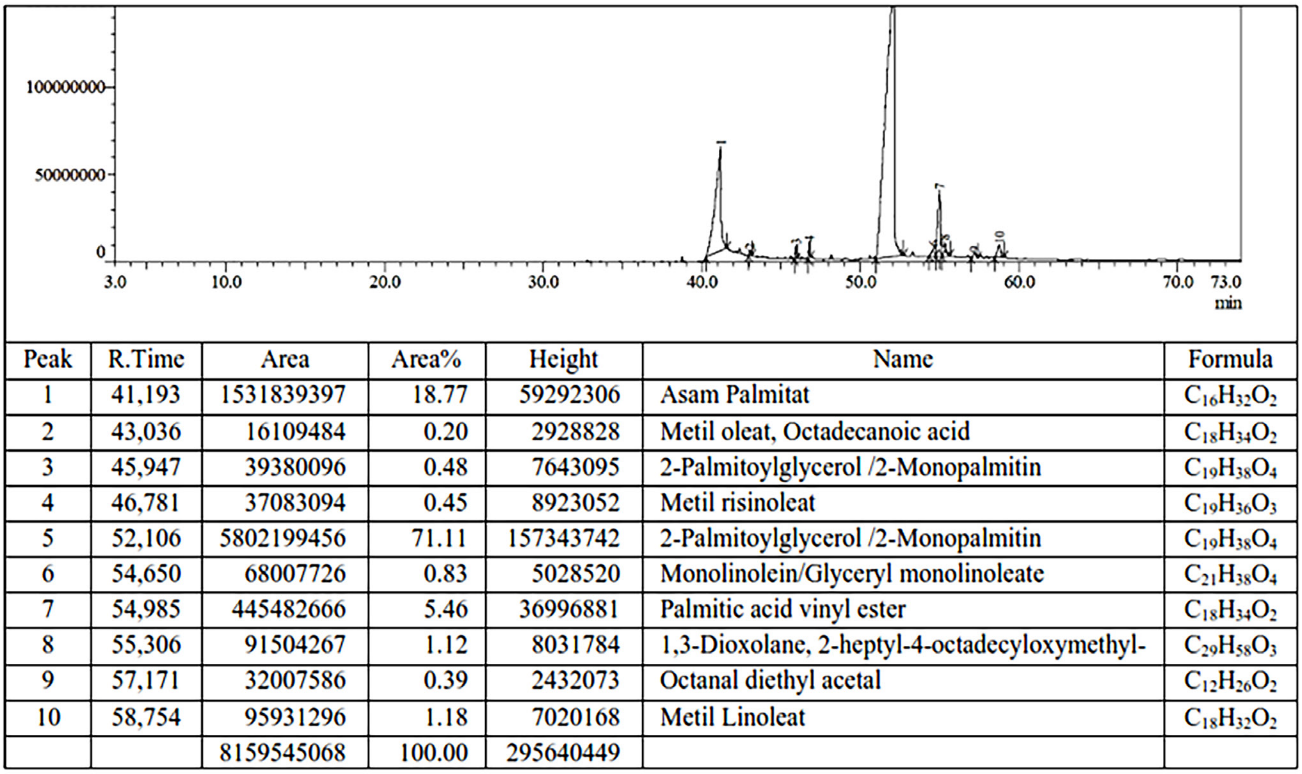
3.3 Product composition

GCMS analysis was performed to determine the quantities of MGs, DGs, and TGs in the emulsifier product. Fig. 5 shows the results of the GCMS test for the emulsifier product carried out at a molar ratio of glycerol to palmitic acid of 1:6, at 180 °C for 180 min using 5 wt.% of betaine hydrochloride–propionic acid DES catalyst. Peak 1 with a concentration 18.77% was identified as palmitic acid. The conversion of palmitic acid under these reaction conditions was 90.3%, i.e., there was still unreacted palmitic acid. MG as 2-monopalmitin (one palmitic acid group bound at the carbon position number 2 of glycerol) was identified as much as 72.8% at peak 5. In this emulsifier product DGs and TGs were not identified. For the application of this process in the industry, it is necessary to separate the unreacted palmitic acid and the by-products to obtain an emulsifier product with high purity.

Maquirriain et al. [9] reported that the reaction mixture became very dark using an acidic homogeneous catalyst (sulfuric acid, p-toluene sulfonic acid, methane sulfonic acid) due to secondary reactions and decomposition of the glycerol to acrolein. In this work, the glycerolysis

Table 2 Catalytic activity in the glycerolysis of fatty acids

No	Fatty acids	Catalyst	Optimum condition	Reaction conversion	Ref.
1	Oleic acid	Allyl triphenylphosphonium bromide – p-toluenesulfonic acid monohydrate DES	Fatty acid:glycerol molar ratio 1:6, catalyst loading 5 wt.%, reaction time 30 min, temperature 150 °C	95%	[10]
2	Free fatty acid	Allyl triphenylphosphonium bromide – p-toluenesulfonic acid monohydrate DES	Fatty acid:glycerol molar ratio 1:6, catalyst loading 5 wt.%, reaction time 10 min, reaction temperature 160 °C	90%	[11]
3	Free fatty acid	Methanesulfonic acid	Fatty acid:glycerol molar ratio 1:3, concentration of catalyst 0.35 equiv/L, temperature 100 °C,	95%	[9]
4	Stearic acid	Choline chloride–sorbitol DES	Fatty acid:glycerol molar ratio 1:6, catalyst loading 5 wt.%, reaction time 180 min, temperature 180 °C	97.6%	[19]
5	Palmitic acid	Betaine hydrochloride–propionic acid DES	Fatty acid:glycerol molar ratio 1:6, catalyst loading 5 wt.%, reaction time 180 min, temperature 180 °C	90.3%	This work



Peak	R.Time	Area	Area%	Height	Name	Formula
1	41,193	1531839397	18.77	59292306	Asam Palmitat	$C_{16}H_{32}O_2$
2	43,036	16109484	0.20	2928828	Metil oleat, Octadecanoic acid	$C_{18}H_{34}O_2$
3	45,947	39380096	0.48	7643095	2-Palmitoylglycerol /2-Monopalmitin	$C_{19}H_{38}O_4$
4	46,781	37083094	0.45	8923052	Metil risinoleat	$C_{19}H_{36}O_3$
5	52,106	5802199456	71.11	157343742	2-Palmitoylglycerol /2-Monopalmitin	$C_{19}H_{38}O_4$
6	54,650	68007726	0.83	5028520	Monolinolein/Glyceryl monolinoleate	$C_{21}H_{38}O_4$
7	54,985	445482666	5.46	36996881	Palmitic acid vinyl ester	$C_{18}H_{34}O_2$
8	55,306	91504267	1.12	8031784	1,3-Dioxolane, 2-heptyl-4-octadecyloxymethyl-	$C_{29}H_{58}O_3$
9	57,171	32007586	0.39	2432073	Octanal diethyl acetal	$C_{12}H_{26}O_2$
10	58,754	95931296	1.18	7020168	Metil Linoleat	$C_{18}H_{32}O_2$
		8159545068	100.00	295640449		

Fig. 5 GCMS spectrum of glycerolysis of palmitic acid product using betaine hydrochloride–propionic acid DES at reaction temperature of 180 °C, loading catalyst of 5 wt.%

reaction carried out at a molar ratio of glycerol to palmitic acid 1:6, at 180 °C for 180 min using 5 wt.% of betaine hydrochloride–propionic acid DES catalyst produced a yellow solid emulsion. The by-products identified in the glycerolysis product are palmitic vinyl ester (5.46%), fatty acid ester (1.83%), and 1,3 dioxolane (1.12%).

3.4 Catalyst reusability

DES has a greater density than oil. Additionally, the solubility of DES in glycerol is higher than its solubility in the oil phase. Therefore, the application of DES as a catalyst in the glycerolysis reaction will provide an advantage because DES will be in the bottom layer after the reaction takes place. That way, DES is very easy to recycle for reuse in the next reaction process. If the DES structure does not change during the reaction even at high temperatures it can be recycled.

To ensure that the catalyst used has economic value and is expected to be used commercially, a reusability test of acid DES catalysts was carried out. Fig. 6 shows the conversion of palmitic acid with reused catalyst. DES has high thermal and chemical stability [22], so the application of DES at high temperatures does not affect its molecular structure (Fig. 3). Therefore, the DES activity did not decrease significantly and the color of the product did not change even though it was used repeatedly in the glycerolysis of palmitic acid. DES catalyst can be directly recycled without the need for treatment and its activity not significantly reduced.

In the synthesis of quinoline derivatives using choline chloride – tin(II) chloride DES as a catalyst, it was revealed that the DES could be used at least four times without significant loss of product yield [31]. In addition, choline chloride–urea DES could be reused 5 times without significantly decreasing the reaction conversion, indicating that this DES had good catalyst reusability in the methanolysis of polycarbonate [29]. Amesho et al. [32] also revealed that choline chloride–malonic acid DES had excellent catalytic activity in the production of 5-hydroxymethylfurfural with only a slight decrease in activity after five recycling processes.

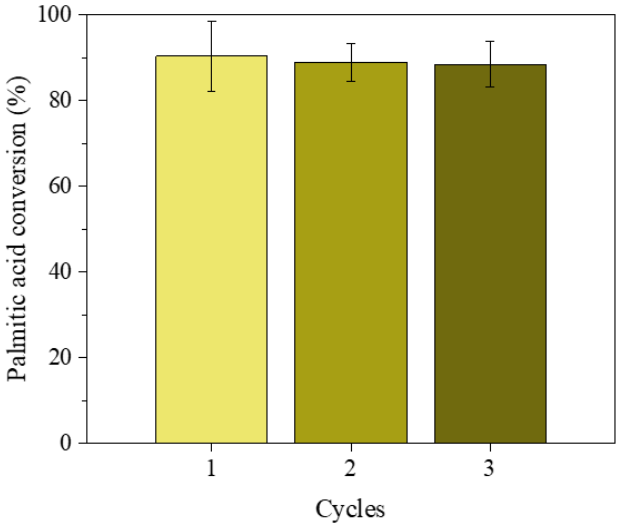


Fig. 6 Palmitic acid conversion at different DES catalyst recycling runs

4 Conclusions

Acidic DES has good catalytic activity in the glycerolysis of palmitic acid with reaction conversion reaching 90.3% at a molar ratio of glycerol to palmitic acid of 1:6, stirring speed 300 rpm, reaction temperature 180 °C, catalyst loading 5 wt.% and reaction time 180 min. The use of this catalyst is also selective to produce MGs emulsifier as much as 72.8%. In addition, the results of this study revealed that this acidic DES catalyst can be reused and its activity did not decrease significantly. However, the use of this catalyst contained 18.77% palmitic acid in the yellow product, resulting in palmitic acid vinyl ester as a side product. The emulsifier products need to be purified to separate residual palmitic acid and by-products.

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