

Solvent-free synthesis of oleic acid-based wax esters using recyclable acidic deep eutectic solvent

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SUMMARY: Wax esters have been widely used in cosmetics and pharmaceutical products. Oleic acid wax esters can be used to replace spermaceti oil or jojoba oil. In this work, the acidic deep eutectic solvent (DES) composed of choline chloride and *p*-toluenesulfonic acid (1:4, mol/mol) was used as an efficient recyclable catalyst for the synthesis of oleic acid-based liquid wax esters through an esterification reaction. The esterification conversion of cetyl alcohol reached 99.1% under the following optimal reaction conditions: 5% DES as catalyst, molar ratio of fatty acid to alcohol of 1.3:1 and reaction temperature of 70 °C for 3h. The catalyst recovery experiments showed that this low-price acidic DES catalyst could be reused five times with uniform activity. Moreover, DES-catalyzed solvent-free esterification could be applied in the preparation of other oleic acid-based wax esters and excellent conversions (> 96%) could be obtained under such mild conditions.

KEYWORDS: Liquid wax esters; Esterification; Deep eutectic solvents; Solvent-free; *p*-toluenesulfonic acid

RESUMEN: *Síntesis libre de solventes de ceras a base de ácido oleico utilizando ácido eutéctico profundo reciclable.* Las ceras se han utilizado ampliamente en productos cosméticos y farmacéuticos. Las ceras de ácido oleico se pueden utilizar para reemplazar al espermaceti o al aceite de jojoba. En este trabajo se utilizó el ácido eutéctico profundo (DES) compuesto por cloruro de colina y ácido *p*-toluensulfónico (1:4, mol/mol) como un catalizador reciclable eficiente para la síntesis de ceras líquida a base de ácido oleico mediante reacción de esterificación. La conversión de esterificación del alcohol cetílico podría alcanzar el 99,1% en las condiciones óptimas de reacción, mostrada como sigue: 5% de DES como catalizador, relación molar de ácido graso a alcohol de 1,3:1 y temperatura de reacción de 70 °C durante 3 h. Es importante destacar que los experimentos de recuperación del catalizador mostraron que este catalizador DES ácido de bajo precio podría reutilizarse cinco veces con una actividad uniforme. Además, la esterificación sin disolvente catalizada por DES podría aplicarse en la preparación de otras ceras a base de ácido oleico y podrían obtenerse excelentes conversiones (> 96%) en tales condiciones suaves.

PALABRAS CLAVE: Ácido *p*-toluensulfónico; Cera líquida; Disolventes eutécticos profundos; Esterificación; Libre de disolventes

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1. INTRODUCTION

Wax esters are the main components of natural waxes, which are composed of long-chain (>12 carbon atoms) fatty acids and alcohols (Doan *et al.*, 2017; Gunawan *et al.*, 2005). Wax esters are widely used in many fields. For example, they are the key ingredients in lipsticks and moisturizers in cosmetic formulations (Li, 1999; Keng *et al.*, 2009). In the pharmaceutical industry, wax esters are used as anti-foaming agents in penicillin production (Ungcharoenwiwat and H-Kittikun, 2013). In addition, wax esters are widely used in the food industry as lubricants, polishes and plasticizers (Salis *et al.*, 2003; Canizares *et al.*, 2020; Mandu *et al.*, 2020).

Wax esters are classified as saturated wax esters or unsaturated wax esters depending on their degree of unsaturation. The main raw materials of natural unsaturated wax esters are spermaceti oil and jojoba oil (Aissa *et al.*, 2012). However, the sperm whale is an endangered species, and the whaling ban has prompted researchers to look for the alternatives to natural spermaceti oil (Papadaki *et al.*, 2017). Jojoba oil has some similar properties to spermaceti oil, and can be used as a good substitute. However, the main limitations to the use of jojoba oil are its cost and availability (Keng *et al.*, 2009). Therefore, it is highly desirable to produce unsaturated wax esters using a chemically synthesize method.

The synthesis of wax esters has been studied for the past decades (Lima *et al.*, 2018). Wax esters can be synthesized via chemical (Aracil *et al.*, 1992) and enzymatic methods (Poisson *et al.*, 1999). Although the enzymatic reaction is mild, it also has many disadvantages, such as longer reaction time, use of organic solvents and high cost (Salis *et al.*, 2003; Deng *et al.*, 2011). Traditionally, conventional chemical catalysts such as mineral acids (e.g., H₂SO₄), organic acids (e.g., *p*-toluenesulfonic acid) and heterogeneous catalysts (e.g., ion exchange resins, zeolites) are used as esterification catalysts (Al-Arafi and Salimon, 2012; Khalkar *et al.*, 2012; Kolah *et al.*, 2007). However, these traditional acid-catalysts have many problems, such as difficulty in catalyst recovery or separation and side reactions (Ieda *et al.*, 2018).

In recent years, acidic ionic liquids have been used for the synthesis of wax ester (Kohno *et al.*, 2019; Yıldırım *et al.*, 2018). For example, Brønsted acidic ionic liquid ([C₁₆ImSO₃H]Cl) has been used to

synthesize wax esters from stearic acid with myristyl alcohol (Yıldırım *et al.*, 2018). However, ionic liquids (ILs) also have some limitations, such as high cost and complex preparation process (Han and Armstrong, 2007). As a new generation of ionic liquid or its substitute, deep eutectic solvent (DES) has attracted attention because of its unique physicochemical properties, such as biodegradability, non-toxic and non-volatile (Zhang *et al.*, 2012). DESs are usually composed of hydrogen bond donors (HBD) (such as alcohols, carboxylic acids, or metal halides) and salts (such as choline chloride), which exhibit high purity and environmentally friendly properties (Ünlü *et al.*, 2019). DESs have been widely used in many fields, such as extraction (Hadi *et al.*, 2015), separation (Shishov *et al.*, 2017), catalysis (Sert, 2015) and CO₂ absorption (Isaifan and Amhamed, 2018). For instance, DESs have been successfully used as catalyst for the esterification of carboxylic acid with simple alcohols (Santi *et al.*, 2012; Sunitha *et al.*, 2007; Yasmin *et al.*, 2018; Williamson *et al.*, 2017; Pan *et al.*, 2016; Cao *et al.*, 2016; Tang *et al.*, 2014).

With the aim of developing low-cost and sustainable catalysts for the preparation of liquid wax esters, an efficient synthesis of oleic acid-based wax esters using choline-based DESs as catalyst under mild conditions was investigated in this work. The DES composed of choline chloride and *p*-toluenesulfonic acid could promote the synthesis of wax esters through esterification of oleic acid with various long-chain fatty alcohols (e.g., cetyl alcohol) in solvent-free conditions. Recovery of the acidic DES catalyst was examined as well.

2. MATERIALS AND METHODS

2.1. Materials

Oleic acid (80%) and cetyl alcohol (99%) were purchased from Aladdin Chemical Reagent Co., Ltd (Shanghai, China). Choline chloride (99%), zinc chloride (ZnCl₂, 99%), zinc bromide (ZnBr₂, 98%), and *p*-toluenesulfonic acid (PTSA, 98%) were purchased from Macklin Biochemical Co. Ltd (Shanghai, China). Oleic acid (99%) was purchased from Sigma-Aldrich Co. Ltd (Shanghai, China). Methanol, anhydrous sodium sulfate (Na₂SO₄) and methanesulfonic acid (MSA, 98%) with analytical purity were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd (Tianjin, China). Lauryl alcohol

(99%), myristyl alcohol (98%) and stearyl alcohol (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The *n*-hexane used was of HPLC grade, while other chemicals were of analytical reagent grade.

2.2. Preparation of the deep eutectic solvents (DESs)

The DESs based on choline chloride and hydrogen bond donors (HBD) with different molar ratios were prepared by continuously stirring in an oil bath at 80 °C until a uniform and transparent liquid was formed. The compositions of the acidic DESs used in this work are shown in Table 1.

2.3. Synthesis of wax esters

1.5 mmol of oleic acid (0.42g), 1.0 mmol of cetyl alcohol (0.24g) and catalyst 10% (w/w) of cetyl alcohol (0.024g) were added into the reaction tube. Then the mixture was heated with stirring in the aluminum heating block at 60 °C for 2 h. After the reaction, the mixture was cooled to room temperature and the product was extracted with *n*-hexane. The *n*-hexane layer (wax ester layer) was washed with warm distilled water more than three times to remove the catalyst until the aqueous solution was neutral. Before the product was analyzed, *n*-hexane was removed with a rotary evaporator under reduced pressure. Finally, the product was dried and analyzed by gas chromatography (GC).

2.4. Analytical methods

2.4.1. Determination of wax esters

The contents of wax esters, fatty acids and alcohols in the reaction mixture were quantified using a GC-7890B gas chromatography (Agilent) equipped

with a DB-1ht capillary column (28 m×250 μm×0.1 μm) and a flame ionizing detector (FID). The column temperature was programmed at 100 °C, held for 0 min, increased to 180 °C at a rate of 10 °C·min⁻¹, maintained for 2 min; then increased to 230 °C at 10 °C·min⁻¹; finally elevated to 330 °C at 20 °C·min⁻¹, and held for 2 min. The injector and detector temperatures were set at 350 and 360 °C, respectively.

The content of the product was quantified with hexadecane as the internal standard. The residual of cetyl alcohol was calculated by the equation:

$$M_i = f \times m_{si} \times \frac{A_i}{A_{si}}$$

where M_i is the mass of residue cetyl alcohol, m_{si} is the mass of the internal standard hexadecane, A_i and A_{si} are the peak area of cetyl alcohol and hexadecane, respectively, f is the response factor:

$$f = \frac{\frac{A_{si}}{M_{si}}}{\frac{A_i}{M_i}}$$

The conversion of cetyl alcohol was calculated by equation shown below:

$$\text{Conversion of cetyl alcohol (\%)} = \left(1 - \frac{M_i}{M_o}\right) * 100\%$$

Where M_o is the total mass of cetyl alcohol.

2.4.2. Characterization of purified wax esters

¹H NMR and ¹³C NMR spectroscopy were used to characterize the wax esters. ¹H NMR spectra were recorded on Bruker NMR spectrometer (500 MHz). Chemical shifts were recorded in parts per million

TABLE 1. Composition of the DESs used in this work

| Abbreviation | HBA | HBD | Molar ratio |
|--------------|------------------|--------------------------------|-------------|
| DES-1 | Choline chloride | Zinc chloride | 1:2 |
| DES-2 | Choline chloride | Zinc bromide | 1:2 |
| DES-3 | Choline chloride | <i>p</i> -toluenesulfonic acid | 1:1 |
| DES-4 | Choline chloride | Methanesulfonic acid | 1:2 |
| DES-5 | Choline chloride | <i>p</i> -toluenesulfonic acid | 1:2 |
| DES-6 | Choline chloride | <i>p</i> -toluenesulfonic acid | 1:3 |
| DES-7 | Choline chloride | <i>p</i> -toluenesulfonic acid | 1:4 |

DES-deep eutectic solvent; HBA-hydrogen bond acceptor; HBD-hydrogen bond donors.

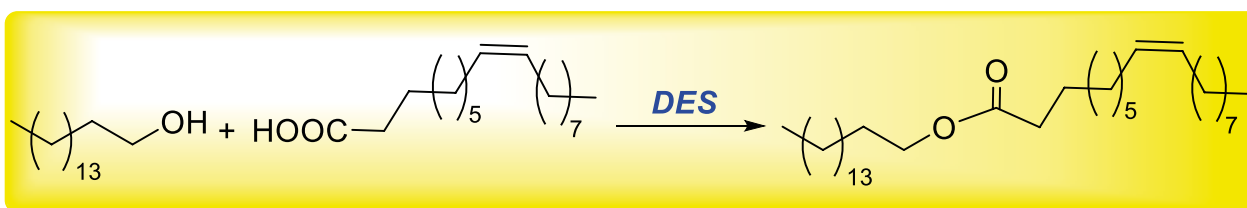


FIGURE 1. Esterification of oleic acid and cetyl alcohol. DES-deep eutectic solvent

(ppm) referenced to 0.0 ppm for tetramethylsilane (TMS). The ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer (125 MHz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of Chloroform-d.

2.5. Recovery of DES catalyst

For investigating the reusability of acidic DES catalyst, the reaction mixture was extracted with *n*-hexane into a separation funnel after the reaction was terminated. As obvious stratification occurred, the lower layer (DES phase) was used for the next batch of esterification experiments after drying in vacuo at 60 °C for 3h.

2.6. Statistical analysis

All the experiments were replicated three times, and the results are expressed as mean \pm standard deviation (SD). The ANOVA analysis was performed at 95% confidence level ($p < 0.05$), along with Duncan for comparisons between groups using Statistical Product and Service Solutions (SPSS).

3. RESULTS AND DISCUSSION

3.1. The composition of oleic acid

The commercial oleic acid (technical grade, ~80%) used in this experiment was analyzed by the GC method after methylation (Table 2). The fatty acid composition showed that the purity of oleic acid purchased (technical grade) was 79.16%, which met the demand of the large-scale preparation of wax esters. In fact, such purity of oleic acid (technical grade) was suitable for the preparation of liquid wax esters owing to its low price.

3.2. Screening of DES catalysts

The esterification of oleic acid and cetyl alcohol to synthesize wax esters was selected as the model reaction to optimize the reaction conditions (Figure 1).

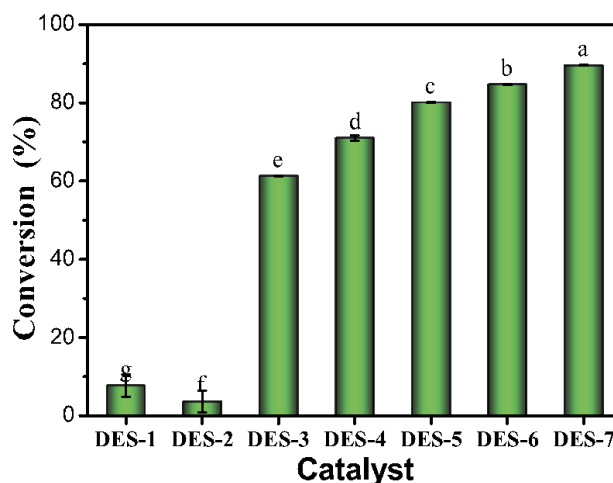


FIGURE 2. Effects of DES on the esterification of oleic acid and cetyl alcohol. Reaction conditions: temperature 60 °C, molar ratio of oleic acid to cetyl alcohol 1.5:1, catalyst 10% (w/w) cetyl alcohol, reaction time 2h. Values are means \pm SD of conversions of cetyl alcohol individually in three times. Duncan for comparisons between groups using Statistical Product and Service Solutions (SPSS). Different lower-case letters were significantly different ($p < 0.05$)

Firstly, the effects of different DESs on the conversion of cetyl alcohol were studied. DESs were synthesized by combining ChCl with different HBDs (Table 1). As shown in Figure 2, seven acidic DESs (DES-1~DES-7) were used to catalyze the esterification of oleic acid and cetyl alcohol to synthesize wax ester (cetyl oleate). The catalytic efficiency of Lewis acidic DESs (DES-1: ChCl/ZnCl₂, DES-2: ChCl/ZnBr₂) was lower than that of Brønsted acidic DESs (DES-4: ChCl/MSA; DES-3, DES-5~7: ChCl/PTSA). For Brønsted acidic DES, the catalytic efficiency of PTSA-based DESs (DES-3, DES-5~7) were better than that of MSA-based DESs. Indeed, the original *p*-toluenesulfonic acid was more acidic than methanesulfonic acid. With the increase in the molar ratio of ChCl to PTSA (1:1 to 1:4), the catalytic efficiency of PTSA-based DESs was enhanced. The results showed that PTSA-based DES(DES-7) had the highest con-

version (89.6%) (Figure 2). Therefore, DES-7 (ChCl/PTSA=1:4, mol/mol) was chosen as the best catalyst for the synthesis of wax ester.

3.3. Effect of reaction temperature

It is well known that reaction temperature plays a crucial role in exothermic reactions such as esterification. Therefore, the effect of reaction temperature was studied (Figure 3a). The results showed that the occurrence of esterification reaction was found to be slow when the temperature was lower than 50 °C, which might be because the melting point of cetyl alcohol (50 °C) prevented the reaction process. When the reaction temperature was increased from 50 °C to 70 °C, the conversion of cetyl alcohol was increased significantly (97.8%). Continuing increase of the reaction temperature to

80 °C caused the conversion of cetyl alcohol to remain unchanged. Therefore, 70 °C was chosen as the suitable reaction temperature for the esterification reaction of oleic acid and cetyl alcohol. Comparison with the previous esterifications using Lewis acidic ionic liquid ChCl/ZnCl₂ or [C₁₆ImSO₃H]Cl as catalysts conducted at 110 °C (Sunitha *et al.*, 2007; Yıldırım *et al.*, 2018) resulted in a more mild (70 °C) reaction temperature.

3.4. Effect of the amount of DES catalyst

The amount of catalyst was evaluated in order to achieve the highest conversion of cetyl alcohol (Figure 3b). As the amount of DES-7 was increased (1-5%, w/w), the conversion of cetyl alcohol was increased (6.9-96.7%). However, further increase in the amount of DES-7 (10-20%, w/w) had no significant improve-

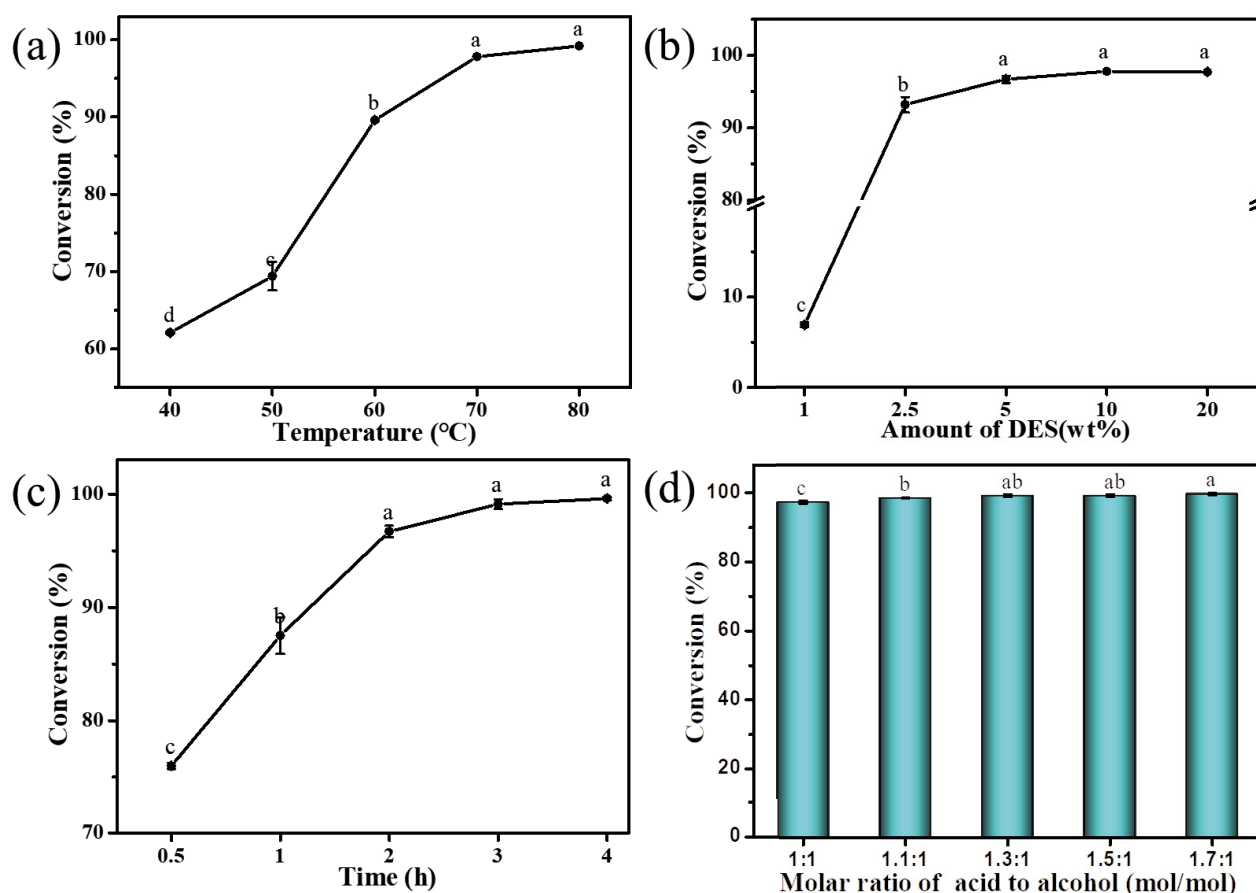


FIGURE 3. Effects of (a) reaction temperature, (b) amount of DES, (c) reaction time, (d) molar ratio of acid-to-alcohol on the conversion of cetyl alcohol. Reaction conditions: (a) 1.5:1, DES-7 concentration 10% (w/w), 2h; (b) 70 °C, 1.5:1, 2h; (c) 70 °C, DES-7 concentration 5% (w/w), 1.5:1; (d) 70 °C, DES-7 concentration 5% (w/w), 3h. Values are means \pm SD of conversions of cetyl alcohol individually in three replicates. Duncan's test was used for comparisons between groups using Statistical Product and Service Solutions (SPSS). Different lower-case letters were significantly different ($p < 0.05$)

ment on the conversion of cetyl alcohol (97.7-97.8%). Therefore, 5% DES-7 was selected as the optimal amount of catalyst for such esterification reactions.

3.5. Effect of reaction time

Reaction time is also one of the important factors for the reaction conditions. The reaction time varied from 0.5 to 4h to evaluate the suitable reaction conditions (Figure 3c). The conversion of cetyl alcohol was increased rapidly (76.0-99.1%) when the reaction time was increased from 0.5 to 3h. But further prolonging the reaction time (4h) led to no further increment in the conversion of cetyl alcohol. It was observed that the conversion of cetyl alcohol reached its maximum (99.1%) after a reaction time of 3h. Therefore, 3h was chosen as the optimal reaction time for the esterification reaction.

3.6. Effect of molar ratio of oleic acid to cetyl alcohol

As the molar ratio of substrates is also one of the important factors affecting the conversion of cetyl alcohol, the molar ratio of substrates (oleic acid/cetyl alcohol) was studied (Figure 3d). When the molar ratio of oleic acid to cetyl alcohol was 1:1, a higher conversion of 97.2% was detected. When the molar ratio of oleic acid to cetyl alcohol was increased from 1:1 to 1.3:1, the conversions of cetyl alcohol were increased from 97.2 to 99.1%. Then the conversion of cetyl alcohol exhibited no change as the molar ratio of oleic acid to cetyl alcohol increased to 1.5:1. Because the esterification of oleic acid with cetyl alcohol was an equilibrium-limited chemical reaction, the use of an excess of oleic acid would be better to promote the conversion of cetyl alcohol. Notably, an excess amount of oleic acid could not only cause a waste of starting materials, but it also affects the separation and purification process of final wax ester products. Therefore, 1.3:1 was selected as the optimal molar ratio of oleic acid to cetyl alcohol.

3.7. Catalyst recovery

The reusability of the acidic DES catalyst used in this work was evaluated and the results are listed in Figure 4. DES containing ChCl and PTSA could be reused for the esterification of oleic acid with cetyl alcohol. It was found that the conversion of cetyl alcohol decreased slightly (93.9%) after re-using the DES catalyst five times. These results are in agreement with the observations described by Taysun *et al.* (Taysun

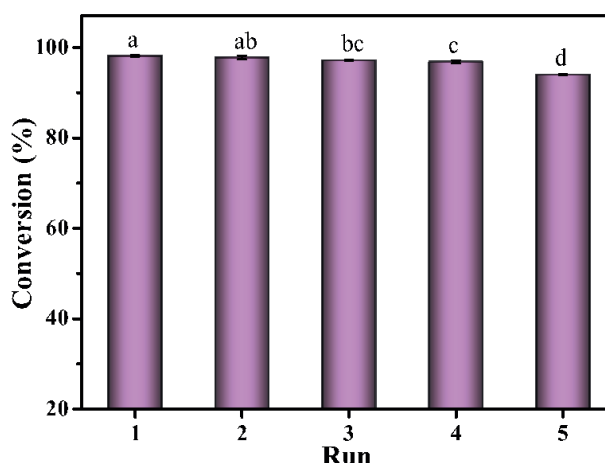


FIGURE 4. Reusability of DES-7 for the esterification of oleic acid and cetyl alcohol. Reaction conditions: temperature was 70 °C, catalyst 5% (w/w) of cetyl alcohol, molar ratio of oleic acid to cetyl alcohol was 1.3:1, reaction time was 3h. Values are means \pm SD of conversions of cetyl alcohol individually in three replicates. Duncan's test was used for comparisons between groups using Statistical Product and Service Solutions (SPSS). Different lower-case letters were significantly different ($p < 0.05$)

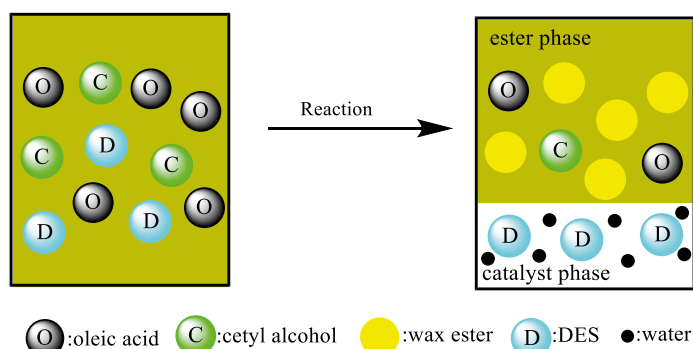


FIGURE 5. Phase separation of DES-7 after the esterification reaction

TABLE 2. Composition analysis of oleic acid (industrial purity) *

| Fatty acids | Structure | Content (wt%) |
|---------------|-----------|-------------------------------|
| Lauric acid | C12:0 | 1.92 \pm 0.09 ^d |
| Myristic acid | C14:0 | 0.41 \pm 0.01 ^e |
| Palmitic acid | C16:0 | 4.44 \pm 0.07 ^e |
| Stearic acid | C18:0 | 1.89 \pm 0.05 ^d |
| Oleic acid | C18:1 | 79.09 \pm 0.09 ^a |
| Linoleic acid | C18:2 | 12.24 \pm 0.06 ^b |

Different lower-case letters were significantly different ($p < 0.05$)
 *Values are means \pm SD of composition analysis of oleic acid individually in three replicates. Duncan's test was used for comparisons between groups using Statistical Product and Service Solutions (SPSS).

et al., 2017), who proved the good reusability of DES catalysts (4-8 cycles without any treatment) (Sunitha *et al.*, 2007). Indeed, the above results demonstrated that the acidic DES catalyst had good catalytic activity and stability in the reaction using for several batches of esterification reactions. Importantly, the DES phase could be separated easily from the wax ester phase through static layering after the esterification reaction (Figure 5). Therefore, the acidic DES catalyst was also an efficient recyclable catalyst for esterification reactions.

3.8. Comparison of acidic catalysts

The catalytic activity of three acidic catalysts with the same amount of PTSA was compared (Table 3). The results showed that there was no significant difference in the catalytic activity of the three catalysts (DES-7, ChCl&PTSA and PTSA). It could be observed that when PTSA was solely added as esterification catalyst, the final product's mixture presented a homogeneous system with a brown color (Figure 6c). However, with the addition of ChCl with PTSA as co-catalyst (ChCl&PTSA) (Figure 6b), the products mixture presented a two-phase system with a light brown color. This phenomenon indicated that the added ChCl might form a deep eutectic solvent with PTSA *in situ*, thus producing the phase separation effect. Comparing Figures 6a and 6b, there was little difference in the conversion of cetyl alcohol (96.4 and 97.3%). Both could cause the separation effect, but the color of the product mixture in Figure 6a was light yellow, suggesting that less PTSA dissolved in the wax ester phase by using DES-7 as catalyst (Figure 6a). Therefore, the acidic DES composed of ChCl and PTSA (1:4, mol/mol) was selected as the best recyclable catalyst for the synthesis of wax ester and exhibited excellent phase separation ability.

TABLE 3. Different catalysts used in the esterification*

| Catalyst | Conversions of cetyl alcohol (%) |
|----------------------------|----------------------------------|
| DES-7 (ChCl: PTSA=1:4) (a) | 96.4±0.14 ^b |
| ChCl&PTSA (b) | 97.3±0.28 ^a |
| PTSA (c) | 97.8±0.28 ^a |

Different lower-case letters were significantly different ($p < 0.05$)
 *Values are means \pm SD of conversions of cetyl alcohol individually in three replicates. Duncan's test was used for comparisons between groups using Statistical Product and Service Solutions (SPSS). Where DES-deep eutectic solvent; ChCl-Choline chloride; PTSA-*p*-toluenesulfonic acid.

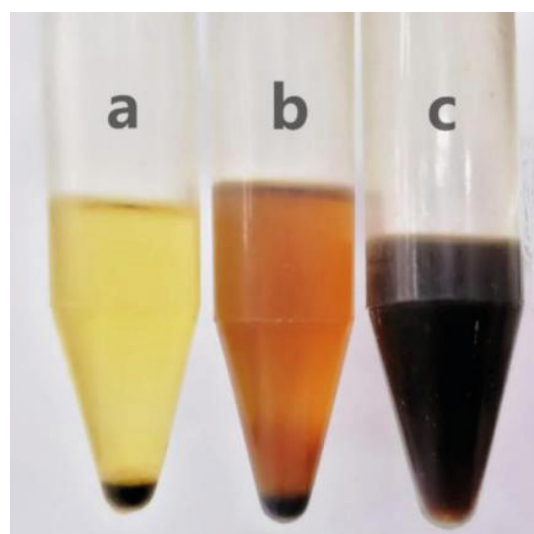


FIGURE 6. Phase separation of three acidic catalysts after esterification. (a): DES-7, (b): ChCl&PTSA, (c): PTSA. Reaction conditions: temperature 70 °C, catalyst 5% (w/w) alcohol, molar ratio of oleic acid to alcohol was 1.3:1, reaction time was 3h. Values are means \pm SD of conversions of cetyl alcohol individually in three replicates. Duncan's test was used for comparisons between groups using Statistical Product and Service Solutions (SPSS). Different lower-case letters were significantly different ($p < 0.05$)

3.9. Analysis and separation of cetyl oleate

The gas chromatogram (GC) of the liquid wax ester (cetyl oleate) synthesized under the optimal conditions is shown in Figure 7. The unreacted fatty acid (oleic acid with purity of 99% was used here) and ce-

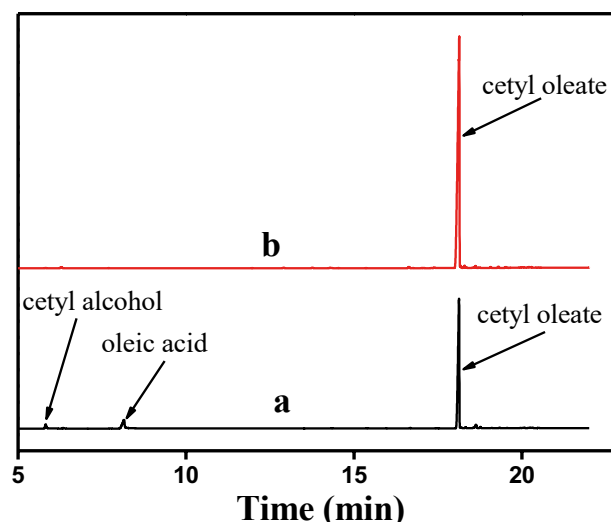


FIGURE 7. Gas chromatogram of cetyl oleate after esterification. (a) before purification, (b) purified with column chromatography. Purification condition: silica gel (200–300 mesh). Elution was carried using hexane/diethylether mixtures (80:20, v/v)

tyl alcohol, and the product wax ester were identified at 5.82 min, 8.14 min and 18.14 min, respectively (Figure 7a), indicating that no side reaction occurred in the esterification reaction between oleic acid and cetyl alcohol catalyzed by the DES catalyst. After purified by silica gel column chromatography (Figure 7b), the cetyl oleate was obtained as a light-yellow liquid with a purity of 99%, which was identified by ^1H NMR and ^{13}C NMR. ^1H NMR (500MHz, CDCl_3): δ =0.86 (br t, 6H), 1.26 (br d, 46H), 1.62 (br t, 4H), 2.00 (br t, 4H), 2.28 (br t, 2H), 4.05 (tr, J =10Hz, 2H), 5.33-5.35 (br m, 2H). ^{13}C NMR (125MHz, CDCl_3): δ =14.25, 22.84, 25.17, 26.09, 27.32, 27.37, 28.82, 29.26, 29.29, 29.32, 29.41, 29.47, 29.51, 29.68, 29.73, 29.81, 29.84, 29.92, 32.08, 34.55, 64.54, 129.89, 130.13, 174.10.

3.10. Preparation of different oleic acid-based wax esters

Under the optimized reaction conditions, the substrate scope was examined as well (Figure 8). The esterification reactions between oleic acid (99% purity) and various long-chain fatty alcohols were conducted. To our delight, the solvent-free esterification reactions catalyzed by DES-7 could afford excellent conversions for various long-chain fatty alcohols, including lauryl alcohol, myristyl alcohol and stearyl alcohol, and the conversions reached 96.4-99.1%.

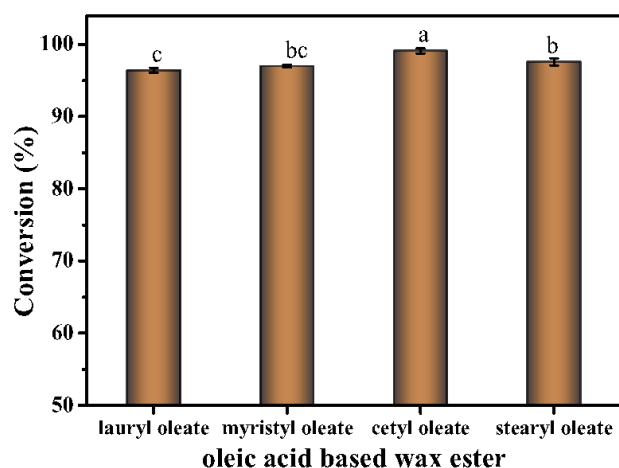


FIGURE 8. Esterification of oleic acid with long-chain alcohols. Reaction conditions: temperature 70 °C, catalyst 5% (w/w) alcohol, molar ratio of oleic acid to alcohol was 1.3:1, reaction time was 3h. Values are means \pm SD of conversions of cetyl alcohol individually in three replicates. Duncan's test was used for comparisons between groups using Statistical Product and Service Solutions (SPSS). Different lower-case letters were significantly different ($p < 0.05$)

After purified by silica gel column chromatography, the liquid wax esters, including lauryl oleate, myristyl oleate and stearyl oleate were obtained with a purity of 99%. It was concluded that this acidic DES-catalyzed esterification reaction was an efficient and sustainable method for the preparation of liquid wax esters.

4. CONCLUSIONS

In this work, the acidic DES composed of ChCl and PTSA (1:4, mol/mol) could be used as an efficient and recyclable catalyst for the synthesis of oleic acid-based liquid wax esters through esterification reaction. The esterification conversion of cetyl alcohol reached 99.1% under optimal reaction conditions as follows: 5% DES as catalyst, molar ratio of fatty acid to alcohol of 1.3:1, reaction temperature of 70 °C for 3h. The catalyst recovery experiments showed that this low-cost DES catalyst could be reused 5 times with uniform activity. Moreover, this solvent-free esterification could be used to the preparation of other oleic acid-based wax esters (lauryl oleate, myristyl oleate and stearyl oleate) and excellent conversions ($> 96\%$) were obtained under such mild conditions.

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