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Short communication

Tunable aryl imidazolium ionic liquids (TAILs) as environmentally benign catalysts for the esterification of fatty acids to biodiesel fuel

Mayur Thul[a,1], Amit Pantawane[a,1], Wesley Lin[b], Yi-Jyun Lin[a], Po-Fang Su[c], Shao-An Tseng[d], Hsin-Ru Wu[e], Wen-Yueh Ho[f,*,2], Shun-Yuan Luo[a,*]

[a] Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
[b] Department of Chemistry, Morrison Academy, Taichung 406, Taiwan
[c] Department of Chemistry, National Hsin Chu Senior Industrial Vocational School, Hsinchu, Taiwan
[d] Department of Chemistry, Hsinchu Chien Kung Senior High School, Hsinchu, Taiwan
[e] Instrumentation center, MOST, National Tsing Hua University, Hsinchu 30013, Taiwan
[f] Department of Cosmetic Science and Institute of Cosmetic Science, Chia Nan University of Pharmacy and Science, Tainan 717, Taiwan

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ABSTRACT

Herein, we describe the synthesis of tunable aryl imidazolium ionic liquid catalysts and tested for esterification of fatty acids to biodiesel. In this work, six tunable aryl imidazolium ionic liquids (TAILs) **1a-1f** were prepared. These ionic liquids were used as the economical and reusable catalysts for the synthesis of biodiesel fuels. The reaction has been preceded in a monophase at 80 °C for 4 h, after which the product was separated from the catalyst system by a simple liquid/liquid phase separation at room temperature with excellent yields. With the simple post-process, the catalyst is reusable at least 6 times. This novel method offers a short reaction time, good yields, and environmentally benign characteristics.

1. Introduction

Due to a developing global need for energy and its emerging impact on the climate, it has become progressively crucial to find a sustainable fuel substitute. Long-chain fatty acid esters, which are commonly known as biodiesel fuel, is prepared from vegetable oils and fatty acids by esterification [1,2] and also, from animal fats through the trans-esterification of triglycerides in the presence of acid or base catalysts. [3–6] In comparison to fossil fuels, biodiesel is more technically producible, economically competitive, environmentally tolerable, and easily accessible. [7] Despite long-chain esters used as biofuel, short-chain esters have been used significantly in the food, and pharmaceutical industries due to their distinctive fruity odor and flavors. [8] However, flavored esters obtained by the eradication of plants and animals are not feasible due to their existence in small abundance. Thus, it could be prepared an adequate amount of naturally flavored esters by using chemical methods. For the low-cost manufacturing of biodiesel in the chemical, the method was used cheaper feedstocks, such as non-edible oils and waste frying oils. [9–11] The low-cost feedstock also consists of a significant amount of free fatty acids, which would be converted to long-chain ester with alcohol by using base or acid catalyst. For that esterification strength of the base catalyst was reduced extremely, in comparison to the acid catalyst, hence it is stated that the importance of acid catalysts. [12] In general, the solid acid catalysts such as Cs-doped heteropolyacid, [13] $SO_4^{-2}/TiO_2–SiO_2$, [14] carbohydrate-derived solid acid [15] and liquid inorganic acid catalysts such as H_2SO_4, [16] and HNO_3 [17] are used extensively for the preparation of esters. However, homogeneous acids cause decomposition in the reaction vessel and need to be counterbalanced with a huge amount of base after the reaction, which leads environmentally unsafe. [18] Solid acid catalysts also have their disadvantages due to their effortless deactivation and consumption of products which make their applications limited. [19]

In recent years, ionic liquids are earning broad consideration as mediums for the array of reactions. [20–24] Their properties such as having low vapor pressure, allow for exceptional solubility, and the ability to vary structures to employ parameters like density, solubility, etc. These properties have gained much interest among researchers in

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* Corresponding authors.
E-mail address: syluo@dragon.nchu.edu.tw (S.-Y. Luo).
[1] M. Thul and A. Pantawane contributed equally.
[2] Designed the project.

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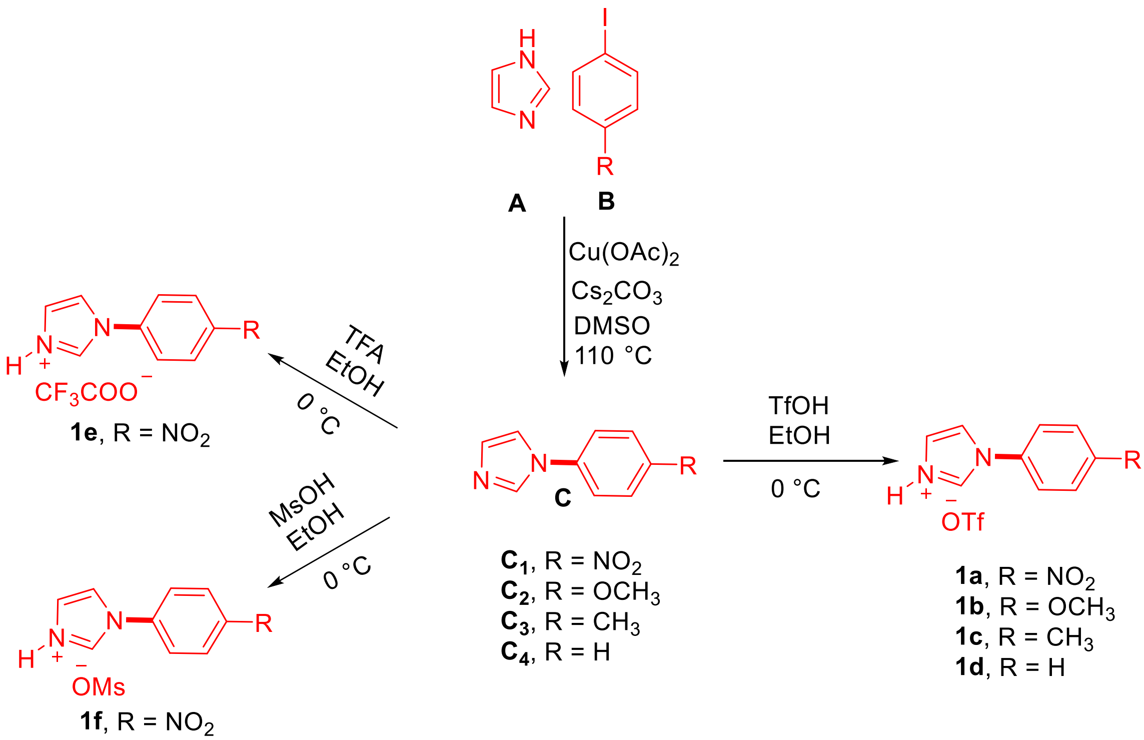


Scheme 1. Tunable Aryl imidazolium ionic liquid (**TAILs**:**1a-1f**).

chemistry. [25–29] In this paper, the Brønsted acidic ionic liquids have been created to serve as the catalyst as well as the solvent for the esterification reactions. Immense conversions have been accessed as the water formed in the reaction adequately solvated by the ionic liquids. Typically, the ionic liquid and water form one phase, and the ester remains in a different phase. Because of this, the product can be easily differentiated from the catalyst. Consequently, ionic liquids serve as an eco-friendlier substitute for conventional solvents. In the last decade, along with the rapid advancement of room temperature ionic liquids, their applications in esterification have been extensively studied. There are some instances, where the catalyst and substrate were dissolved into nearly neutral ionic liquids such as [bmim][BF$_4$] and [bmim][PF$_6$] to promote esterification. [30] Moreover, the preparation of these ionic liquids contains such synthetic steps. Herein, we have been demonstrated the development of tunable aryl imidazolium ionic liquid (TAIILs) catalysts from simple imidazoles also show high activity for the esterification reaction of fatty acids and study the structure-activity relationship.

2. Experimental section

2.1. Chemicals and instruments

All chemicals (analytical reagent grade) were commercially

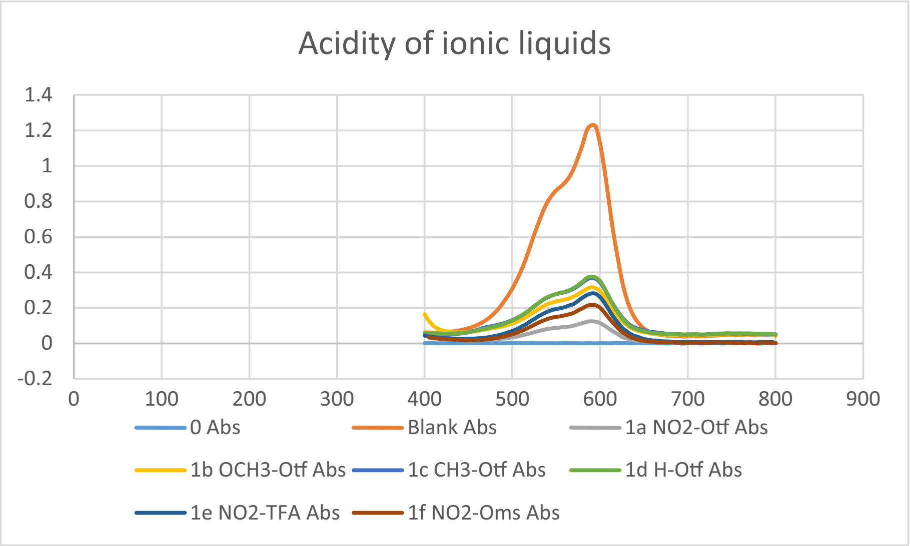


Fig. 1. Absorption spectra of TAILs in crystal violet dye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
H_0 values of the tunable aryl imidazolium ionic liquids (TAILs) 1a-1f. $H_0 = pK(I)_{aq} + \log([I]/[IH^+])$.

Compound	λ_{max}	[I] (%)	$[IH^+]$ (%)	H_0
Blank	1.2280	100	0	–
1a	0.1235	10.06	89.94	−0.15
1b	0.3159	29.25	70.05	0.43
1c	0.3681	29.95	70.05	0.43
1d	0.3765	30.63	69.37	0.45
1e	0.2812	22.90	77.10	0.27
1f	0.2176	17.72	82.28	0.13

λmax: Maximum absorption, [I]: Concentration of indicator, [IH+]: Concentration of protonated indicator, H0: Brønsted acidity, Indicator: Crystal violet.

available and were used without further purification unless otherwise stated. Ether was purified and dried from a safe purification system containing Al_2O_3. Flash column chromatography was carried out on silica gel 60. TLC was performed on pre-coated glass plates of silica gel 60 F254 detections was executed by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$ (0.5 g), $(NH_4)_6Mo_7O_{24}$ (24.0 g), and H_2SO_4 (28.0 mL) in water (500.0 mL) and subsequent heating on the hot plate. ^1H NMR and ^{13}C NMR spectra were recorded with 400 MHz instruments. Chemical shifts are in ppm from Me_4Si generated from the $CDCl_3$ lock signal at δ 7.26. IR spectra were taken with an FT-IR spectrometer using NaCl plates. Mass spectra were analyzed on an instrument with an EI source.

2.2. General procedure for the synthesis of biodiesel

A magnetic stir bar placed in a sealed tube, Free Fatty Acids (FFAs), methanol, and ionic liquids were added. The esterification was then carried out for a length of time at a specific temperature with vigorous stirring. After the reaction was completed, the residue was cooled to room temperature and kept at the same temperature until phase separation. The reaction mixture was extracted with ether and water. The upper phase (volume) mainly containing the desired ester could be isolated simply by liquid/liquid phase separation, concentrated, and column chromatography; the bottom phase ionic liquid in water from the reaction could be reused after removal of water under reduced pressure. For several experiments separated organic phase was directly concentrated and the product was confirmed by NMR spectrometry/ mass spectrometry.

2.3. Preparation of TAIILs

The preparation of ionic liquids **1a–1f** (Scheme 1) [31] is described below. Ionic liquids **1a–1f** was synthesized in two steps. The first step is the Ullmann-type coupling reaction: a combination of **A** and **B** in the presence of 10 mol% copper(II) acetate and cesium carbonate gave aryl imidazole $\mathbf{C_1}$, $\mathbf{C_2}$,$\mathbf{C_3}$, and $\mathbf{C_4}$ in 74%, 80%, 76%, and 88% yields respectively (Scheme 1). In the second step, the aryl imidazole $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$, and, $\mathbf{C_4}$ were dissolved in ethanol and were treated with triflic acid, methane sulfonic acid, or trifluoroacetic acid in an ice bath to yield acidic ionic liquids **1a** − **1 f.** (Scheme 1).

3. Result and discussion

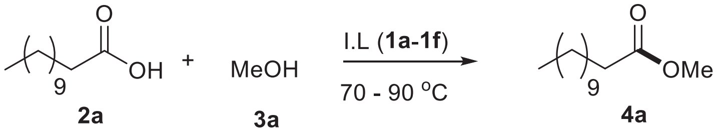
3.1. Hammets acidity of different catalysts

Preparation of the catalysts' like tunable aryl imidazolium ionic liquids (TAIILs) involves a two-step atom-economic reaction, and the new catalysts obtained are somewhat yellow and white solids. A characteristic of our prepared catalysts similar to that of other ionic liquids was observed. Neither of the new species fumes or manifests any noticeable degree of vapor pressure. In sharp contrast, acids dissolved in conventional ionic liquids for esterification frequently emit noxious vapors and harm the environment. Such instability indicates that the donor acid is completely incorporated into their respective TAIIL structures rather than to remain simply as mixtures of added strong acids with dissolved zwitterion, in which case some characteristics of the reactants would be expected. Generally, tunable aryl imidazolium ionic liquids are comprised of imidazolium-based cations containing relatively inert anions. The thermal stabilities of these aryl imidazolium ionic liquids are greater than most of those of the traditional ionic liquids. [32] Hence, they could be used as reaction media for high-temperature organic reactions as well.

In the present work, the functionalized aryl imidazolium ionic liquids are solid at room temperature and have potential applications in relatively low reaction temperature. The solubility experiment showed that these TAILs are miscible with water and relatively readily soluble in polar solvents such as methanol, ethanol, and acetone, and they are partially immiscible with nonpolar solvents such as alkanes and aromatic hydrocarbons. The solubility of these catalysts in organic solvents

Table 2
Esterification of lauric acid with methanol in the presence of different reaction conditions[a]

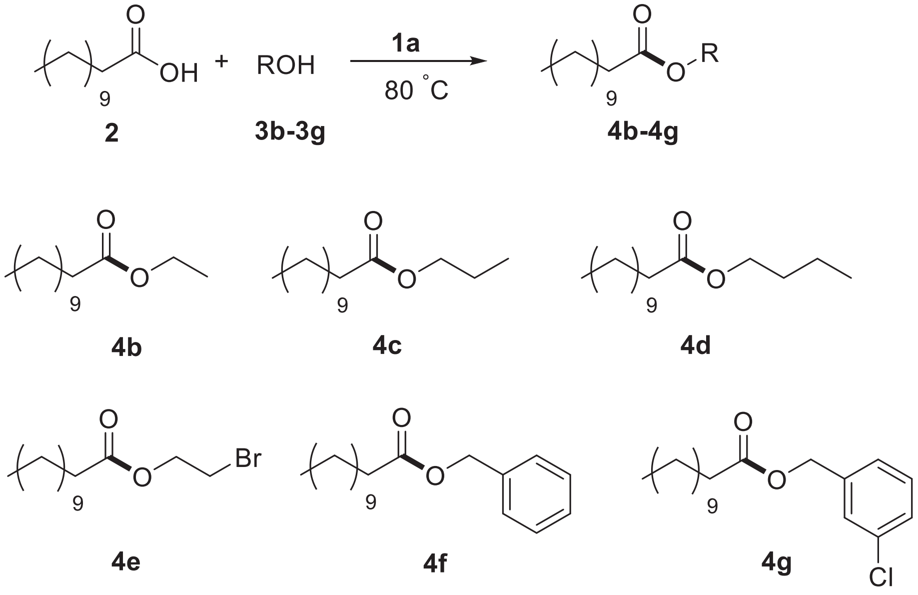
Entry	Methanol (equiv.)	Ionic liquid (equiv.)	Temperature	Time[a] (h)	Yield (%)[b]
1	7	**1a** (0.20)	80 °C	4	98%
2	7	**1a** (0.10)	80 °C	4	85%
3	7	**1a** (0.35)	80 °C	4	98%
4	7	**1a** (0.20)	70 °C	4	95%
5	7	**1a** (0.20)	90 °C	4	97%
6	7	**1a** (0.20)	80 °C	2	93%
7	7	**1a** (0.20)	80 °C	5	98%
8	10	**1a** (0.20)	80 °C	4	98%
9	5	**1a** (0.20)	80 °C	4	91%
10	7	**1b** (0.20)	80 °C	4	92%
11	7	**1c** (0.20)	80 °C	4	90%
12	7	**1d** (0.20)	80 °C	4	88%
13	7	**1e** (0.20)	80 °C	4	94%
14	7	**1f** (0.20)	80 °C	4	90%



[a] Reaction conditions: all reactions were carried out using **2a** (1 mmol).
[b] isolated yield, the products were identified with ^1H NMR.

Table 3
Esterification of lauric acid with different alcohols[a]

Entry[a]	Alcohol[b]	Time (h)	Yield(%)[c]
1	**3b** (Ethanol)	4	**4b** (96%)
2	**3c** (Propanol)	4	**4c** (93%)
3	**3d** (Butanol)	4	**4d** (97%)
4	**3e** (1-bromoethanol)	4	**4e** (70%)[d]
5	**3f** (Benzyl alcohol)	6	**4f** (80%)[d]
6	**3 g** (3-chlorobenzyl alcohol)	6	**4 g** (87%)[d]



[a] Reaction condition: Lauric acid (1 mmol), catalyst **1a** (0.2 mmol), temperature 80 °C.
[b] **3b-3e** (7.0 mmol) and **3f-3 g** (1.0 mmol).
[c] Isolated yield. The products were identified with ^{1}H NMR.
[d] Purified with column chromatography.

drop down as follows: **1a** > **1b** > **1c** > **1d** > **1e** > **1 f**. To some extent, they have similar structures and solubilities to those of the phase transfer catalyst. As a result, they have potential applications in acid-catalyzed organic reactions such as Friedel–Crafts acylation, thioesterification [32], Per-*O*-acetylation, and benzylidene ring-opening reaction [31]. In previous reports, Tong et al. investigated the Hammett acidity of Brønsted-Acidic ionic liquids. [33] The acidity of $H_2PO_4^-$ and $CF_3CO_2^-$ is lower than that of SO_3H- functionalized ionic liquids with HSO_4^- and p-CH_3 (C_6H_4) SO_3^-used by Y. Zhao et al. [34]

The Brønsted acidities of these TAILs were evaluated for the determination of the Hammett acidity functions by using UV–visible spectroscopy. The acidities of these TAILs have been examined using crystal violet dye as the indicator, and the results are shown in Fig. 1. From this, the Hammett function (H_0) could be calculated, and the results are listed in Table 1. When an acidic IL was added, the absorbance of the unprotonated form of the indicator decreased as shown in Fig. 1 the absorbance of the unprotonated form of the indicator on six acidic TAILs decreased as follows: **1a** > **1f** > **1c** > **1b** > **1e** > **1d** (Fig. 1).

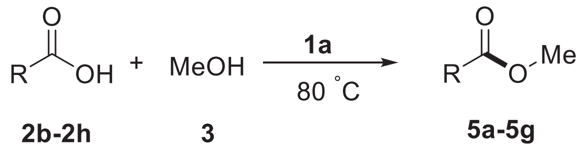
An array of ionic liquids was tested to compare the catalytic activity of different catalysts in the esterification reaction. Initial studies of **2a** and **3a** determined the optimal conditions; the results are shown in Table 2. The study of Brønsted acidic ionic liquid **1a-1f** of Table 2 suggested that **1a** was the best catalyst for the esterification reaction, providing the product **4a** in excellent yield 98% (Table 2, entry 1). The ionic liquids **1b-1f** (Table 2, entries 10–14) provided less yield as compared to **1a**, most likely because of their weaker acidity. As a result, ionic liquid **1a** was used to examine the effect of catalyst loading in esterification. The reactions were operated with catalyst loading range from 0.05 mmol to 0.5 mmol at 80 °C with 1:7 (lauric acid: methanol) molar ratio for 4 h (Table 2 entries 1–3). The yield of methyl laurate raised until 0.2 mmol of catalyst loading. Among the many entries tested, significant conversion of lauric acid was accomplished in 98% (Table 2, entry 1) when only 0.2 mmol of ionic liquid **1a** was used. A larger amount of catalyst loading resulted in no obvious increase in the yield. Seemingly it is enough to catalyze the esterification of lauric acid with methanol methodically at minimal loading for ionic liquid **1a**. It is feasible that improved reaction results are obtained when the reaction temperature is the boost or the reaction time is extended (Table 2, entries 4–7). On the effect of various molar ratios of lauric acid to methanol (Table 2, entries 8–9), the results demonstrate that the yield was prolonged while hiking the extent of methanol because the surplus of one of the reactants makes the equilibrium alter towards the product side.

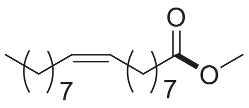
Once the optimized conditions were established, the results revealed that ionic liquid **1a** proceeded for esterification smoothly, from which satisfactory conversions were obtained in all cases under this procedure. It is also worth noting that the length of the n-alkyl chains of alcohol (Table 3, entries 1–3) has not been a significant effect on the conversion of fatty acids to corresponding esters in excellent yields, where we use 2-bromoethanol (entry 4) resulting in 70% yield. We extended this current method to different aromatic alcohols such as benzyl alcohol and 3-chloro benzyl alcohol. Similarly, the results were presented in good yields (Table 3, entries 5–6). The type of alcohol used affects the synthesis reaction for esterification very obviously. This is perhaps because of the different dissociation energy of alcohol in the oil phase. For alcohol, the more substituted alkyl group the alcohol gets, the weaker dissociation energy the alcohol has.

Having obtained good results in the synthesis of laurate esters using a catalytic amount of ionic liquid **1a**, we extended this method substrate

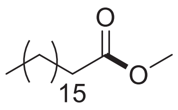
Table 4
Esterification of different acids with methanol[a]

Entry	Acid[a]	Time (h)	Yield(%)[b]
1	**2b** (Oleic acid)	4	**5a** (96%)
2	**2c** (Stearic acid)	4	**5b** (92%)
3	**2d** (Myristic acid)	4	**5c** (98%)
4	**2e** (Tridecanoic acid)	4	**5d** (90%)
5	**2f** (Benzoic acid)	12	**5e** (76%)
6	**2 g** (p-toulic acid)	12	**5f** (69%)[c]
7	**2 h** (2-Chloro-5-iodobenzoic acid)	12	**5 g** (89%)[c]

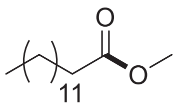




5a



5b



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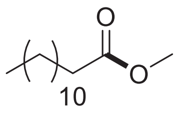
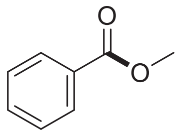
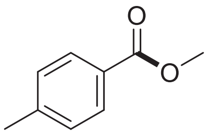


5d



5e



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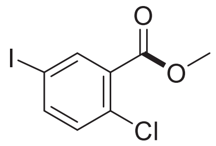

5g

[a] Reaction conditions: acid 1.0 mmol, methanol (7.0 mmol), ionic liquid **1a** (0.2 mmol).
[b] isolated yield, the products were identified with ^{1}H NMR.
[c] Purified with column chromatography.

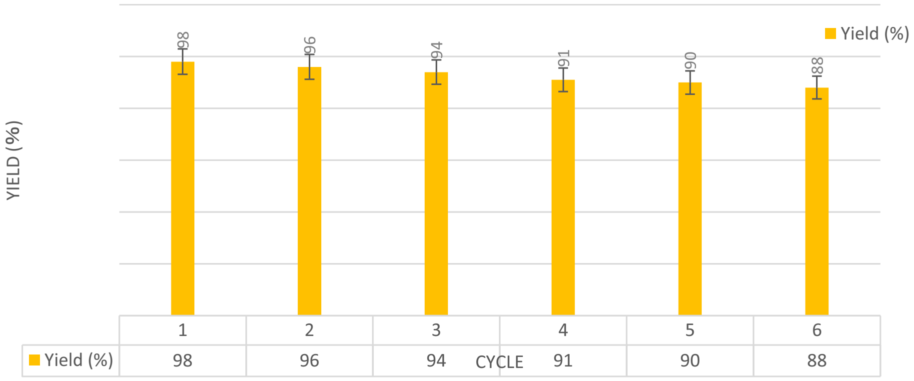

Fig. 2. Reusability of TAIIL for esterification.

scope to some long-chain aliphatic acids and aromatic acids. Currently, the esterification of fatty acids with alcohols is commercially achieved by a conventional method using liquid catalysts, such as sulfuric acid, hydrofluoric acid, and p-toluenesulfonic acid. However, scientific literature also contains a good number of reports about the use of heterogeneous acid catalysts for esterification. For instance, esterification has been carried out using ion-exchange resins such as Amberlyst-15 and Nafion with good results. [35] From the results demonstrated by the literature, it could be concluded that the ionic liquid **1a** is also a more suitable catalyst and also, proved in this method. It is shown that the different long-chain unsaturated fatty acids (Table 4, entries 1) afford 96% in excellent yield. Other, acids (Table 4, entry 2–4) had a significant yield of 90%–98% respectively. While benzoic acid and p-toluic acid turned out to be slightly less reactive, gaining a yield of 76% and 69% (Table 4, entries 5–6). Interestingly, di-halogen substituted benzoic acid such as 2-chloro-5-iodobenzoic acid gave the corresponding product **5 g** in high yield (89%, c4, entry 7).

*3.2. Reuse of ionic liquid **1a***

The recycling achievement of these TAILLs was investigated using the above model reaction. After the reaction was completed, the products were confined from the catalytic system by liquid-liquid phase separation. Further, the catalysts were reused in the next run after the removal of water under a vacuum. As shown in Fig. 2, TAIILs could be reused at least six times and the yield was decreased about.

10% in the last attempt. According to the above method (section 1), after the separation of the product and removal of water under reduced pressure, the slow degradation may be due to the slight loss of the catalyst after each cycle (Fig. 2). Therefore, **1a** was further investigated as a catalyst for the esterification of lauric acid with methanol for bulk scale.

4. Conclusion

In summary, TAIILs were found to be novel catalysts for the synthesis of biodiesel fuels from various free fatty acids and alcohol with gratifying yields of 69–98% under optimal reaction conditions. These catalysts have the advantages of high activity to fatty acids esterification and practical convenience in the product separation from the catalytic system. The TAIILs can be reused at least 6 times, which delivers the method as a potential application in the commercial production of biodiesel.

Credit Author Statement

S.-Y. Luo and W.-Y. Ho designed the research. H.-R. Wu analyzed the data. M. Thul, A. Pantawane, Y.-J. Lin, and W. Lin prepared the compounds. M. Thul, A. Pantawane, P.-F. Su and S.-A. Tseng prepared ionic liquid. M. Thul wrote the manuscript with the help of S.-Y. Luo.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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