ARTICLE IN PRESS

Materials Today: Proceedings xxx (xxxx) xxx

Contents lists available at ScienceDirect

Materials Today: Proceedings

journal homepage: www.elsevier.com/locate/matpr

One-pot liquefaction of cellulose to ethyl levulinate via 1-sulfonic acid-3-methyl imidazolium trichlorozincate as Brønsted-Lewis catalyst

Kirrthana Krishnasamy [a], Mohd Asmadi [a,*], Nor Aishah Saidina Amin [a], Muzakkir Mohammad Zainol [b], Zaki Yamani Zakaria [a], Sureena Binti Abdullah [c]

[a] *Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia*
[b] *School of Chemical Engineering, College of Engineering, Universiti Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia*
[c] *Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia*

A R T I C L E I N F O

Article history:
Available online xxxx

Keywords:
Cellulose
Ionic liquid
Brønsted-Lewis
Biofuel additive
Alkyl levulinate

A B S T R A C T

The direct conversions of cellulose to ethyl levulinate (EL) via Brønsted acidic ionic liquid (BAIL), Lewis acidic ionic liquid (LAIL), and Brønsted-Lewis acidic ionic liquid (BLAIL) conducted in this study is a sustainable approach. Initially, BAIL 1-sulfonic acid-3-methyl imidazolium chloride [SMIM][Cl] was prepared by the mixing of 1-methylimidazole, dry dichloromethane, and chlorosulfonic acid. Then, Lewis acidic site was provided to the BAIL by the addition of zinc chloride ($ZnCl_2$), to synthetize BLAIL 1-sulfonic acid-3-methyl imidazolium trichlorozincate, [SMIM][$ZnCl_3$]. Meanwhile, LAIL 1-butyl-3-methyl imidazolium trichlorozincate [BMIM][$ZnCl_3$] was prepared by the addition of $ZnCl_2$ to a neutral 1-butyl-3-methyl imidazolium chloride [BMIM][Cl]. These three catalysts were then characterized and employed in the one-pot liquefaction process that was conducted in a stainless-steel batch reactor at 180 °C for 10 hr, by charging 0.6 g of cellulose, 40 mL of ethanol and 3 g of catalyst. A parameter study, mainly temperature (120–200) °C, time (2–10) hr, and cellulose loading (0.2–1.0) g, were then conducted to determine the selected parameters to obtain high EL yield. Among the employed ionic liquids (ILs), BLAIL [SMIM][$ZnCl_3$] exhibited the highest catalytic activity, which was contributed mainly by its co-existence of Brønsted and Lewis acidic sites as detected in Fourier-Transform Infrared (FTIR) analysis, and its high acidic value. The maximum EL yield (20.27 wt%) was obtained under conditions of 180 °C, 6 hr, 0.6 of cellulose, and 3 g of [SMIM][$ZnCl_3$]. The outcome of this study provides an insight on the potential of novel [SMIM][$ZnCl_3$] in facilitating the direct cellulose ethanolysis to EL.
Copyright © 2023 Elsevier Ltd. All rights reserved.
Selection and peer-review under responsibility of the scientific committee of the 2nd Regional Congress on Membrane Technology 2022 in Conjunction with the 16th AUN/SEED-NET Regional Conference on Environmental Engineering 2022.

1. Introduction

In recent years, the increasing energy demands are causing a spike in the usage of fossil fuels, leading to rapid depletion and massive emissions of greenhouse gaseous. In an effort to contribute to the environmental sustainability, extensive studies are being conducted on the use of biomass as feedstocks, due to its renewable, abundance and non-toxic nature [1]. Biomass is mainly comprised of cellulose, hemicellulose, and lignin, which is capable to be converted to various high-end chemicals such as furfurals, alkyl levulinates, levulinic acid, and furfuryl alcohol [2,3]. The production of alkyl levulinates gained the attention of many due to its promising characteristics. Methyl, ethyl and butyl levulinates are biofuel octane-booster additives that enhances the fuel flow properties with high flashpoint stability and lubricity, improved viscosity and density, reduced engine out smoke number, and promotes cleaner emissions [4].

Among the alkyl levulinates, EL has several advantages which makes it more prominent. Long degradation time and the release of unburnt hydrocarbons are one of the major issues associated with fuel blends. Fortunately, EL has shorter degradation time which helps in minimizing the impact on the environment [5]. Moreover, it was observed that EL blend with 30 % heptane decreased the nitrogen oxides (NOx) emissions, compared to the blends with butyl levulinate, ketones and valeric esters [5]. Inter-

* Corresponding author.
E-mail address: mohdasmadi@utm.my (M. Asmadi).

https://doi.org/10.1016/j.matpr.2023.02.024
2214-7853/Copyright © 2023 Elsevier Ltd. All rights reserved.
Selection and peer-review under responsibility of the scientific committee of the 2nd Regional Congress on Membrane Technology 2022 in Conjunction with the 16th AUN/SEED-NET Regional Conference on Environmental Engineering 2022.

Please cite this article as: K. Krishnasamy, M. Asmadi, N. Aishah Saidina Amin et al., One-pot liquefaction of cellulose to ethyl levulinate via 1-sulfonic acid-3-methyl imidazolium trichlorozincate as Brønsted-Lewis catalyst, Materials Today: Proceedings, https://doi.org/10.1016/j.matpr.2023.02.024