CHEMICAL ENGINEERING TRANSACTIONS

VOL. 45, 2015

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

**ISBN** 978-88-95608-36-5; **ISSN** 2283-9216

DOI: 10.3303/CET1545152

# Synthesis of Ethyl Levulinate from Levulinic Acid over Solid Super Acid Catalyst

Dorairaaj Sivasubramaniam, Nor Aishah Saidina Amin

Chemical Reaction Engineering Group (CREG), Faculty of Chemical Engineering, Universiti Teknologi Malaysia 81300 Skudai, Johor, Malaysia
noraishah@cheme.utm.my

In this study, 40 % $H_3PW_{12}O_{40}/ZrO_2$ catalyst was synthesized, characterized and tested for conversion of levulinic acid (LA) and ethanol (EtOH) to ethyl levulinate (EL). The catalyst was prepared through wet-impregnation method. Catalyst characterization using BET and $NH_3$-TPD revealed that the catalytic performance was dominantly influenced by the acid sites and surface area of the catalyst. The perfomance of the catalyst was tested based on reaction time (30 min to 4 h) and reaction temperature (120 °C to 160 °C) with 1:5 levulinic acid to ethanol ratio. The 40 % $H_3PW_{12}O_{40}/ZrO_2$ catalyst exhibited high catalytic performance at 150 °C with time taken 3 h for 99 % yield of ethyl levulinate.

## 1. Introduction

Lignocellulosic biomass is a major source for production of many bio-based chemicals (Barontini et al. 2015). The lignocellulosic biomass is also nontoxic and biodegradable (Delhomme et al. 2014). Biomass could be in the form of sugar, starch, oil crops, wheat straw, giant reed, oil palm frond, empty fruit bunch, and animal manure, which are currently utilized for the production of liquid fuels and chemicals to replace fossil fuels (Tang et al. 2014). Levulinic acid is largely obtain by the dehydration lignocellulosic biomass (Cirujano et al. 2015). Derivatives of levulinic acid are utilized as a bio-based chemical mainly in the production of gasoline and diesel fuel. Esters of levulinic acid are promising for flavouring and solvents (Kuwahara et al. 2014). Specifically, ethyl levulinate is an interesting chemical because this compound is utilized for diesel miscible biofuel (Fernandes et al. 2012).

Traditionally, esterification reaction was conducted in the presence of mineral acids such as $H_2SO_4$, $H_3PO_4$ or HCl (Bart et al. 1994) but homogeneous acid catalysts are unrecycleable and always costly in its operation. Moreover, it is a corrosive chemicals to equipment (Neves et al. 2013) and have some drawbacks in the catalyst such as limited catalytic activity, environmental problems, toxic waste generation (Melero et al. 2013). For instance, one pot synthesis of ethyl levulinate from lignocellulosic biomass in the presence of homogeneous mineral acids produce quantitative yield but have some serious drawbacks such as high temperature, limited catalyst recyclability and only utilized low molecular weight alcohols, bulkier alcohols was not effective for the reaction (Melero et al. 2013). Hence, heterogeneous catalyst were introduced for esterification of levulinic acid and ethanol that could eliminate all the disadvantages of homogeneous catalyst.

As alternatives to the homogeneous catalysts, heteropoly acid catalyst is well established area and has green benefits. Heteropolyacids divided into several examples such as $H_4SiW_{12}O_{40}$, $H_4MoW_{12}O_{40}$ and $H_4PW_{12}O_{40}$ (Huang et al. 2008). Among heteropolyacid catalyst, phosphotungstic acid ($H_4PW_{12}O_{40}$) catalyst is highly utilized catalyst for many reactions because of its high bronsted acidity site and sustainable acid catalyst (Cirujano et al. 2015). Heteropoly phosphotungstic acid could be applied as a heterogeneous and homogeneous catalyst depending on the composition and presence of support catalyst. As recently revealed that heteropolyacids soluble in ethanol and methanol. Hence, heteropolyacids was utilized in the presence of its supported catalyst to make it easily separable from the reaction mixture. There was a study conducted for the production of biodiesel via transesterification

Please cite this article as: Sivasubramaniam D., Saidina Amin N.A., 2015, Synthesis of ethyl levulinate from levulinic acid over solid super acid catalyst, Chemical Engineering Transactions, 45, 907-912 DOI:10.3303/CET1545152

reaction under mild condition in the presence heteropolyacids but it was found that heteropolyacid is highly soluble in water and polar solvents.

Moreover, it has low surface area which depletes its heterogeneous characteristics. Hence, to overcome this problems previous studies intended to utilized supported heteropoly phosphotungstic acid ($H_3PW_{12}O_{40}$) for the production of biodiesel from the transesterification of rapeseed oil and ethanol and found that hydrous zirconia supported heteropolyacids provide a high catalytic activity which involved the combination of lewis acid sites and hydoxyl group (Morin et al., 2007). Moreover, heteropoly phosphotungstic acid been utilized as an individual catalyst for the production of EL with quantitative yield, but its solubility in solvent and difficult in the separation of catalyst from reaction mixture become disadvantages of the catalyst. Hence, to overcome these problems heteropoly phosphotungstic acid been impregnated on the metal oxide surface.

In this paper, the study reported on the production of ethyl levulinate (EL) from levulinic acid over 40 % $H_3PW_{12}O_{40}/ZrO_2$. Firstly, the study was conducted under different temperature (120 to 160 °C) and time taken (30 min to 4 h). This paper also focused on the characterization of catalyst that prepared using wet impregnation method. The characterization mainly on the acidity site of the catalyst using $NH_3$-TPD and surface area using BET. These two properties important in evaluated catalytic perfomance of 40 % $H_3PW_{12}O_{40}/ZrO_2$ in the production of EL via esterification of LA.

## 2. Experimental Section

### 2.1 Chemicals

All the chemicals were supplied from Merck, Germany. The Keggin-type heteropolyacid used in the reaction was phosphotungstic acid ($H_3PW_{12}O_{40}$), Zirconium Oxide ($ZrO_2$) was used for the catalyst preparation. Ethanol was used as a solvent for the reaction and alcohol for the esterification reaction.

### 2.2 Catalyst preparation

The catalyst was prepared via impregnation method. The catalyst was prepared by mixing the solid form of zirconium oxide ($ZrO_2$) with Keggin-type heteropolyacid ($H_3PW_{12}O_{40}$). The preparation was in wt% such as 40 wt %. The zirconium oxide powder was weighted and added to 30 mL of water, follows the stated amount of Keggin-type heteropolyacid ($H_3PW_{12}O_{40}$). Mixture then stirred at 80 ºC for 2 h and dry under oven for 12 h at 100 ºC to remove excess water. Finally, the prepared catalyst was calcined at 450 ºC for 5 h.

### 2.3 Catalyst Characterization

The acidity properties of catalysts were analysed using $NH_3$-temperature programme desorption ($NH_3$-TPD). Brunauer- Emmet-Teller (BET) method was applied to study surface area, pores volume and size distribution using Micrometrics ASAP2020 analyzer with isotherm nitrogen adsorption.

### 2.4 Catalytic activity

The conversion of levulinic acid to ethyl levulinate was carried out in the presence of 30 mL of ethanol as solvent for the reaction, solid acid catalyst and the reaction was performed in a high pressure stirred autoclave reactor at 150 ºC. Finally, the product was analysed using GC-FID to obtain the yield of products. The reaction was repeated with various temperature and reaction time taken.

## 3. Results and Discussion

### 3.1 Catalyst Characterization

#### 3.1.1 Brunauer- Emmet-Teller (BET)

The BET values in Table 1 indicate that impregnation of $H_3PW_{12}O_{40}$ on $ZrO_2$ increased the surface area of the solid catalyst. The surface area was 18.81 $m^2/g$ for 40 % $H_3PW_{12}O_{40}/ZrO_2$ which shows that the impregnated catalyst surface area was higher than parent-$ZrO_2$ catalyst because porous characteristics of $ZrO_2$ that enables to increase its own surface area when impregnated with other catalyst (Katryniok et al. 2010). In the present study, $ZrO_2$ prevents $H_3PW_{12}O_{40}$ soluble in polar solvent and easy for the separation from reaction mixture. Based on the total surface area obtained, it was confirmed that surface area influenced by the catalytic performance for the production of EL.

*Table 1: BET results for $H_3PW_{12}O_{40}$ impregnate on $ZrO_2$ at different loadings*

| Catalyst | Specific surface area ($m^2g^{-1}$) |
|---|---|
| $H_3PW_{12}O_{40}$ | 4.55 |
| $ZrO_2$ | 14.95 |
| 40% $H_3PW_{12}O_{40}/ZrO_2$ | 18.81 |

### 3.1.2 $NH_3$-temperature programmed desorption ($NH_3$-TPD)

The acidity of the catalyst highly influences the esterification reaction of LA. Table 2 compares the acidity of the parent catalyst with the impregnated ones. The acidity of the impregnated catalyst was higher compared to individual $ZrO_2$ catalyst due to the introduction of $H_3PW_{12}O_{40}$ on $ZrO_2$. Generally, $H_3PW_{12}O_{40}$, known as super acid, contains strong Bronsted acid sites. $H_3PW_{12}O_{40}$ is also known as superacid catalyst. Bronsted acidity of HPA modified by their acid-base titration and redox properties by restructuring their chemical composition. Moreover, HPA is capable to accept and release electrons, high proton mobility, easy work up procedures, easy filtration, and minimization of cost and waste generation because of the reusable and recycle characteristics of this catalyst (Allameh et al. 2010). Previously, $H_3PW_{12}O_{40}$ shows slight depletion of the heat of ammonia adsorption, this is due to its high stability (Morin et al. 2007). Hence, 40 % $H_3PW_{12}O_{40}/ZrO_2$ catalyst displayed the highest acidity

*Table 2: $NH_3$-TPD profile for the $H_3PW_{12}O_{40}/ZrO_2$ with different loading*

| Catalyst | Acidity (mmol/g) |
|---|---|
| $H_3PW_{12}O_{40}$ | 1.68 |
| $ZrO_2$ | 0.27 |
| 40 % $H_3PW_{12}O_{40}/ZrO_2$ | 0.64 |

### 3.2 Esterification of Levulinic acid (LA)

Traditionally, Ethyl levulinate has been produced through the esterification reaction of levulinic acid and ethanol. The reaction was conducted using various catalysts (homogeneous and heterogeneous catalyst). Initially, homogeneous catalyst was utilized for the esterification reaction and produce high yield of EL. However, homogeneous acid catalyst especially sulphuric acid have some serious drawback which harmful to the reaction equipment and environment (Lee et al.2010). Traditionally, esterification reaction was conducted using mineral acid such as $H_2SO_4$, HCl and $H_3PO_4$ as homogeneous acid catalyst (Zhao et al. 2014). There were some serious drawbacks by utilizing the homogeneous acid catalyst such as recyclability and generation of toxic waste which reduce the yield of EL (Su et al. 2013). Homogeneous catalyst known as harmful substance and generate high quantity of toxic waste (Pasquale et al. 2012). Hence, heterogeneous catalyst was chose as an alternative catalyst for homogeneous catalyst which could eliminate the disadvantages of the homogeneous catalyst.

Heteropoly phosphotungstic acid ($H_3PW_{12}O_{40}$) supported zirconia ($ZrO_2$) was chose as stable catalyst for many reaction and have high surface area. Therefore, in this study $H_3PW_{12}O_{40}$ supported $ZrO_2$ was applied for esterification of LA and screen different reaction time and reaction temperature for the conversion of LA to EL. These two parameters highly influence the production of EL from the esterification reaction of LA.

### 3.2.1 Effect of Parameters

#### Reaction Time

Reaction time is highly influencing the production of ethyl levulinate. When the reaction was conducted at 150 °C for 30 min, only 10 % EL yield obtained from the reaction. When the reaction time was increased to 1 h, the EL yield was 37 %. This due to LA is not fully converted to EL in 1 h which indicates the probability of the reaction might stop after the production of intermediate compound.

Furthermore, high yield (99 %) was successfully obtained when the reaction time was increased to 3 h which is considered as an optimal time taken for the formation of EL. In the reaction condition, 3 h is the best time taken at 150 °C because this condition is the longer time taken for LA to be fully converted to EL by using the solid super acid catalyst.

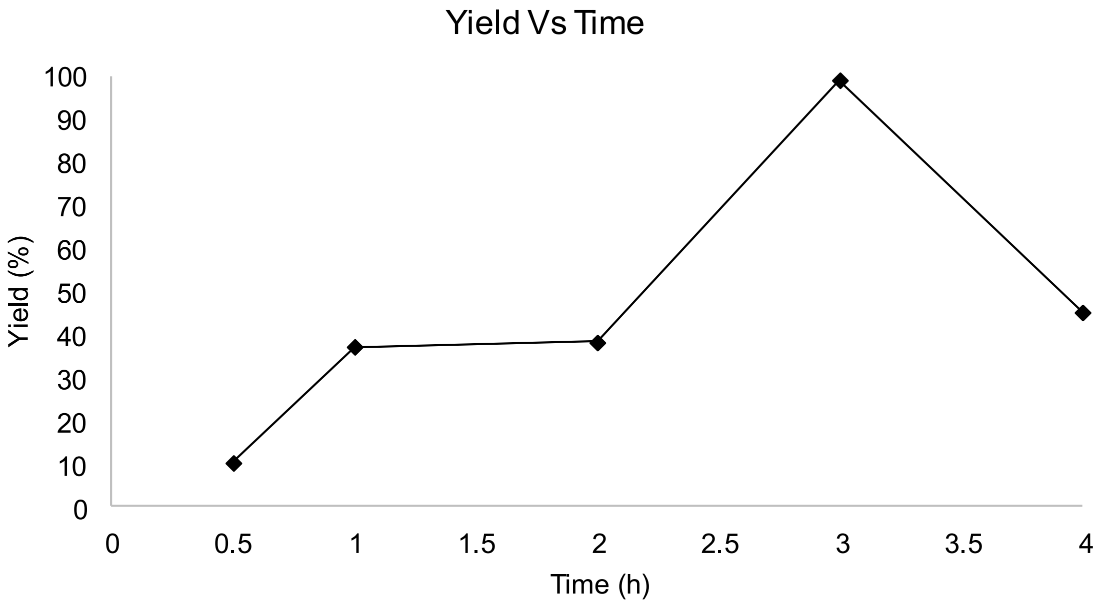

*Figure 1: Graph of reaction time influenced the production ethyl levulinate*

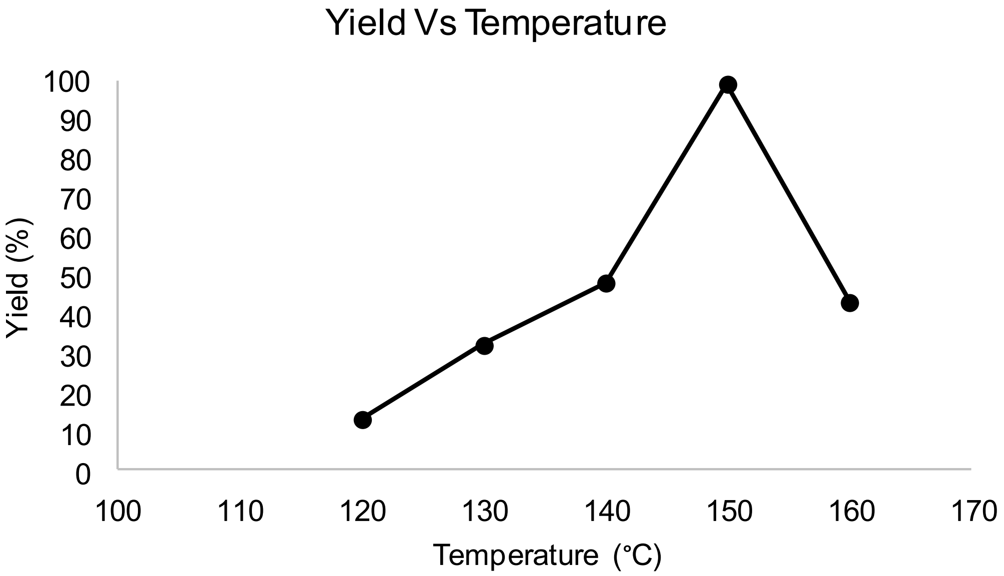

*Figure 2: Graph of temperature influence the production of ethyl levulinate*

**Reaction Temperature**

Screening temperature based on the five different sets including 120 °C, 130 °C, 140 °C, 150 °C, 160 °C. The best temperature to obtain high yield of EL was 150 °C at 3 h known as an optimal condition for the reaction to produce 99 % yield of EL. When the temperature was increased to 160 °C, the yield of EL has been reduced to 43 % due to the decomposition of EL and more undesired products such as soluble polymers and insoluble humins formed through the esterification (Zhao et al. 2014). Hence, 150 °C is an optimum temperature for the conversion of LA to EL via esterification reaction to produce high yield of EL.

## 4. Conclusion

Ethyl levulinate (EL) can be obtained from the esterification reaction between levulinic acid and ethanol. The individual catalyst $H_3PW_{12}O_{40}$ and $ZrO_2$ and the impregnated catalyst was characterized using BET and $NH_3$-TPD shows its surface area and total acidity of the catalyst. Hence, it was concluded that the surface area of the individual catalyst were lower than impregnated catalyst because of the porous characteristics of $ZrO_2$ which provides itself to increase the surface area and increase its catalytic activity. 40 % $H_3PW_{12}O_{40}/ZrO_2$ was utilized as a solid acid catalyst for the esterification reaction of levulinic acid. It was found that 40 % $H_3PW_{12}O_{40}/ZrO_2$ exhibit high catalytic performance by produced EL with 99 % yield at 150 °C in 3 h.

### Acknowledgement

The authors would like to express their gratitude for the financial support from Universiti Teknologi Malaysia under Research University Grant (RUG) vote no 07H14 and Ministry of Higher Education (MOHE).

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