Sulfated Zirconia Catalyst for Hydrolysis of Palm Oil Lignocellulosic Wastes

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Abstract

The waste plant materials remaining from palm oil extraction consist of cellulose, hemicellulose and lignin. They are potential sources of cellulose, which can be used as raw material for production of fermentable sugar. In this study, a single stage of heterogeneous acid catalyst hydrolysis were carried out in ionic liquid solution over sulfated zirconia catalysts prepared by modified sol gel method. Among the sulfated zirconia catalysts tested, sulfated zirconia prepared by SFE showed the highest hydrolysis catalytic activity up to 37.20 % in EFB treated and 53.95 % in frond treated. In addition, the process variable of reaction time hydrolysis was also investigated over both sulfated zirconia catalyst. The objective of this research is to do catalytic hydrolysis of lignocellulosic waste by using sulfated zirconia catalyst prepared by sol gel method.

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Keywords: Cellulose; empty fruit bunches; frond; hydrolysis; palm oil; sulfated zirconia catalysts.

Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BMIMCl</td>
<td>1-butyl-3-methylimidazolium chloride</td>
</tr>
<tr>
<td>CTAC</td>
<td>cetyltrimethylammonium chloride</td>
</tr>
<tr>
<td>DNS</td>
<td>dinitrosalicylic acid</td>
</tr>
<tr>
<td>EFB</td>
<td>empty fruit bunches</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>1 psi</td>
<td>6,894.76 Pascals</td>
</tr>
<tr>
<td>TRS</td>
<td>total reducing sugar</td>
</tr>
</tbody>
</table>

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### 1. Introduction

Lignocelluloses biomass is one of the most abundant biomass and non-food bio-feedstock used in bioethanol production. Comparing with other biomass, lignocelluloses biomass is more efficient and environmentally friendly. Lignocelluloses biomass as an organic residue consists of mainly cellulose, lignin and hemicelluloses, whose basic units are sugars that can be fermented into ethanol or other chemicals. The carbohydrate polymers (cellulose and hemicellulloses) are tightly bound to the lignin. Up to 80% of the lignocelluloses are polysaccharides [1]. Lignocelluloses plant structures also contain a variety of plant-specific chemicals in the matrix, called extractives (resins, phenolics, and other chemicals), and minerals (calcium, magnesium, potassium, and others).

Palm oil production is on a steeply rising path. The EFB are waste by-products of palm oil industries that are being investigated for further uses. Currently, palm oil mills typically use the shell and the drier part of the fibre product stream, rather than EFB, to fuel their boilers, as the raw EFB contain nearly 60% water [2].

As the most abundant source of biomass and because of its non-edible nature, cellulose is a promising alternative for the sustainable production of chemicals and fuels [3]. Hydrolysis of cellulose to glucose is a key technology for effective use of lignocellulose because glucose can be efficiently converted into various chemicals, biofuels, foods and medicines [4-7]. Cellulose hydrolysis can be achieved with enzymes [8], dilute acids [9] and sub- or super-critical water [7,10-12] however, these processes have significant drawbacks such as high cost of enzymes, difficulty in separation of catalysts, corrosion of reactors, waste effluents and severe reaction conditions. Some of these problems can potentially be overcome with the application of solid acid/base catalysts. Onda et al. [13] showed highly selective hydrolysis of cellulose into glucose under hydrothermal conditions at 423 K in the presence of sulfonated activated carbon (AC-SO$_3$H) and demonstrated that this catalyst was superior to zeolite, mixed-oxide TiO$_2$-ZrO$_2$ [14] and ionic liquids [15].

Many studies have been contributed to the hydrolysis of cellulose catalyzed by mineral acids at relatively lower temperatures (523 K). Although high yields of glucose can be achieved using concentrated H$_2$SO$_4$ (30% to 70%), the hydrolysis of cellulose with dilute acids (1%), which is more feasible at a commercial scale, affords lower glucose yields [16]. Solid acids such as carbon materials bearing SO$_3$H groups and layered transition metal oxides (e.g., HNbMoO$_6$) have also been examined for the hydrolysis of cellulose, but the yield of glucose is low [17]. Higher glucose yield (40% to 60%) could only be attained in the conversion of the cellulose with a decreased crystallinity after a pretreatment with trifluoroacetic acid or ball milling [16,18]. The use of ionic liquids as reaction media could also enhance the efficiency for cellulose conversions in the presence of an acid catalyst [19].

The conversion of cellulose into glucose and the simultaneous hydrogenation of glucose into sugar alcohols, such as sorbitol and mannitol on Ru/C [20], polymer stabilized Ru nanoclusters [21], and Pt and Ru supported by H-USY and c-Al$_2$O$_3$ [22] has been reported. In order to replace the mineral acids in the acid hydrolysis of cellulose, solid acid catalysts such as sulfonated activated carbon (AC-SO$_3$H) [23], sulfonic acid mesoporous materials [24,25], and Brønsted acidic zeolites [21,22] were used. Higher glucose yields were reported for sulfate modified catalysts than for acidic zeolites.

The research was aimed to implement hydrolysis process of lignocellulosic materials over sulfated zirconia catalysts. The prepared catalysts were prepared by using modified sol gel method then dried by different method, i.e. immersed by CTAC surfactant and SFE and characterized their physical and chemical properties before tested their catalytic activity.

### 2. Experimental method

#### 2.1. Catalyst preparation

The precursor employed in the preparation of the sol-gel catalyst was zirconia butoxide in $n$-butanol. The
Sulfated zirconia was prepared as follows: 16.778 mol of zirconium (IV) butoxide and 16.516 n-butanol was introduced into a glass system at low temperature (0 °C) under constant stirring. Then, 6.718 mL of n-butanol; 0.496 mL of distilled water and 0.684 mL of HNO₃ were drop-wise added to the solution and continue stirred constantly. After that, 0.489 mL of H₂SO₄ was added to the reaction system and the resulting suspension was maintained and stirred constantly until gelling was achieved. The wet gel was treated through two methods to compare the result. First method was surfactant immersion, the wet gel was immersed overnight at room temperature (25 °C) in an n-butanol solution of CTAC surfactant, decanted and then dried under vacuum for 24 h at 70 °C. The second method was SFE which conducted at 60 °C, extractor pressure of 2000 psi, CO₂ flow of (5 to 6) mL·min⁻¹, separator pressure of 500 psi. Finally, all samples calcined for 2 h at 500 °C.

2.2. Catalytic activity test

0.2 g of raw material, 3.8 g of ionic liquid, [bmim]Cl as solvent, 0.25 mL of aquadest as anti solvent and 0.1 g of catalyst were placed into batch reactor. The hydrolysis reaction was carried out at 160 °C for 3 h. After reaction finished, 10 mL of aquadest was added into reactor then filtered. The TRS in liquid product was analyzed by using DNS method.

2.3. Liquid hydrolysis product analysis

0.25 mL of DNS reagent and 0.25 mL of liquid hydrolysis product were mixed and boiled in water bath at 5 °C to 100 °C for 5 min then cooled in room temperature. The solution was diluted by adding 2 mL of water then measured by using UV-Vis Spektrofotometer at 540 nm. TRS concentration was measured by using standard curve of glucose.

3. Results and discussion

3.1. Catalysts properties

The properties of catalysts prepared were characterized, in term of specific surface area, pore volume, pore size, total acidity and surface acidity. Table 1 shows that SZ SFE resulted in higher specific surface area, pore volume, pore size and acidity than SZ immersing.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Specific surface area (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
<th>Pore size (nm)</th>
<th>Total acidity (mmol·g⁻¹)</th>
<th>Surface acidity (mmol·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ immersing</td>
<td>81.79</td>
<td>0.063</td>
<td>15.32</td>
<td>5.85</td>
<td>0.61</td>
</tr>
<tr>
<td>SZ SFE</td>
<td>119.90</td>
<td>0.39</td>
<td>64.53</td>
<td>13.41</td>
<td>2.33</td>
</tr>
</tbody>
</table>

3.2. Catalytic activity test

Sulfated zirconia catalysts prepared were tested their catalytic activity for hydrolysis process to produce TRS. Table 2 shows that pre-treatment by using NaOH can remove 14.5 % of lignin in EFB and 3.1 % of lignin in frond. Then, these raw materials will be used for hydrolysis by using SZ catalyst.
Table 2. Compositional analysis of palm oil lignocellulosic waste

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Lignin (%)</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EFB untreated</td>
<td>36.40</td>
<td>30.85</td>
<td>13.94</td>
</tr>
<tr>
<td>EFB treated</td>
<td>21.97</td>
<td>52.30</td>
<td>21.32</td>
</tr>
<tr>
<td>Frond untreated</td>
<td>29.50</td>
<td>40.01</td>
<td>30.78</td>
</tr>
<tr>
<td>Frond treated</td>
<td>26.36</td>
<td>47.84</td>
<td>8.23</td>
</tr>
</tbody>
</table>

Variation of raw material used was investigated to see their catalytic activity in hydrolysis of lignocellulose. Palm oil lignocellulosic wastes used are frond and EFB, both untreated and treated by using NaOH.

Table 3. Catalytic activity of SZ catalyst in lignocellulosic hydrolysis

<table>
<thead>
<tr>
<th>Raw material</th>
<th>SZ\textsubscript{immersing} TRS yield (%)</th>
<th>SZ\textsubscript{SFE} TRS yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>17.85</td>
<td>23.13</td>
</tr>
<tr>
<td>EFB untreated</td>
<td>8.61</td>
<td>16.77</td>
</tr>
<tr>
<td>EFB treated</td>
<td>17.51</td>
<td>37.20</td>
</tr>
<tr>
<td>Frond untreated</td>
<td>9.37</td>
<td>19.75</td>
</tr>
<tr>
<td>Frond treated</td>
<td>16.57</td>
<td>28.16</td>
</tr>
</tbody>
</table>

(Raw material 0.2 g; catalyst 0.1 g; Ionic Liquid BMIMCl 3.8 g; 160 °C; 3h)

Table 3 shows that pretreatment by using NaOH in EFB increased the TRS yield, from 8.61 % to 17.51 % and in frond, from 9.37 % to 16.57 % by using SZ\textsubscript{immersing} and 16.77 % to 37.20 % and in frond, from 19.75 % to 28.16 % by using SZ\textsubscript{SFE}. Increasing of TRS yield correlated with decreasing of lignin content and increasing of cellulose content after pretreatment. Optimization of hydrolysis process was done by variation of hydrolysis time by using EFB and frond treated by NaOH.

Figure 1 and Figure 2 elucidated that SZ\textsubscript{SFE} catalyst gave higher % TRS yield than SZ\textsubscript{immersing} both for hydrolysis of EFB treated and frond treated. Hydrolysis for 3 h gave the highest % TRS yield up to 37.20 % in EFB treated by...
using SZ$_{SFE}$. While, hydrolysis for 4 h gave the highest % TRS yield up to 53.95 % in frond treated by using SZ$_{SFE}$.

Fig. 2. Hydrolysis of frond treated by NaOH

4. Conclusion

SZ catalyst have successfully been synthesized by sol gel method, SZ$_{immersing}$ and SZ$_{SFE}$. Characterization resulted that SZ$_{SFE}$ has higher specific surface area, pore size, pore volume and acidity than SZ$_{immersing}$. The hydrolysis of both in cellulose and lignocellulose in BMIMCl ionic liquid, SZ$_{SFE}$ showed superior catalytic activity than SZ$_{immersing}$. SZ$_{SFE}$ catalyst showed the highest hydrolysis catalytic activity up to 37.20 % in EFB treated and 53.95 % in frond treated. Therefore, sulfated zirconia catalyst may have potential application in the hydrolysis reaction of lignocellulosic biomass in order to get fermentable sugar as intermediate product for ethanol production.

References


