Potential of lignocellulosic biomass for octane and jet fuel precursors production through catalytic transformation technologies

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Introduction

Uncertainty on reserves

New alternatives to produce valuable chemicals and fuels

Oil crude

Prices

Energy demand has generated a renewed interest in producing fuels from biomass

Climate change

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**Introduction**

- **Colombia as tropical country**
- **Lignocellulosic biomass**
  - Cellulose
  - Hemicellulose
  - Lignin
  - ✓ Availability
  - ✓ Relatively low cost
- **Sugarcane bagasse**
- **Coffee cut-stems**
- **Fique bagasse**

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W. Shen et al. (2011) reported that jet fuels range alkanes could be obtained from lignocellulosic biomass by a novel route, wherein C5 sugar was firstly produced by hydrolysis of biomass and then converted into furfural.

**Figure 1** Sequence of hydrolysis, dehydration and aldol-condensation reactions to produce precursor jet fuel from lignocellulosic biomass.
Materials and methods. Overview

Experimental steps

Raw materials → Dilute-acid pretreatment → Dehydration reaction → Aldol-condensation reaction

Sample analysis

- Sugars and furan-based compounds determination
- Alkane precursor determination

Simulation procedure

To the simulation tool, the experimental results are fed → Aspen Plus v8.2 → Aspen process economic analyzer v8.2 → Waste Reduction Algorithm

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Materials and methods

Raw materials

Table 1 Composition of the lignocellulosic biomass used in this work (% wt dry basis).

<table>
<thead>
<tr>
<th>Component</th>
<th>Sugarcane bagasse</th>
<th>Coffee cut-stems</th>
<th>Fique bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>46.74</td>
<td>40.39</td>
<td>50.79</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>23.62</td>
<td>34.01</td>
<td>14.19</td>
</tr>
<tr>
<td>Lignin</td>
<td>19.71</td>
<td>10.13</td>
<td>12.47</td>
</tr>
<tr>
<td>Ash</td>
<td>1.13</td>
<td>1.27</td>
<td>21.84</td>
</tr>
<tr>
<td>Extractives</td>
<td>8.79</td>
<td>14.18</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Materials and methods

Experimental process description

Figure 2 Flowsheet for process to obtain jet fuel precursor.

1. Pretreatment – acid hydrolysis
   - Raw material
   - Dilute acid
   - Xylose rich hydrolyzate
   - Solids

2. Furfural Production
   - NaCl
   - Furfural

3. Precursor production
   - Methanol
   - Acetone
   - Precursor
Materials and methods

Experimental process description

1. Dilute-acid pretreatment
   110°C, 1:10 (%wt) solid:liquid
   i) H₂SO₄ solution (2 %v/v), 5h.
   ii) H₂SO₄ solution (10% v/v), 30min.

2. Dehydration reaction
   90°C, 1.5h, 500rpm, 2.4g NaCl
   i) H₂SO₄ solution (2 %v/v)
   ii) H₂SO₄ solution (10% v/v)

3. Aldol-condensation reaction
   120°C, 7-10atm, 24h,
   40mg MgO-ZrO₂
   i) 55 wt. % total organics,
      furfural/acetone = 1 by moles,
      methanol/water = 1.85 by volume
Materials and methods

Sample analysis

Sugars and furan-based compounds determination
Sugars and furan-based compounds during the acid hydrolysis, dehydration and aldol-condensation reactions are quantified by the HPLC system (ELITE LaChrom) using an ORH-801 Transgenomic® column.

Alkane precursor determination
Alkane precursor (4-(2-furyl)-3-buten-2-one) identification is made with a gas chromatograph (Agilent Technologies 6850 Series II) equipped with a mass selective detector (MSD 5975B).
Materials and methods

Simulation procedure

Aspen Plus

Aspen process economic analyzer

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Results and discussion

Acid hydrolysis

Table 2 Results of the acid hydrolysis.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Condition 1</th>
<th>Condition 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g xylose/g hem</td>
<td>g furfural/g hem</td>
</tr>
<tr>
<td>SCB</td>
<td>0.81±0.004</td>
<td>0.054±0.001</td>
</tr>
<tr>
<td>CCS</td>
<td>0.50±0.030</td>
<td>0.024±0.002</td>
</tr>
<tr>
<td>FB</td>
<td>0.58±0.017</td>
<td>0.019±0.003</td>
</tr>
</tbody>
</table>

hem: hemicellulose

Xylose and furfural are the interesting products and a platform to obtain the precursor of jet fuels.
Results and discussion

Dehydration reaction

Table 3 Results of dehydration reaction.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Condition 1 (g furfural/g xylose)</th>
<th>Condition 2 (g furfural/g xylose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCB</td>
<td>0.060±0.008</td>
<td>0.060±0.005</td>
</tr>
<tr>
<td>CCS</td>
<td>0.063±0.002</td>
<td>0.067±0.005</td>
</tr>
<tr>
<td>FB</td>
<td>0.092±0.009</td>
<td>0.045±0.005</td>
</tr>
</tbody>
</table>

Rong et al. (2012) reported that xylose dehydration to furfural has a yield below 10% when acid concentration is nearly to 2.5% w/w. On the other hand, the yield reduces to 0.51% when the concentration of sulfuric acid reaches 12.5% w/w[10].
Results and discussion

Aldol-condensation reaction

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Condition 1 (% disappearance of furfural)</th>
<th>Final FA (4-(2-furyl)-3-buten-2-one) yield (g/g of hemicellulose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCB</td>
<td>71.7±0.018</td>
<td>0.14±0.004</td>
</tr>
<tr>
<td>CCS</td>
<td>96.5±0.014</td>
<td>0.12±0.004</td>
</tr>
<tr>
<td>FB</td>
<td>92.9±0.008</td>
<td>0.08±0.002</td>
</tr>
</tbody>
</table>

The data reported in literature indicate a disappearance percentage of 66% in the same conditions of the procedure developed in this work [12].

When aldol-condensation reaction is carried out for operation condition 2, the formation of interest products is not recorded for any raw material.
Results and discussion

Simulation results

- According to results from the technical assessment, SCB, CCS and FB have relative high FA (4-(2-furyl)-3-buten-2-one) yields 0.14, 0.13 and 0.08 grams of precursor per gram of lignocellulosic biomass, respectively. The good content of hemicellulose in these residues, the efficiency in acid hydrolysis and dehydration stages, involve good flows of product.

- The production cost is 6.02, 5.57 and 10.22 USD per kilogram of precursor for SCB, CCS and FB, respectively. In this sense, the economic margins are -20.45, -11.41 and -104.34% for SCB, CCS and FB, respectively.
**Results and discussion**

**Simulation results**

The utilities cost represents approximately more than 50% of total production cost which is related with the great amount of energy that demands the aldol-condensation reaction to generate the FA. As can be seen there are not significant changes in the percentages of distribution between the residues.

**Figure 3** Total costs distribution for SCB, CCS and FB to produce jet fuel precursor.
Results and discussion

Simulation results

SCB is the process with greater flow of FA and released energy that can be exploited, consequently is the friendliest environmental process.

Figure 4 Environmental results for SCB, CCS and FB to produce jet fuel precursor.
Conclusions

- This work contributes to the implementation of simultaneous processes for the transformation of agroindustrial wastes to obtain sugars, furan-based compounds and precursor of liquid alkane range jet biofuel, focusing on the comprehensive utilization of raw materials.

- Additionally, this work shows that MgO-ZrO₂ catalyst allows converting carbohydrate-derived compounds, like furfural, to water-soluble intermediates (precursor FA). These compounds are the base for future production of liquid alkanes.
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References


References


Thank you for your attention

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