Comparison of processing lines to convert lignocellulosic C5 sugar platform to furfural and biogas

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1. Introduction

1.1 Platform products

Feedstocks

- Sugar crops, lignocellulosic crops, algae crops, etc.

Building blocks

Platform product

Pillars

Bulk chemicals

Products

- Physical
- Chemical
- Biochemical
- Thermochemical

Biofuels, energy, organic acids, biofertilizers, etc.

FINAL

STAND-ALONE PROCESSES

BIOREFINERIES

START

Conversion processes

Syngas, biogas, C6 sugar and C5/C6 sugars, plant-based oil, algae oil, organic solutions, lignin, pyrolysis oil.
1. Introduction

1.2 Challenges of lignocellulosic biomass

SEARCH
Lignocellulosic biomass with high availability and low cost

REVISE
Appropriate configurations processes in order to achieve the efficient use of lignin and hemicellulose fractions

CHOOSE
Suitable pretreatment technologies
Enzymes with the best performance

SYSTEMATIC RESEARCH
To demonstrate the best processing alternative to efficiently use and transform C5 sugars to added-value products.

HEMICELLULOSE: C5 SUGARS PLATFORM

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2. Materials and Methods

2.1 Raw material and sample analysis

CCS were obtained from a farm placed at Salamina, a town of north of Departamento de Caldas, located in the center of Colombia.

- Sugars (glucose and xylose): High-Performance Liquid Chromatography (HPLC- ELITE LaChrom).
- Furfural and hydroxymethylfurfural (HMF) spectrophotometry.
- Biogas: Displacement of water volume and biogas analyzer.

- NREL standards (National Renewable Energy Laboratories) for moisture, extractives, ashes calculation.
- TAPPI (Technical Association of the Pulp and Paper Industry) standards were use to determine cellulose, hemicellulose, Klasson lignin and soluble lignin content (T-264-cm-07; T-211-cm-93; T-249-em-85).
2. Materials and Methods

2.2 Stand-alone processes

Figure 1. Flowsheet of stand-alone processes for the obtaining of, A) biogas and B) furfural.
2. Materials and Methods

2.2 Stand-alone processes

**OPERATING CONDITIONS**

- **Particle size reduction**
  - Slices of 3-5mm of width and 10-30mm of diameter. The slices were milled using a knife mill. The material was sieving to pass meshes of 40 (0.425mm) and 60 (0.250mm).

- **Drying**
  - The obtained materials were dried in an oven (Thermo Precision model 6545) at 40°C and 24h.

- **Dilute-acid hydrolysis**
  - Milled CCS sample (25g) were mixed with sulfuric acid at 2% (v/v) to obtain a 1:10 solid-liquid mass ratio [8]. In autoclave the operating conditions were, 115°C and 3h.

- **Anaerobic digestion**
  - The C5 sugars fraction was used for the biogas production at 37°C, 20 days and a pH of 7.0 in a thermostatic bath using as inoculum, sludge from spent coffee grounds treatment in Coffee Factory.

- **Dehydration reaction**
  - Catalyzed by CrCl$_3$ at 180°C and 11bar for 2h $^{11}$. A HP-Autolab Reactor with a maximum capacity of 300mL.
2. Materials and Methods

2.3 Technical, economic and environmental assessment

Mass and energy balances were experimentally obtained and then translated to simulation procedures.

Economic parameters as CAPEX and OPEX were calculated using the software Aspen Process Economic Analyzer v9.

The energy consumption was determined using Aspen Energy Analyzer v9.

Software SimaPro v8.3 (PRe Sustainability, Netherlands) and the Ecoinvent database were used to measure the environmental impact of the cradle-to-gate approach.

- Climate change (CC), Ozone depletion (OD), Terrestrial acidification (TA), Freshwater eutrophication (FE), Human toxicity (HT), Photochemical oxidant formation (POF), Particulate matter formation (PMF), Freshwater ecotoxicity (FET), Agricultural land occupation (ALO) and Fossil depletion (FD).

CAPEX. Fixed capital costs of equipment.

OPEX. Sum of costs of raw materials, utilities, maintenance, labor, fixed and general costs and overhead.

Analysis of scale. 234, 180, 108 and 50 ton/h
3. Results and Discussion

3.1 Experimental results

Table 1. Physicochemical characterization of CCS (% w/w dry).

<table>
<thead>
<tr>
<th>Component</th>
<th>This work</th>
<th>Quintero et al. (2013) [15]</th>
<th>Aristizábal et al. (2015) [16]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>9.11±0.39</td>
<td>4.12</td>
<td>11</td>
</tr>
<tr>
<td>Extractive</td>
<td>9.36±0.12</td>
<td>8.38</td>
<td>14.18±0.85</td>
</tr>
<tr>
<td>Ash</td>
<td>0.96±0.13</td>
<td>2.27</td>
<td>1.27±0.03</td>
</tr>
<tr>
<td>Cellulose</td>
<td>35.13±0.81</td>
<td>37.35</td>
<td>40.39±2.20</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>11.42±0.31</td>
<td>27.79</td>
<td>34.01±1.20</td>
</tr>
<tr>
<td>Lignin</td>
<td>34.01±0.56</td>
<td>19.81</td>
<td>10.13±1.30</td>
</tr>
</tbody>
</table>

High amounts of lignin content hinders the access to hemicellulose and cellulose polymers, therefore, to their monomers (i.e., xylose and glucose).
## 3. Results and Discussion

### 3.1 Experimental results

Table 2. Experimental yields and conversions obtained in the process units.

<table>
<thead>
<tr>
<th>Process unit</th>
<th>Yield</th>
<th>Units</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilute-acid</td>
<td>0.75</td>
<td>g xylose/g hemicellulose</td>
<td>Hemicellulose:</td>
</tr>
<tr>
<td>hydrolysis</td>
<td>0.12</td>
<td>g furfural/g hemicellulose</td>
<td>97.57%</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>g glucose/g cellulose*</td>
<td>Cellulose*:</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
<td>g HMF/g cellulose</td>
<td>25.17%</td>
</tr>
<tr>
<td>Biogas</td>
<td>509.50</td>
<td>mL accumulated biogas/g VS</td>
<td>N.R.</td>
</tr>
<tr>
<td></td>
<td>81.15</td>
<td>mL accumulated CH$_4$/g VS</td>
<td>N.R.</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.07</td>
<td>g furfural/g xylose</td>
<td>Xylose: 63%</td>
</tr>
</tbody>
</table>

N.R. Non-reported

*Minimum hydrolysis due to the use of acid.

Kaparaju et al. (2009) performed assays of the biological methane potential (BMP) at 55°C from wheat straw hydrolysates obtained from hydrothermal pretreatments [21]. For this configuration, a **methane yield of 384 ml/g VS** is obtained.

Martin and Grossman (2016) presented the furfural production using the same process configuration that in this work, and reported a conversion of 82 and 70% for glucose and xylose, respectively [8].

Despite the high lignin content in the CCS, the **acid hydrolysis fulfills with its target**, that is to release sugars contained in material structure, specially, **xylose from hemicellulose with a yield of 0.75**
3. Results and Discussion

3.2 Techno-economic results

Figure 1. Process schemes A) Biomethane production and B) Furfural production.

**PURIFICATION**

**Biomethane:** High pressure water scrubbing

**Furfural:** Distillation

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3. Results and Discussion

3.2 Techno-economic results

Table 3. Energy requirements of both processes.

<table>
<thead>
<tr>
<th>Utility</th>
<th>Biomethane (MJ kg(^{-1}) CCS)</th>
<th>Furfural (MJ kg(^{-1}) CCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling water</td>
<td>1.085</td>
<td>2.247</td>
</tr>
<tr>
<td>Low pressure steam</td>
<td>20.551</td>
<td>N.A.</td>
</tr>
<tr>
<td>Medium pressure steam</td>
<td>0.009</td>
<td>0.009</td>
</tr>
<tr>
<td>High pressure steam</td>
<td>N.A.</td>
<td>3.021</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.007</td>
<td>0.008</td>
</tr>
</tbody>
</table>

N.A. Non-Apply.

Utilities cost without using wastewater as cooling water

**Biomethane:** 31.950 M-USD/year

**Furfural:** 60.976 M-USD/year

Utilities cost using wastewater as cooling water

**Biomethane:** 7.082 M-USD/year

**Furfural:** 9.016 M-USD/year
3. Results and Discussion

3.2 Techno-economic results: Furfural

The equipment costs such as, dehydration reactor and distillation columns are the main contributors to CAPEX.

Raw materials cost represents approximately 86% of OPEX, followed by utilities cost with 10%.

After 108 ton/h of processing capacity, the profits are higher than OPEX.

Figure 2. Distribution of the production costs and profits of furfural production.

<table>
<thead>
<tr>
<th>Processing capacity (ton/h)</th>
<th>M-USD/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CAPEX</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>108</td>
<td>150</td>
</tr>
<tr>
<td>180</td>
<td>200</td>
</tr>
<tr>
<td>234</td>
<td>250</td>
</tr>
</tbody>
</table>

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3. Results and Discussion

3.2 Techno-economic results: Furfural

Figure 3. Analysis of scale of the furfural production and NPV change over the project lifetime.

**Equilibrium scale.** Gains and expenses are equal. VPN curve is constant after zero time.

**Minimum Processing Scale for Economic Feasibility (MPSEF).** Process achieves an NPV equal to zero throughout the project lifetime.

After 135 ton/h the process presents a positive economic behavior. At 180 and 234 ton/h the payback period is 5.64 and 4.04 years, respectively.

At 180 and 234 ton/h the profit margin is -0.07 and 1.44%, respectively.

At 180 and 234 ton/h the profit margin is 2.00 and 1.97 USD/h, respectively.
3. Results and Discussion

3.2 Techno-economic results: Biomethane

The low yield of biomethane does not favor the economic performance of the process. At any scale the profits are lower than OPEX. The biomethane process in any processing scale is unfeasible, despite that this also considers the digestate as co-product.

**Figure 4.** Distribution of the production costs and profits of biomethane production.
3. Results and Discussion

3.3 Environmental results

In general terms, the furfural production has an environmental impact higher than biomethane production. In all impact categories, this process presents a significant contribution (80-90%). In the CC category there is a small exception linked to the emission of gases (CO₂, N₂, O₂, CH₄) in the biomethane purification.

Figure 5. Total environmental impact of the furfural and biomethane production.
3. Results and Discussion

3.3 Environmental results: Furfural

Coffee growing and therefore, the CCS obtaining presents a considerable impact in the categories assessed. The stages of vegetative growth and production are the most representative due to the fertilizers use (i.e., DAP and KCl).

The butanol use as solvent also affects the most of impact categories due to it is obtained by petrochemical route (hydroformylation of propylene).

Impact categories as CC, TA, POF, PMF and FD are influenced by the steam demand as utility and its production process.

Solid waste contributes to FET and ALO categories. Both affected by the final disposition of wet solid.

Figure 6. Sharing of the environmental impact for furfural production.
3. Results and Discussion

3.3 Environmental results: Biomethane

To take the digestate as co-product (biofertilizer) is a positive decision in the biomethane process, because it reduces considerably the emissions.

The steam requirement in the acid hydrolysis presents impact in CC, TA, POF, PMF and PD.

Streams as CCS and solid waste are common in the pretreatment of furfural and biomethane production, therefore, its contribution has the same origin.

For the obtaining of 1 kg of furfural and biomethane are needed 3.39 and 0.2 ha, respectively.

Figure 7. Sharing of the environmental impact for biomethane production.
4.1 Conclusions

The low methane yield could be due to the amounts of inhibitory compounds, 3.4 g/L of furfural and 7.7 g/L of HMF, contained in the CCS hydrolyzed. Additionally, the low concentration of sugars (less than 1.3% w/w) as a substrate source of the microorganism.

The CO$_2$ removal is required to increase the calorific value of the biogas and to be able to sell it commercially. Biogas upgrading represents 7.2% of the capital cost (CAPEX) as an initial investment.

By implementing wastewater as cooling water, the utility cost savings are 78% and 85% for the biomethane and furfural processes, respectively.

Furfural production showed economic gains when the raw material flow is above 135 ton/h. In contrast, biomethane is not feasible for any processing scale, even when the digestate is considered as co-product.

In the cradle to gate approach, biomethane production represents a lower environmental impact compared to furfural. The impact over the production process is represented in greater proportion by butanol and steam, for furfural and biomethane processes, respectively.
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5. References


5. References


THANK YOU

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