Effect of methanol-organosolv pretreatment on anaerobic digestion of lignocellulosic materials

Armando Oliva, Lea Chua Tan, Stefano Papirio, Giovanni Esposito, and Piet N. L. Lens

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Renewable energy accounted only 11% of total final energy consumption in 2018.

Renewables made up less than one-third of demand growth from 2013 to 2018.

The world is not on track to limit global warming (REN21: Renewable global status report, 2020 – Data from 2017).

Biogas:
- Few atmospheric pollutants per unit
- Several applications
- Line distribution already in place
- Globally, domestic supply of biogas was 62 million Nm³ in 2017
- Global electricity generation from biogas increased of 90% (2010-2016)
- We are exploiting only 1.6-2.2% of the potential of anaerobic digestion (World Bioenergy Association: global bioenergy statistics, 2019)
Lignocellulosic composition

- Most abundant bio-resource
- $2 \times 10^5$ Mt of biomass are globally produced every year
- 1000 Mt of dry matter are produced annually in the EU
- Low-cost waste materials
- No competition between food and energy production

Recalcitrance of LMs
- Protection by lignin and hemicellulose
- Cristallinity of cellulose
- Polymerization of cellulose
- Accessible surface (particle size, porosity)

(D. Muley and Boldor, 2017)
Anaerobic digestion process

Increase the efficacy of lignocellulose hydrolysis by improving the accessibility to cellulose

- Removing lignin and/or hemicellulose
- Decreasing the degree of polymerization and crystallinity of the cellulosic component of biomass
Pretreatment methods and raw substrates

Physical Pretreatment for lignocellulosic materials

- Mechanical comminution
  - Microwave
  - Ultrasound
  - Extrusion
  - Dilute acid
  - Alkaline
  - Organosolv
  - Ionic liquid
  - N-Methylmorpholine N-Oxide (NMMO)
  - Steam explosion
  - Hydrothermal
  - Wet oxidation
  - CO₂ explosion
  - Ammonia fibre expansion

Chemical

- Spent coffee grounds
  - 1.2 million tons/year
  - + 24% over prior 10 year average
  - ≈ 70% of the total weight is shell
  - 23% cellulose
  - 22% hemicellulose
  - 31% lignin

- Almond shell
  - 6 million tons/year
  - + 1.3% per year in the last decades
  - ≈ 50% of the fruit mass became a waste
  - 9% cellulose
  - 34% hemicellulose
  - 20% lignin

- Hazelnut skin
  - 0.5 million tons/year
  - + 16% over prior 10 year average
  - High bulk density
  - 10% cellulose
  - 4% hemicellulose
  - 40% lignin

Biological

- Fungal species
- Microbial consortium
- Enzymatic
Organosolv pretreatment

- Lignin dissolution
- Cellulose and hemicellulose in the solid phase
- Partial hemicellulose hydrolysis
- Increase of porosity
## Experimental set-up: pretreatment and anaerobic digestion

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Substrate/Solvent (w/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>50% Methanol</td>
<td>/</td>
<td>130</td>
<td>60</td>
<td>20/200</td>
</tr>
<tr>
<td>1.2</td>
<td>50% Methanol</td>
<td>/</td>
<td>160</td>
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<td>20/200</td>
</tr>
<tr>
<td>1.3</td>
<td>50% Methanol</td>
<td>/</td>
<td>200</td>
<td>60</td>
<td>20/200</td>
</tr>
<tr>
<td>2.1</td>
<td>50% Methanol</td>
<td>0.01M H$_2$SO$_4$</td>
<td>130</td>
<td>60</td>
<td>20/200</td>
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**Mesophilic AD** → 37 °C  
**Wet AD** → 2% TS  
**Inoculum/Substrate** → 1.5 g VS/g VS  

**Inoculum** → Granular Sludge  
**Substrates** → Hazelnut skin  
Spent coffee grounds  
Almond shell  

**Working Volume** → 150 mL  
**Head Space Volume** → 100 mL
- Significant biomethane production enhancement
- Increase of methane production with catalyst addition
- Amorphous aspect of treated HS
- No VFAs accumulation
- pH range: 6.3 – 7.0
Methane production: Spent coffee grounds and almond shell

- Slight increase of biomethane yield (10%)
- High biomethane potential yield of raw SCG
- No VFAs accumulation
- pH range: 6.3 – 7.0

- No biomethane yield enhancement
- Increase of methane content in biogas from 57 to 77%
- No VFAs accumulation
- pH range: 7.0 – 7.6
Recalcitrant nature of the three raw substrates:
- **Hazelnut skin**: 40% lignin, 14% sugars
- **Spent coffee grounds**: 20% lignin, 42% sugars
- **Almond shell**: 31% lignin, 45% sugars

### Pretreated hazelnut skin
- 7-12% lignin removal from hazelnut skin
- Sugar content increased from 13.7 to **17.3%**
- Strong inverse correlation between lignin content and cumulative methane production

### Pretreated spent coffee grounds
- Slight increase of sugars content
- The maximum lignin removal was **10%**

### Pretreated almond shell
- No significant effect
Why is the organosolv pretreatment failing for AS and SCG?

**Chemical composition**
- Lignin Content
  - Almond Shell: 30.58 (± 0.13) g/g TS
  - Spent Coffee Grounds: 20.31 (± 0.29) g/g TS
- Loss of non-structural compounds during the pretreatment (sucrose, glucose, fructose)

**Physical characteristics**
- Porosity
  - AS = 1.40 (± 0.10) g/g
  - SCG = 2.76 (± 0.06) g/g
  - HS = 5.53 (± 0.49) g/g
- Water swelling capacity
  - Almond Shell: 30.58 (± 0.13) g/g TS
  - Spent Coffee Grounds: 20.31 (± 0.29) g/g TS
- Surface morphology (SEM)
Conclusions and future prospective

- Methanol-organosolv pretreatment was particularly effective to enhance biogas production for hazelnut skin.
- Methanol-organosolv pretreatment was slightly effective for spent coffee grounds and ineffective for almond shell.
- Catalyst addition enabled to gain a higher methane production from hazelnut skin with the lowest pretreatment temperature.
- The economic viability of the pretreatment for hazelnut skin is confirmed by the energy assessment, with a net positive energy recovery of 1.35 kWh/kg VS deriving from the extra biomethane produced under the optimal pretreatment condition.

- Maximize and optimize lignin recovery from pretreatment liquor.
- Verify the economic viability of the recovery of valuable compounds before undergoing pretreatment and anaerobic digestion (proteins, phenolic compounds, lipids, non-structural sugars).
- Further studies are required to explore different pretreatments able to raise the biomethane potential of spent coffee grounds and almond shell (ionic liquid, milling).
THANK YOU