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

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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.

- **Overview**
  - Renewable energy
  - Depletion of fossil fuel
  - Global environmental quality
  - 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

- **Biogas**
  - Few atmospheric pollutants per unit
  - Several applications
  - Line distribution already in place
  - Globally, domestic supply of biogas was 62 million Nm$^3$ 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
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**
- Mechanical comminution
  - Microwave
  - Ultrasound
  - Extrusion
- Dilute acid
- Alkaline
- Organosolv

**Chemical**
- Ionic liquid
- N-Methylmorpholine N-Oxide (NMMO)
- Steam explosion
- Hydrothermal
- Wet oxidation
- CO₂ explosion
- Ammonia fibre expansion

**Physico-chemical**
- Fungal species
- Microbial consortium
- Enzymatic

**Biological**

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

**Spent coffee grounds**
- 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
Organosolv pretreatment

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

| Experiment | Solvent            | Catalyst       | Temperature (°C) | Time (min) | Substrate/Solvent (w/v) |
|------------|--------------------|----------------|------------------|------------|-------------------------|
| 1.1        | 50% Methanol       | /              | 130              | 60         | 20/200                  |
| 1.2        | 50% Methanol       | /              | 160              | 60         | 20/200                  |
| 1.3        | 50% Methanol       | /              | 200              | 60         | 20/200                  |
| 2.1        | 50% Methanol       | 0.01M H₂SO₄    | 130              | 60         | 20/200                  |
| 2.2        | 50% Methanol       | 0.01M H₂SO₄    | 160              | 60         | 20/200                  |
| 2.3        | 50% Methanol       | 0.01M H₂SO₄    | 200              | 60         | 20/200                  |

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
Methane production: Hazelnut skin

- 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: $30.58 \pm 0.13$ g/g TS
  - Spent Coffee Grounds: $20.31 \pm 0.29$ g/g TS
- Loss of non-structural compounds during the pretreatment (sucrose, glucose, fructose)

**Physical characteristics**
- Porosity
  - AS = $1.40 \pm 0.10$ g/g
  - SCG = $2.76 \pm 0.06$ g/g
  - HS = $5.53 \pm 0.49$ g/g
- Water swelling capacity
- 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

Any Questions