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

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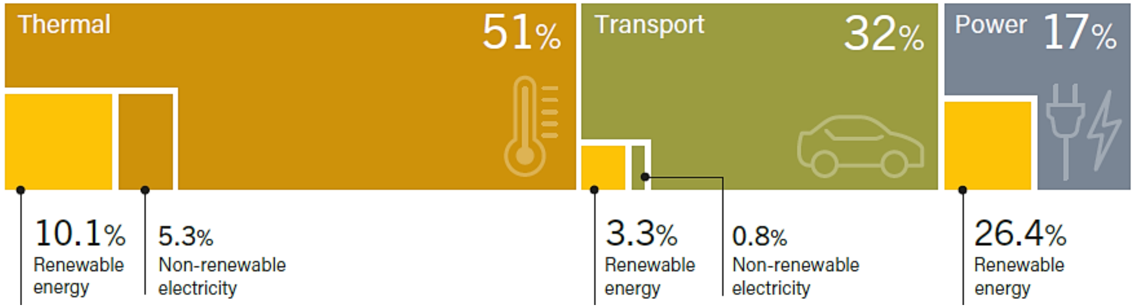
8TH INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT

24 June 2021

Overview

Renewable energy

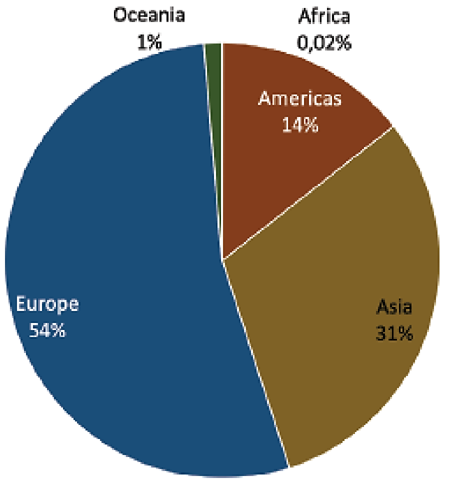
- Depletion of fossil fuel
- Global environmental quality
- Renewable energy accounted **only 11%** of total final energy consumption in 2018
- Renewables made up less than one-third of demand growth from 2013 to 2018
- The world is **not on track** to limit global warming



(REN21: Renewable global status report, 2020 – Data from 2017)

Biogas

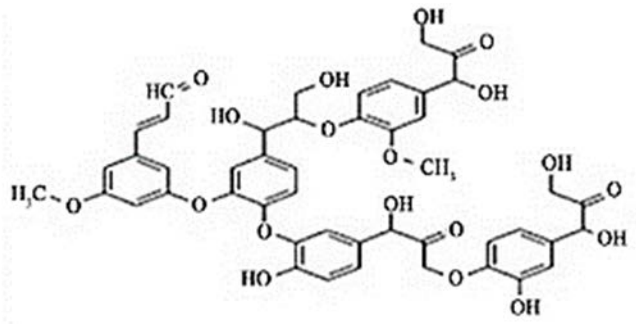
- Few atmospheric pollutants per unit
- Several applications
- Line distribution already in place
- **Globally, domestic supply of biogas was 62 million Nm^3 in 2017**
- Global electricity generation from biogas increased of 90% (2010-2016)
- We are exploiting **only 1.6-2.2%** of the potential of anaerobic digestion

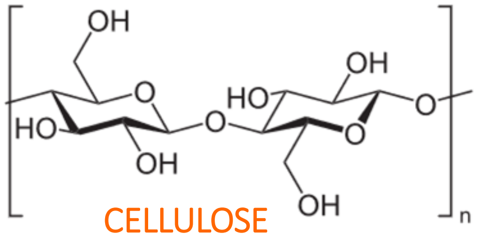


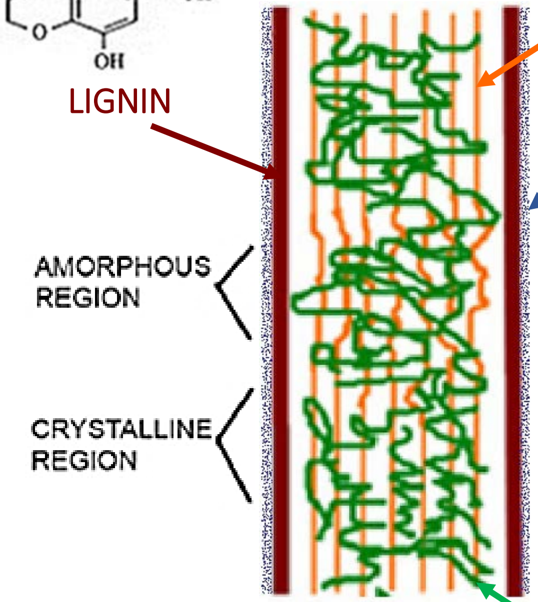
(World Bioenergy Association: global bioenergy statistics, 2019)

Lignocellulosic composition

- Most abundant bio-resource
- 2×10^5 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

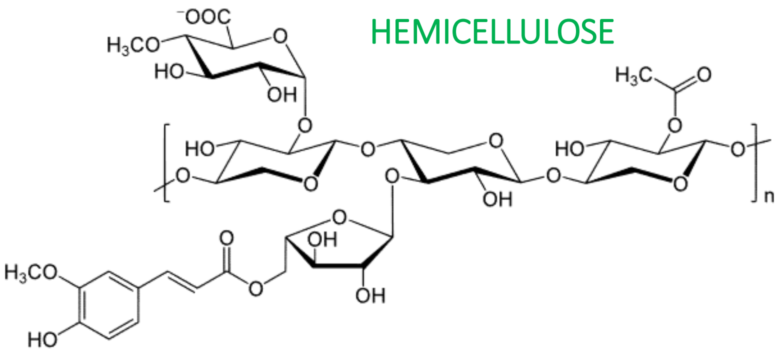






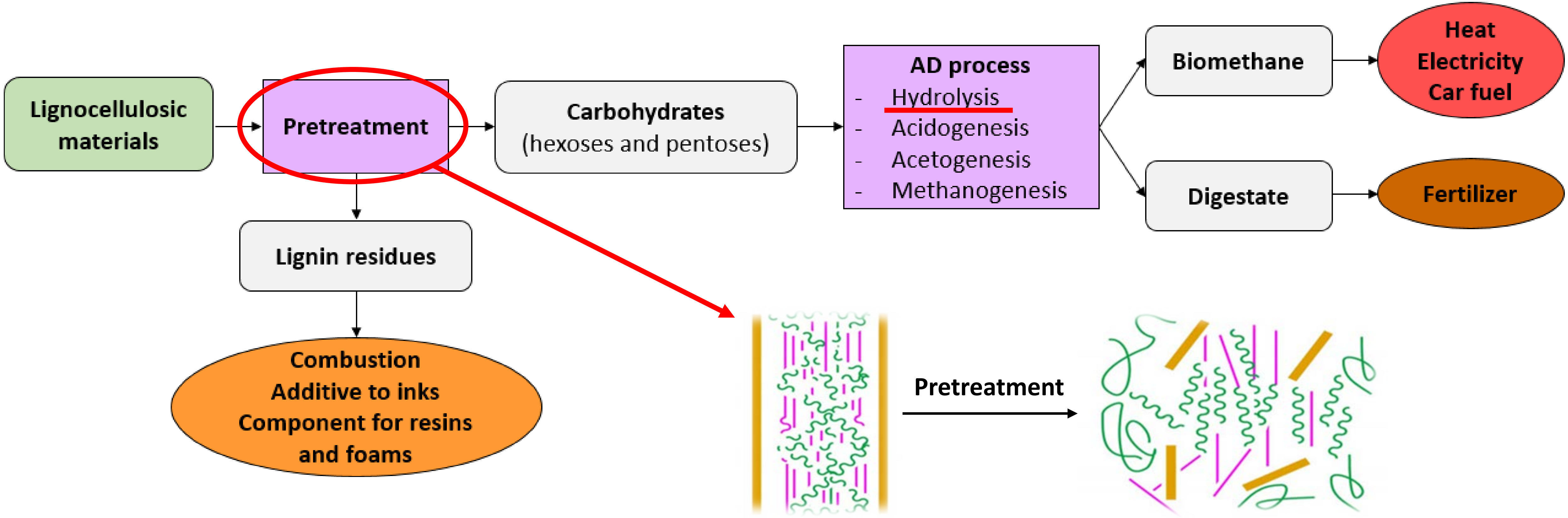
Non-structural sugars
Protein
Nitrate/Nitrite
Ash
Chlorophyll
Waxes

(D. Muley and Boldor, 2017)



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

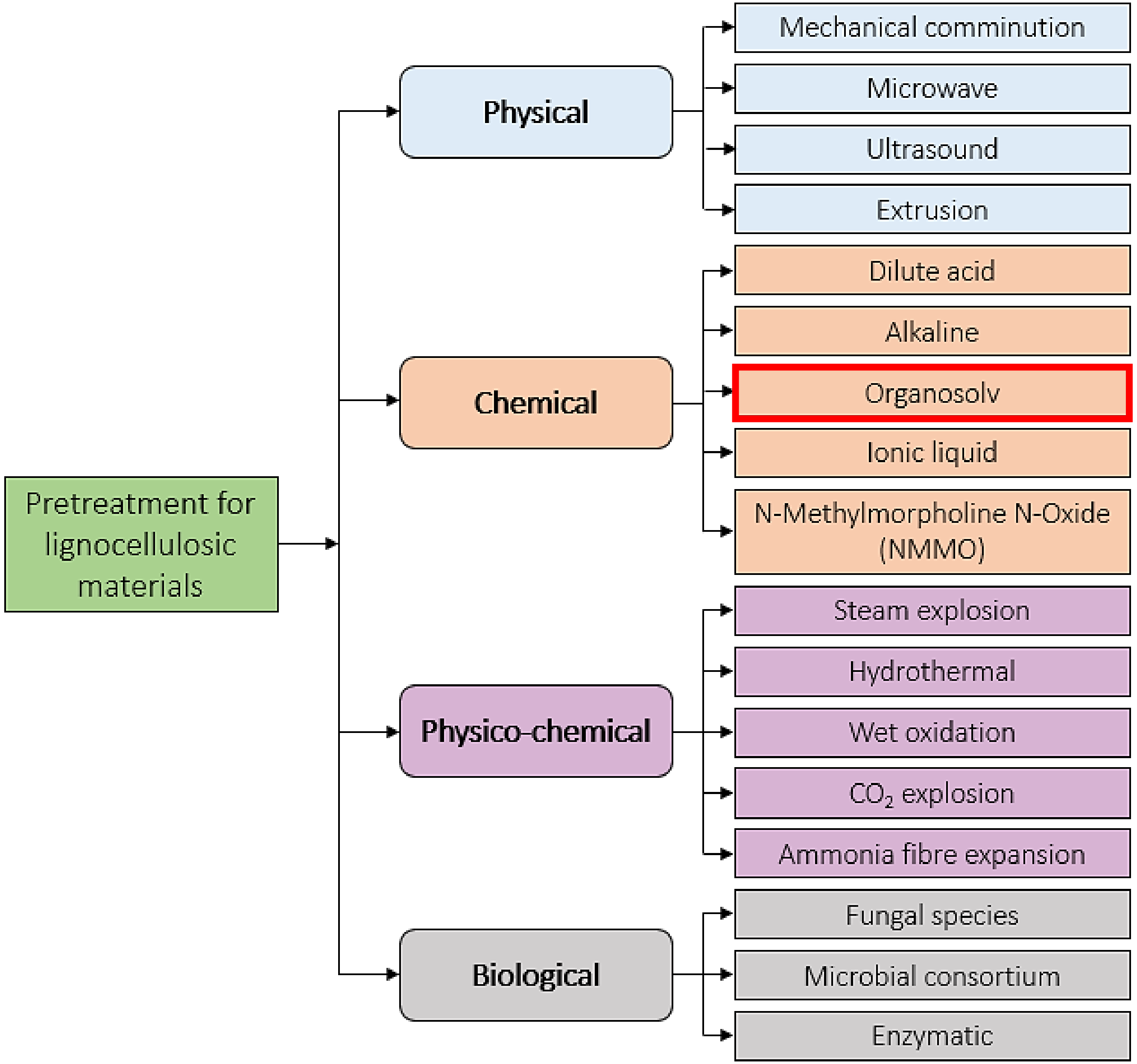
Anaerobic digestion process



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



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

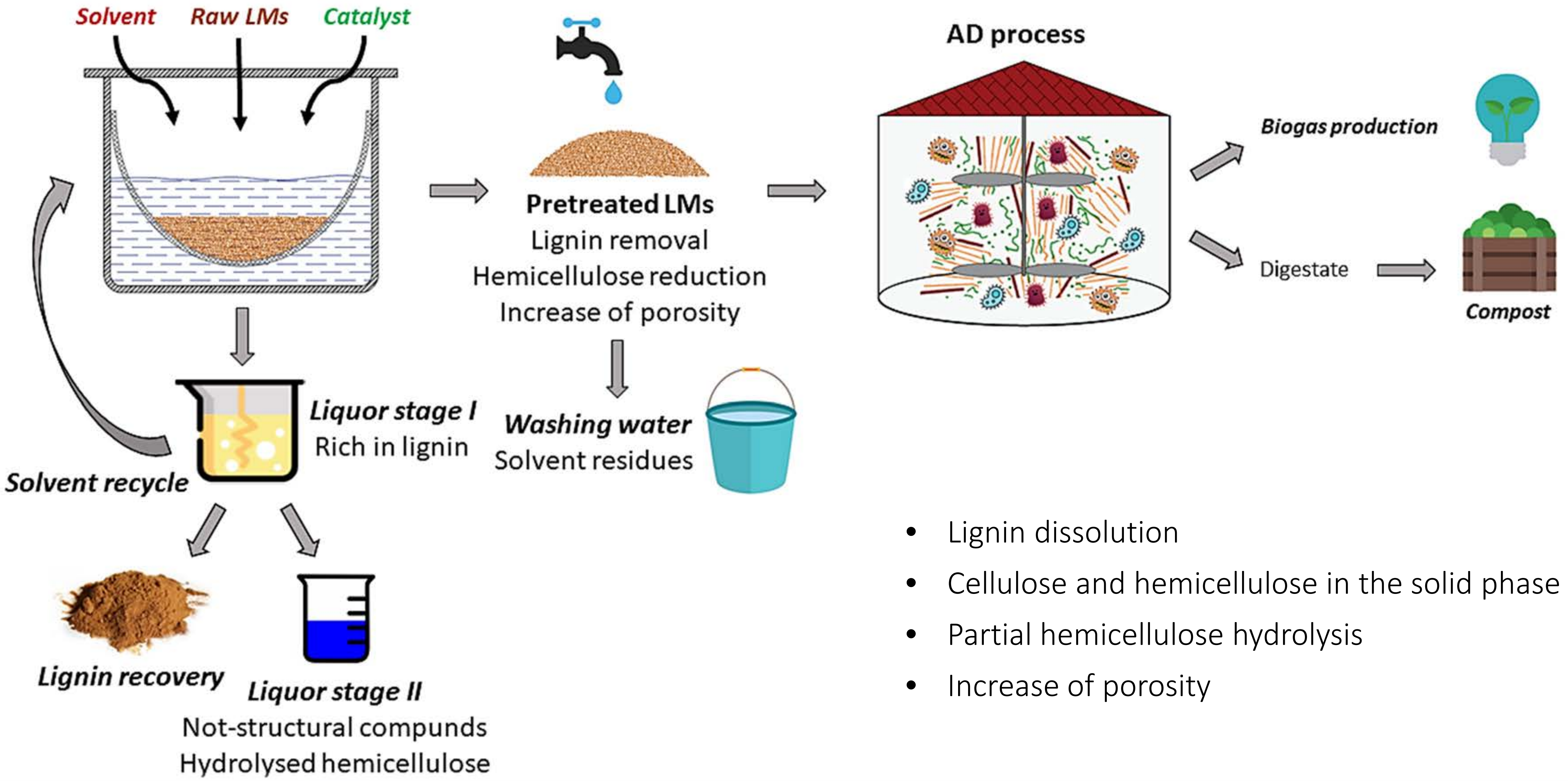
9% cellulose
34% hemicellulose
20% lignin

Hazelnut skin

0.5 million tons/year
+ 16% over prior 10 year average
High bulk density

10% cellulose
4% hemicellulose
40% lignin

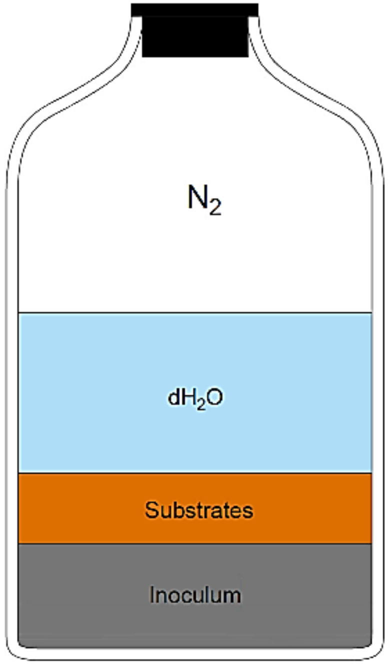
Organosolv pretreatment



- 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 H_2SO_4	130	60	20/200
2.2	50% Methanol	0.01M H_2SO_4	160	60	20/200
2.3	50% Methanol	0.01M H_2SO_4	200	60	20/200



Mesophilic AD → 37 °C
Wet AD → 2% TS
Inoculum/Substrate → 1.5 g VS/g VS

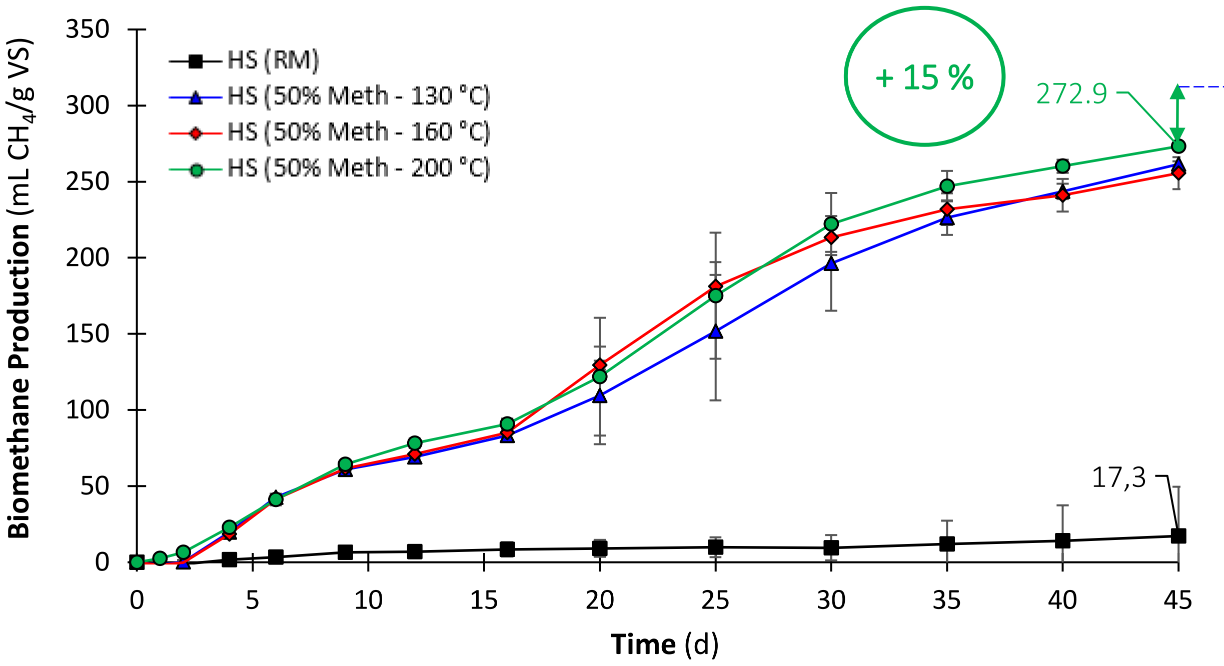
Inoculum → Granular Sludge

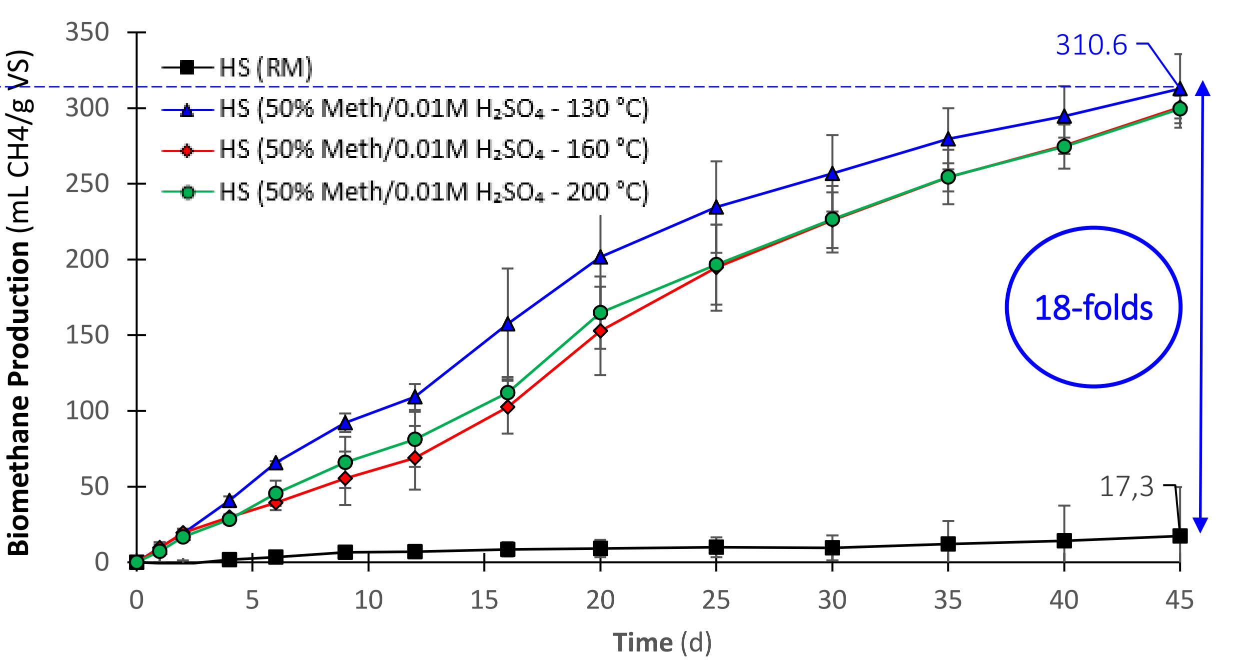
Substrates → Hazelnut skin
Spent coffee grounds
Almond shell

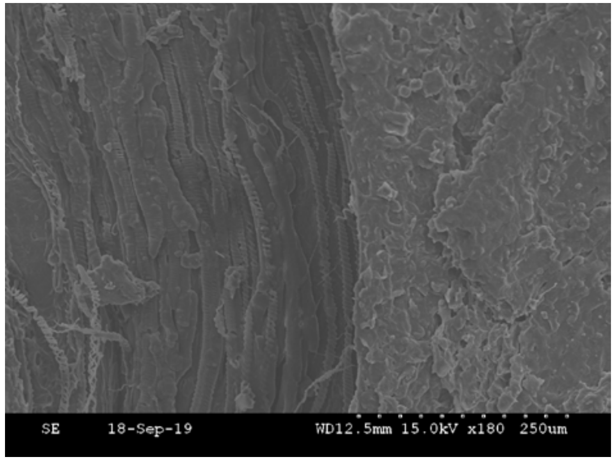
Working Volume → 150 mL

Head Space Volume → 100 mL

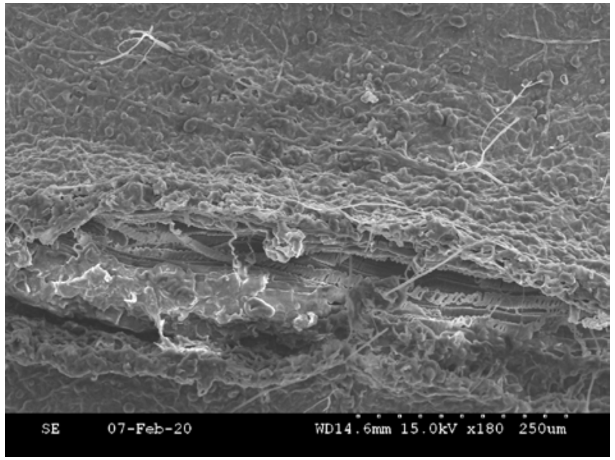
Methane production: Hazelnut skin



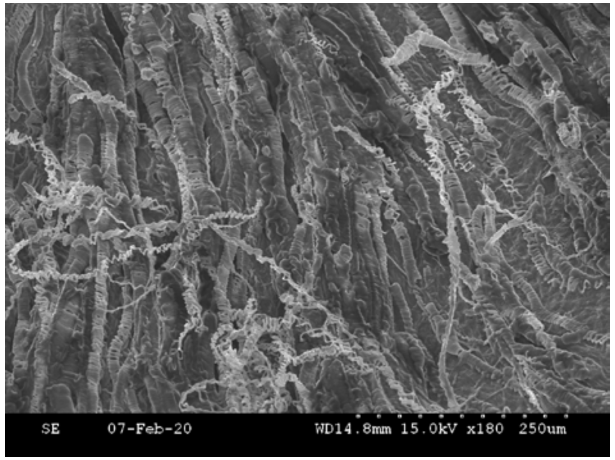




Raw HS



Pretreated HS (130 °C)

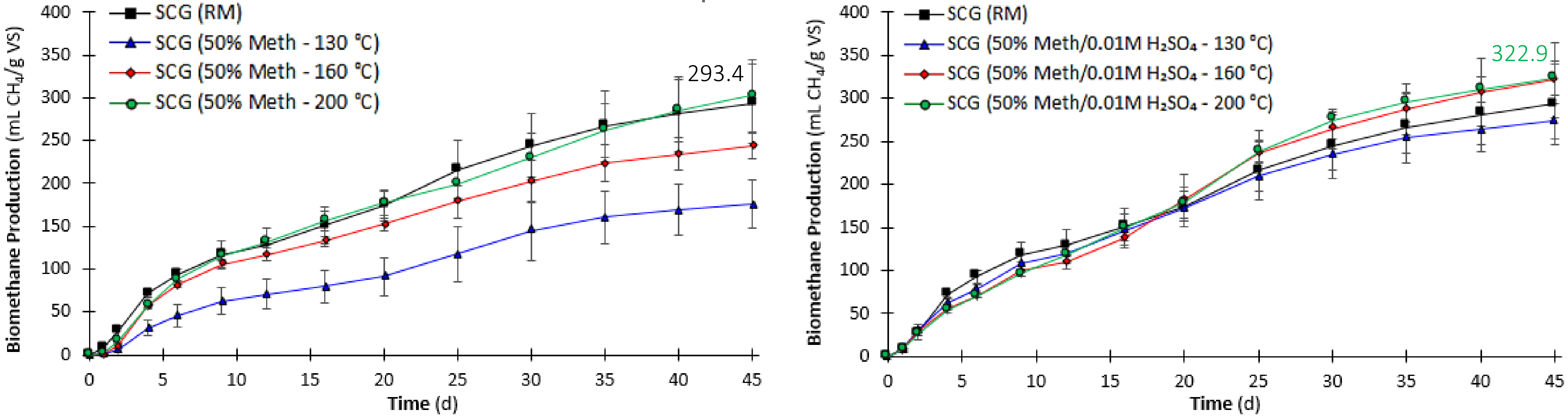


Pretreated HS (130 °C + Cat)

- 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

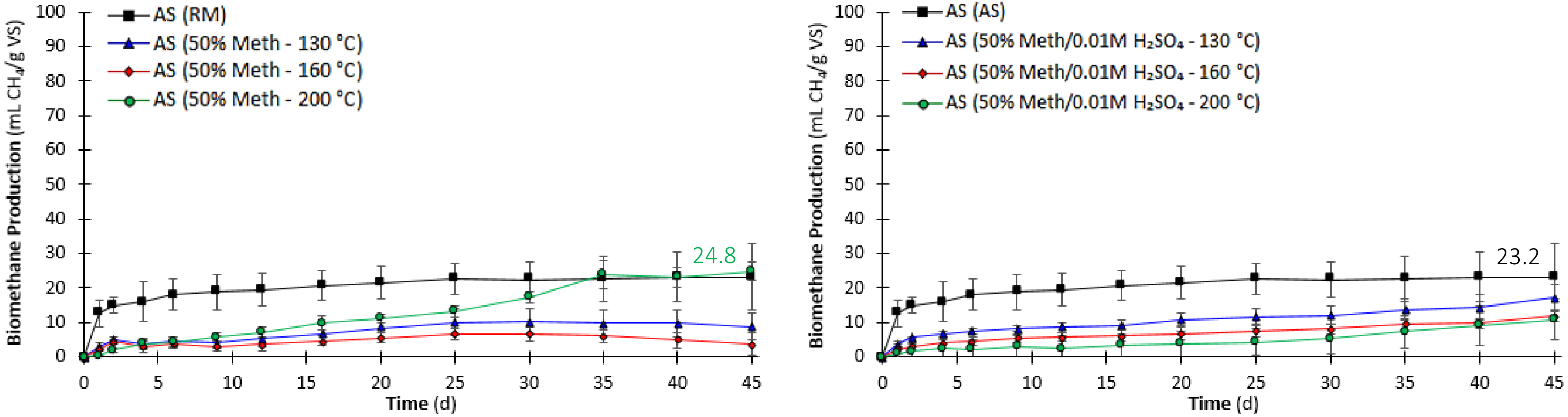
Methane production: Spent coffee grounds and almond shell

Spent Coffee Grounds



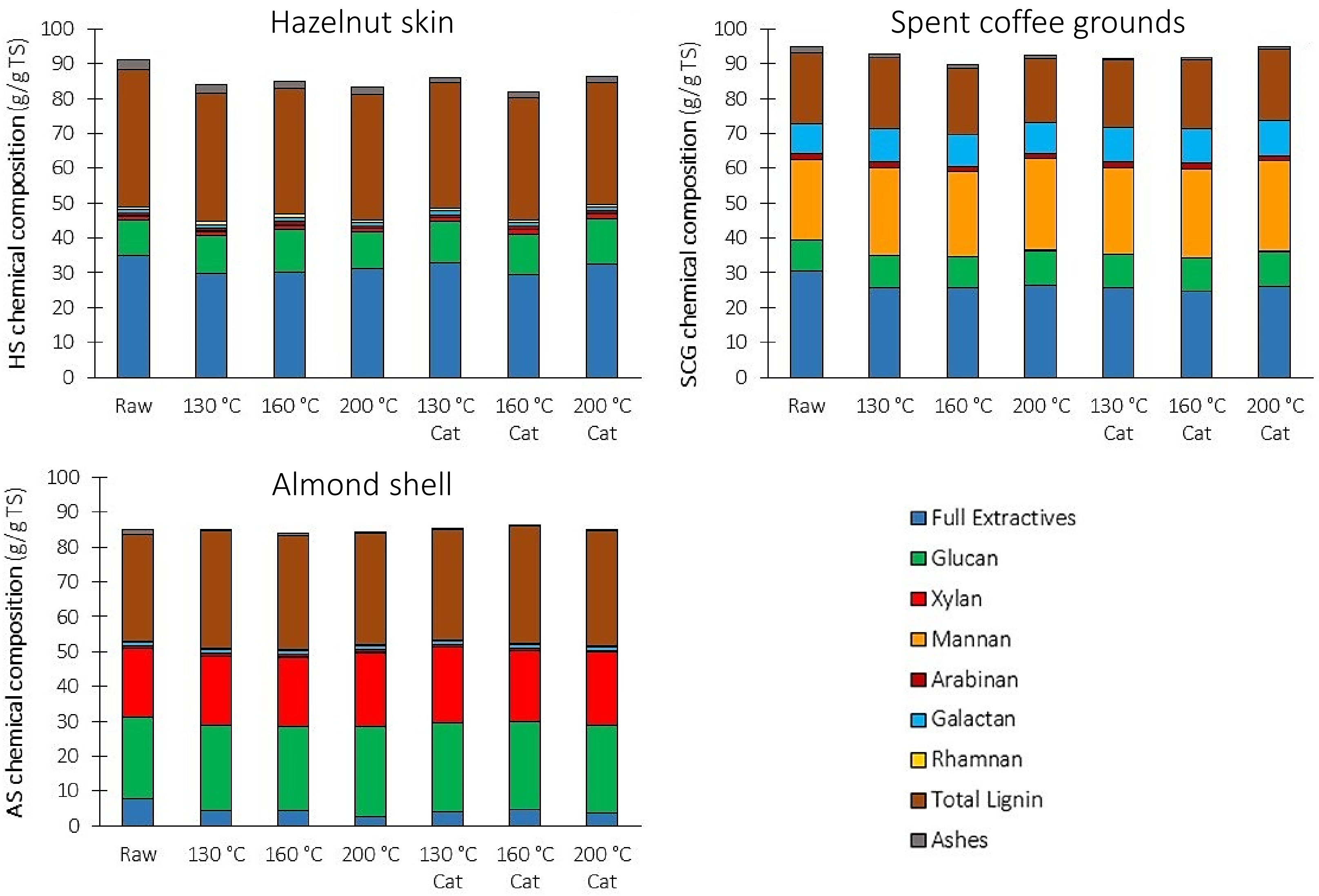
- Slight increase of biomethane yield (10%)
- High biomethane potential yield of raw SCG
- No VFAs accumulation
- pH range: 6.3 – 7.0

Almond Shell



- No biomethane yield enhancement
- Increase of methane content in biogas from 57 to 77 %
- No VFAs accumulation
- pH range: 7.0 – 7.6

Effect on chemical composition



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%**

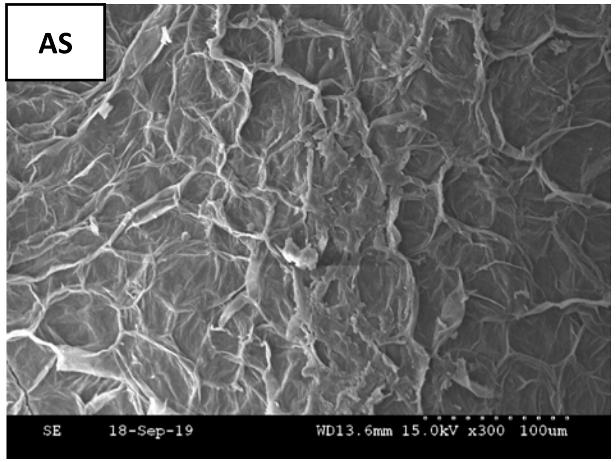
Pretreated almond shell

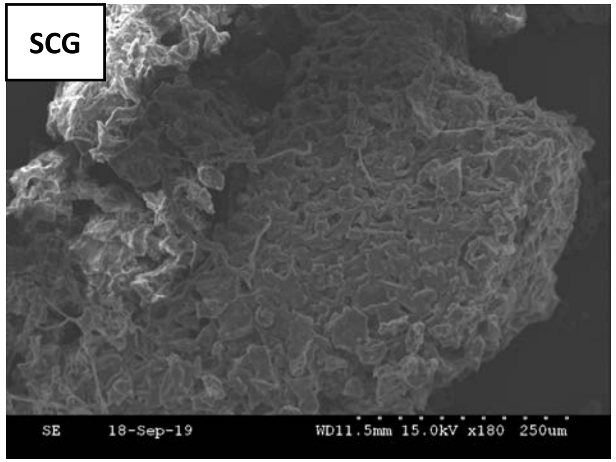
- No significant effect

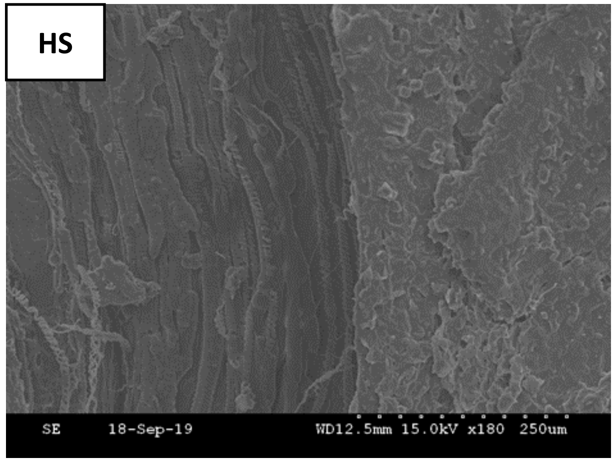
Why is the organosolv pretreatment failing for AS and SCG?

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 →
- Water swelling capacity
  - AS = 1.40 (± 0.10) g/g
  - SCG = 2.76 (± 0.06) g/g
  - HS = 5.53 (± 0.49) g/g
- 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