BiOMeGaFuel

Bio Methanol Production via Chemical Looping Gasification Coupled with Membrane Reactors

SYNGAS PRODUCTION FROM BIOGENIC RESOURCES WITH NEGATIVE CO_2 EMISSIONS THROUGH CHEMICAL LOOPING GASIFICATION (CLG)

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Background and Motivation

❖ Why Biofuels production?

- ❖ Reduce dependence on fossil fuels.
- ❖ Critical to **decarbonizing hard-to-abate sectors**: aviation, shipping, heavy transport.

❖ Why Methanol ?

- ❖ Versatile: used in **combustion engines**, blended fuels, fuel cells, and **chemical feedstock**.
- ❖ **Biomethanol** significantly lowers GHG emissions vs fossil methanol.
- ❖ Maritime progress:
  - ❖ **Stena Germanica**: world's 1st methanol-powered vessel → SOx & particle emissions cut by 90%.
  - ❖ **Maersk**: first methanol-powered vessel launched.
- ❖ Methanol in **fuel cells**: higher efficiency, easier storage vs hydrogen.

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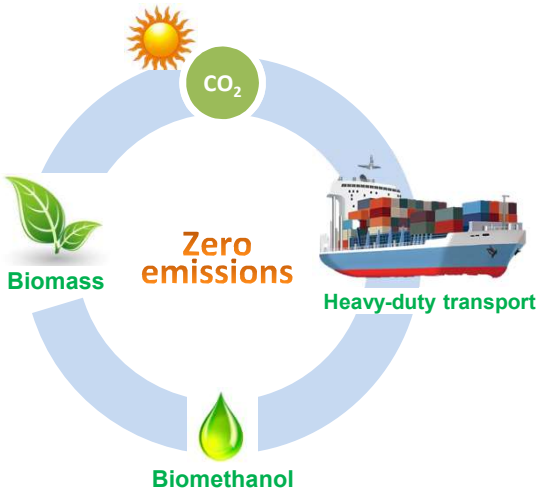
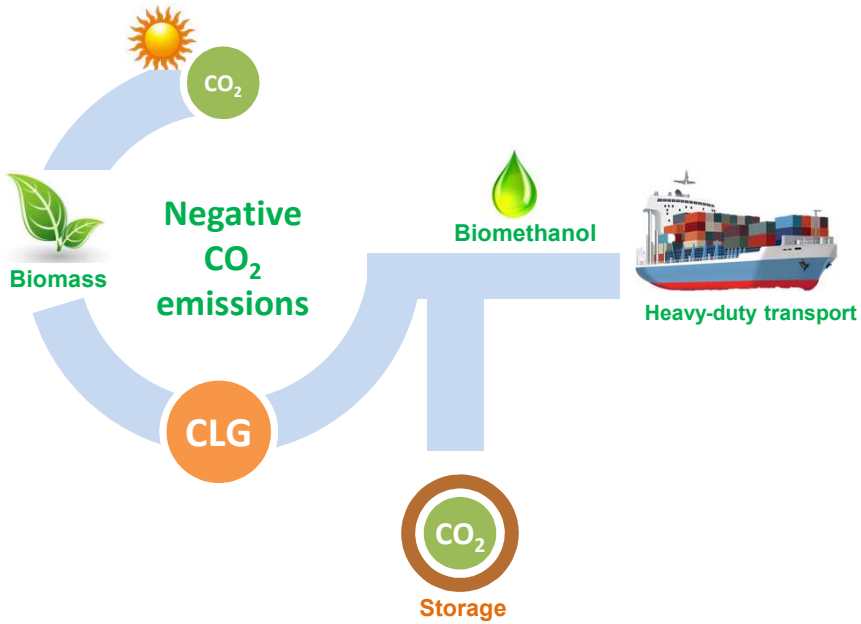
Biomethanol and Negative CO_2 emissions





Chemical Looping Gasification – with CO_2 capture-

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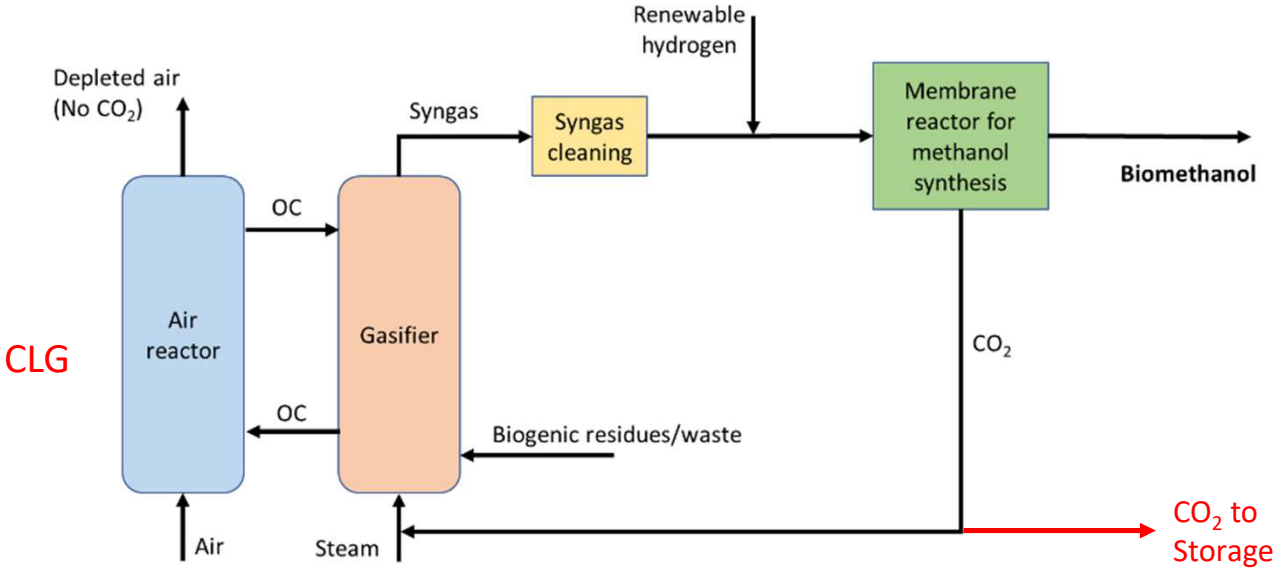
Bio-MeGaFuel concept

Novel efficient, and scalable process to convert **low-value biogenic residues** and organic waste to **biomethanol** through chemical looping gasification coupled with membrane reactors



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Bio-MeGaFuel participants

- The Bio-MeGaFuel project has an expert consortium. It consists of **9 partners from 5 countries** and includes:
  - Three Research Institutes:
    - **RISE** Research Institutes of Sweden
    - **IVL** Swedish Environmental Research Institute
    - **CSIC** The Spanish National Research Council
  - Two Universities:
    - **TUDA** The Technical University of Darmstadt
    - **TU/e** Eindhoven University of Technology
  - Four Companies:
    - **GIDARA Energy** Technology Provider
    - **Perpetual Next**
    - **1Cube**
    - **Blue World Technologies**

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Chemical Looping Gasification

Delivers high quality non-N_2 diluted syngas without the need of ASU and with reduced tar formation.
CO_2 is concentrated in syngas, thus Negative CO_2 emissions can be reached if CCS

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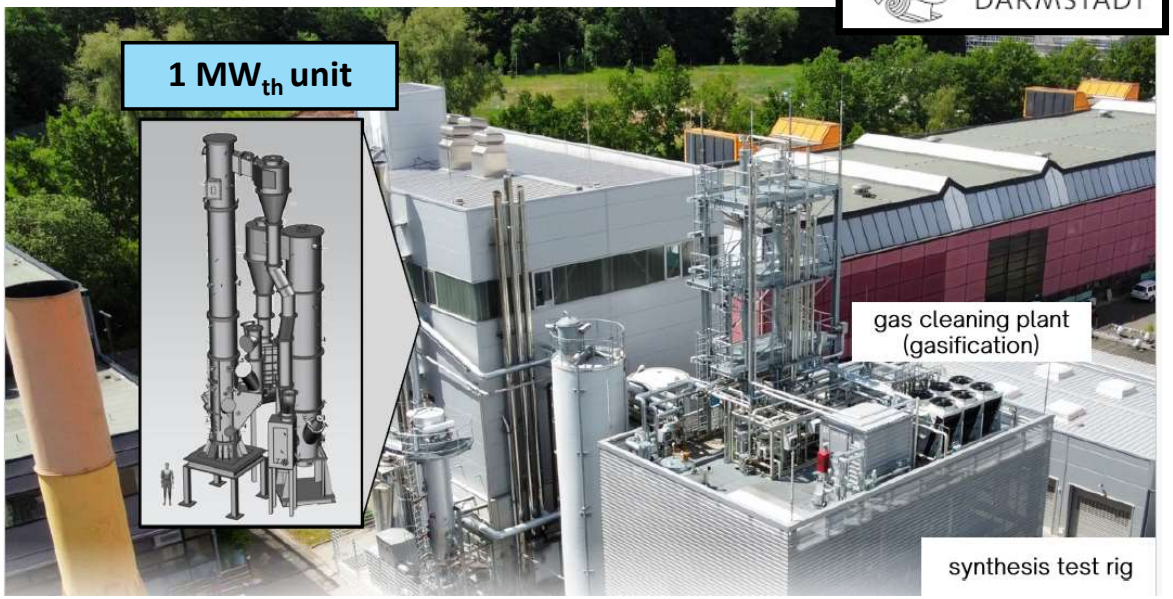
20 kW_{th} unit

TECHNISCHE UNIVERSITÄT DARMSTADT



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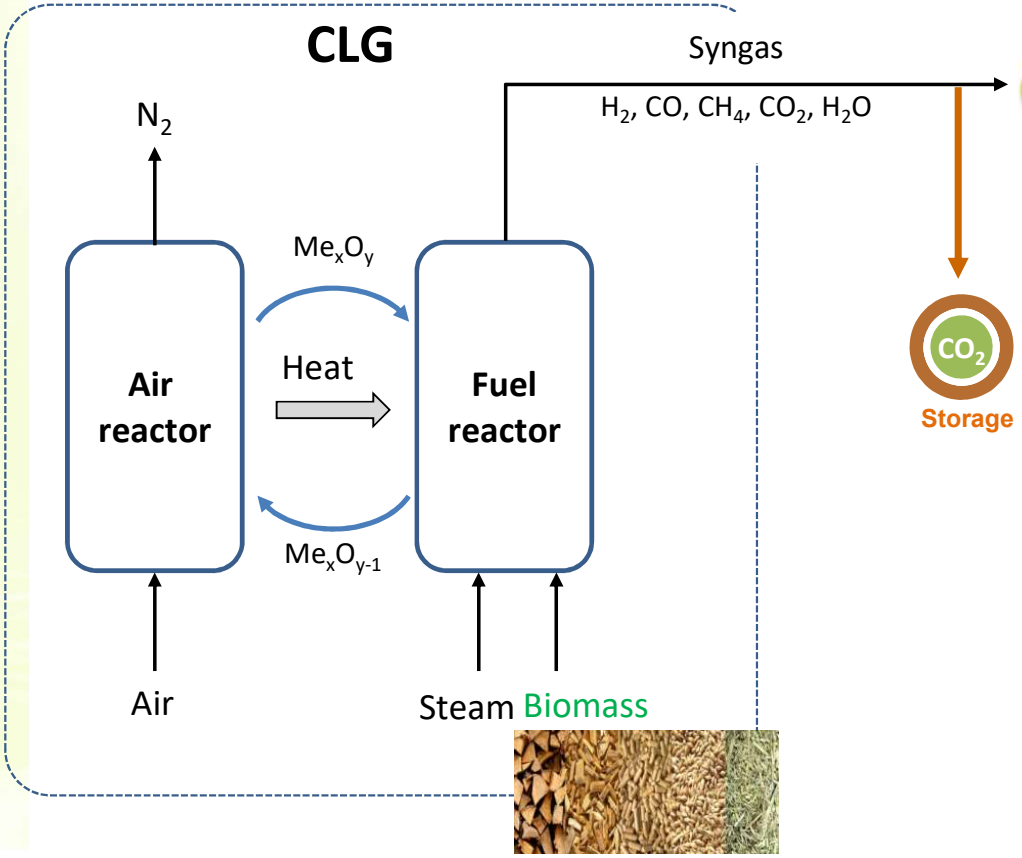
Chemical Looping Gasification



- Pure syngas stream (no N_2 dilution and without using ASU unit)
- Autothermic
- Less steam consumption than conventional gasification processes
- Low tar generation (catalytic cproperties of the Me_xO_y)
- Less corrosion in heat exchangers (located in AR)
- Less emission of CO_2 to the atmosphere (CO_2 concentrated in syngas).

NEGATIVE emissions possible

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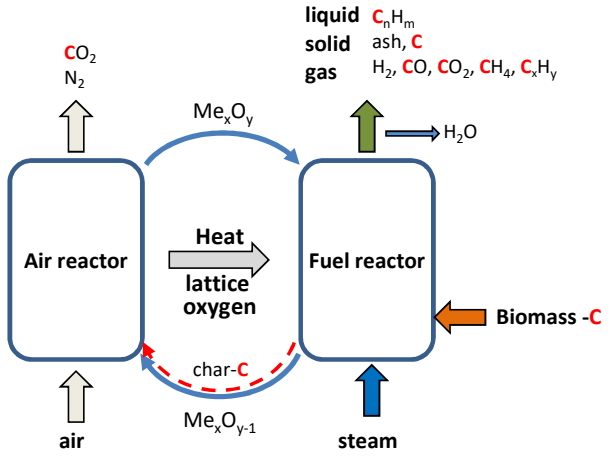
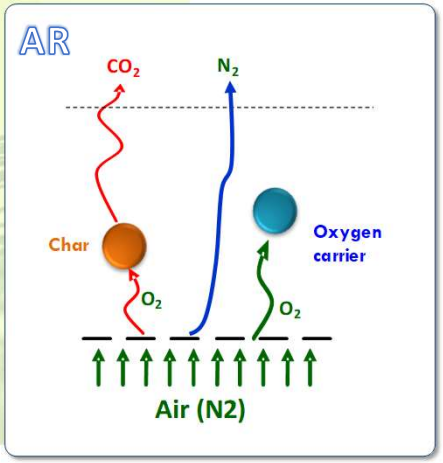
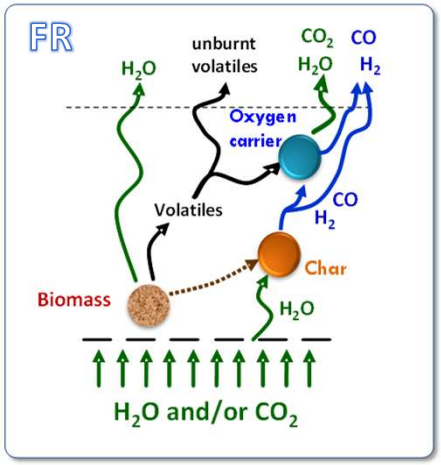
Chemical Looping Gasification







FR

- Drying and devolatization:

  Biomass $\rightarrow$ H_2O + Volatiles + Char

- Char gasification:

  Char + H_2O $\rightarrow$ H_2 + CO

  Char + CO_2 $\rightarrow$ 2 CO

- Volatile oxidation by the oxygen carrirer

  Volatiles / H_2 + CO + Me_xO_y $\rightarrow$ Me_xO_{y-1} + H_2O + CO_2

- Water-Gas Shift

  CO + H_2O $\leftrightarrow$ CO_2 + H_2

AR

- Oxygen carrier oxidation:

  Me_xO_{y-1} + O_2 $\rightarrow$ Me_xO_y

- Char combustion:

  C + O_2 $\rightarrow$ CO_2

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Objective

The objective is to evaluate in a 20 kW_{th} CLG facility the gasification performance and the syngas quality of four representative European second-generation biogenic residues

- Evaluation of different fuel reactor temperatures and oxygen-to-fuel ratios, together with the influence the steam-to-CO_2 ratio used as the gasifying agent
- Providing a basis for optimizing CLG operation and feedstock selection for diverse syngas applications within the European bioeconomy

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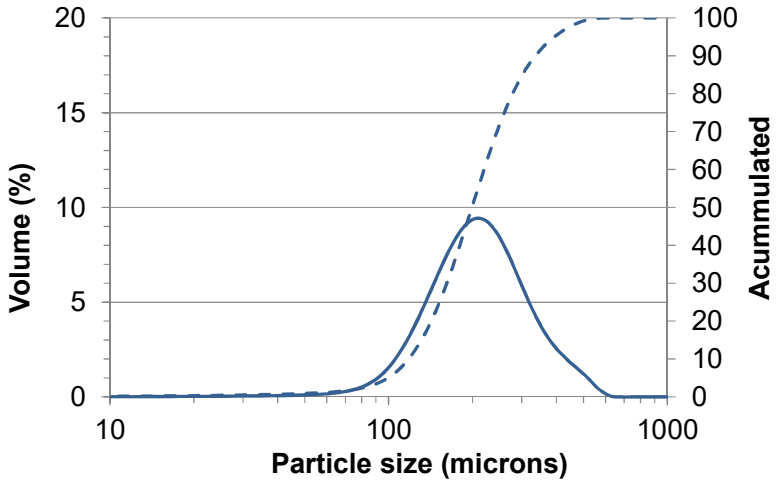
Selection of oxygen carrier

Fresh ilmenite from Titania, Norway.
Calcination: 950 ºC in air for 2 h
Circulated 6 h at 800 ºC in air

Fe_2TiO_5	54.7 wt.%
Fe_2O_3	11.2 wt.%
TiO_2	28.6 wt.%
Inerts	5.5 wt.%



	Calcined ilmenite
Particle size (mm)	100-300
True density (kg/m^3)	4100
$R_{O,ilm}$ (%)	4.0
Porosity (%)	1.2
Crushing strength(N)	2.2
XRD (main species)	Fe_2TiO_5, Fe_2O_3, TiO_2

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Selection of biogenic residues

ANALYSIS (wt.%)	Waste Wood Type B (WWB)	Olive pits (OS)	Buckwheat husk (BW)	Spruce branches (SP)
Size (mm)	L: 10, Ø:6	0.5-3.2	L: 10, Ø:6	0.5-10
Moisture	6.8	7.3	9.7	8.0
Ash	1.7	0.3	2.0	2.5
Volatiles	74.2	74.9	66.4	72.1
Fixed carbon	17.3	17.4	21.8	17.5
C	46.3	46.3	45.0	46.7
H	5.5	5.5	5.2	5.4
N	1.1	1.1	0.6	0.4
S	0	0	<0.1	<0.1
O(by diff.)	38.5	38.5	38.5	37.0
LHV (kJ/kg)	16664	17352	16375	16808

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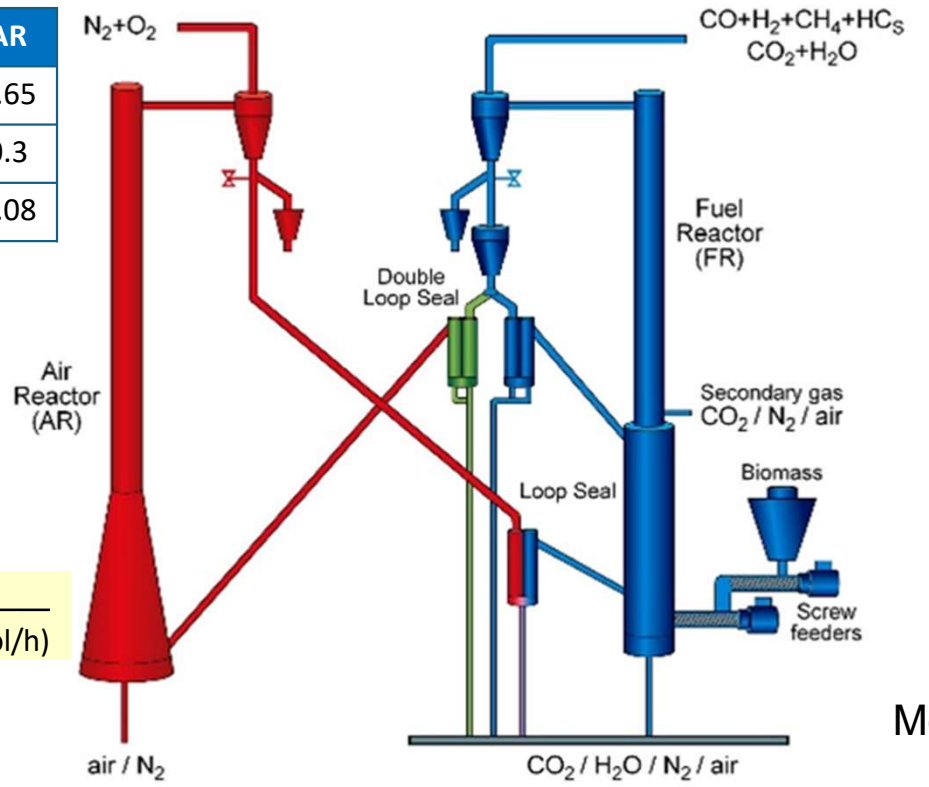
The 20kW$_{th}$ CLG unit at CSIC

	FR	AR
Height (m)	4.0	4.65
Diameter bottom (m)	0.1	0.3
Diameter up (m)	0.08	0.08



FR temperature (T_{FR})
850 – 950 ºC
Oxygen-to-fuel ratio (λ)
0.19-0.50
Steam-to-CO_2 ratio (S/CO_2)
25/75, 50/50, 75/25, 100/0

$$\lambda = \frac{\text{oxygen fed in AR (mol/h)}}{\text{oxygen for full combustion (mol/h)}}$$

More than **85 h of steady-state** operation

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Performance evaluation: Key Performance Indicators

BIOMASS CONVERSION

$$X_b = \frac{carbon\ in\ gaseous\ compounds\ from\ FR\ and\ AR}{carbon\ in\ the\ biomass\ fed}$$

CARBON EMITTED IN AR

$$C_{AR} = \frac{carbon\ in\ gases\ from\ AR}{carbon\ in\ the\ biomass\ fed}$$

SYNGAS YIELD

$$Y_g = \frac{flow\ of\ H_2\ and\ CO\ from\ FR\ (\frac{mol}{h})}{biomass\ feeding\ rate\ (\frac{kg}{h})}$$

HC YIELD

$$Y_{HC} = \frac{flow\ of CH_4\ and\ C_2 - C_3\ from\ FR\ (\frac{mol}{h})}{biomass\ feeding\ rate\ (\frac{kg}{h})}$$

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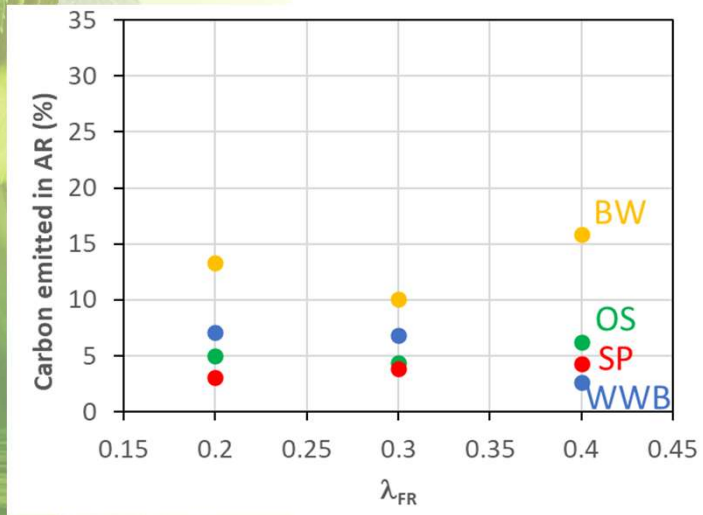
Influence of oxygen-to-fuel ratio (λ)

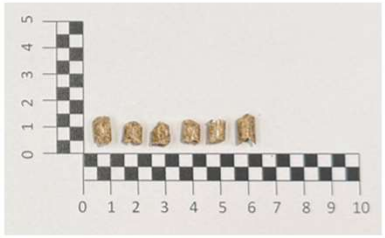
Air reactor

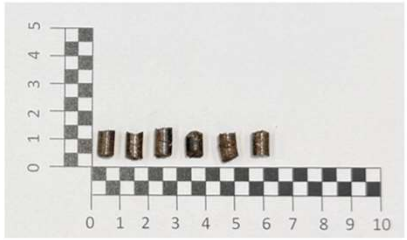


Wastewood-B raw pellets

Buckwheat Husk raw pellets

Spruce


Wastewood-B crushed pellets


Buckwheat Husk crushed pellets

Olive stone

- Biomass conversion higher than 90% for all the biogenic residues
- C_{AR} <5% for spruce (SP) and olive stones (OS). Larger values for WWB and BW pellets due to their larger size

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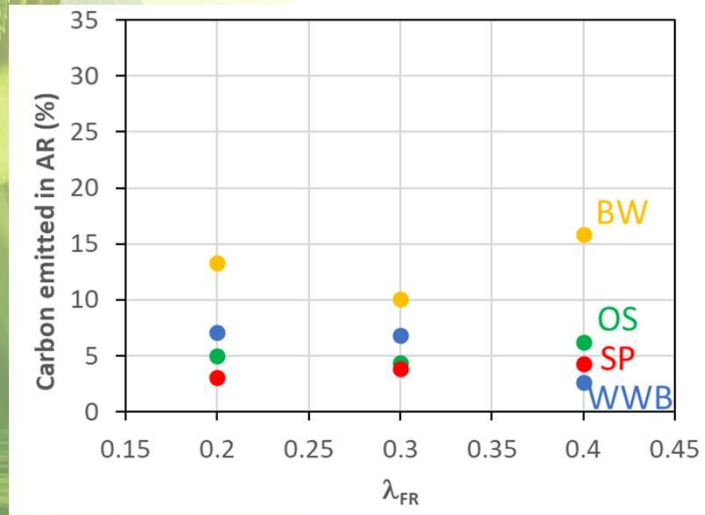
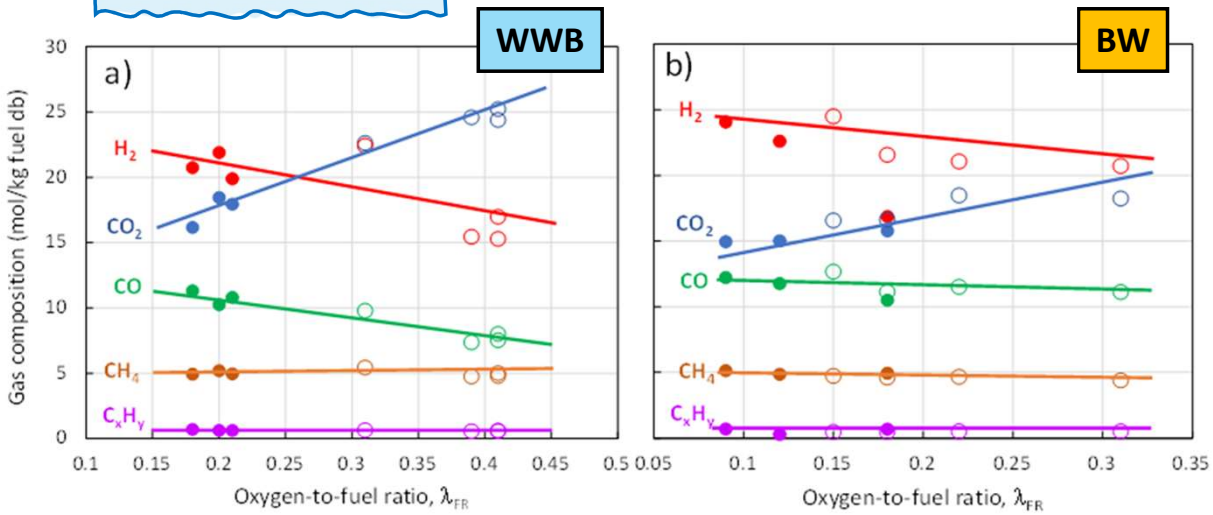
Influence of oxygen-to-fuel ratio (λ)

Air reactor



Fuel reactor



- An increase in λ produced an increase in CO_2 flow and a decrease in the H_2 and CO generated
- High amount of CH_4 and C_2-C_3 hydrocarbons

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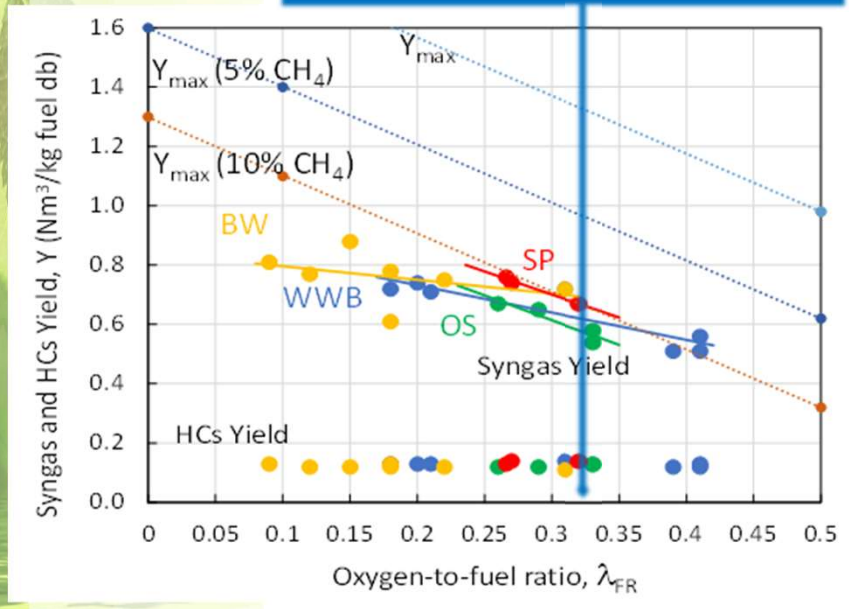
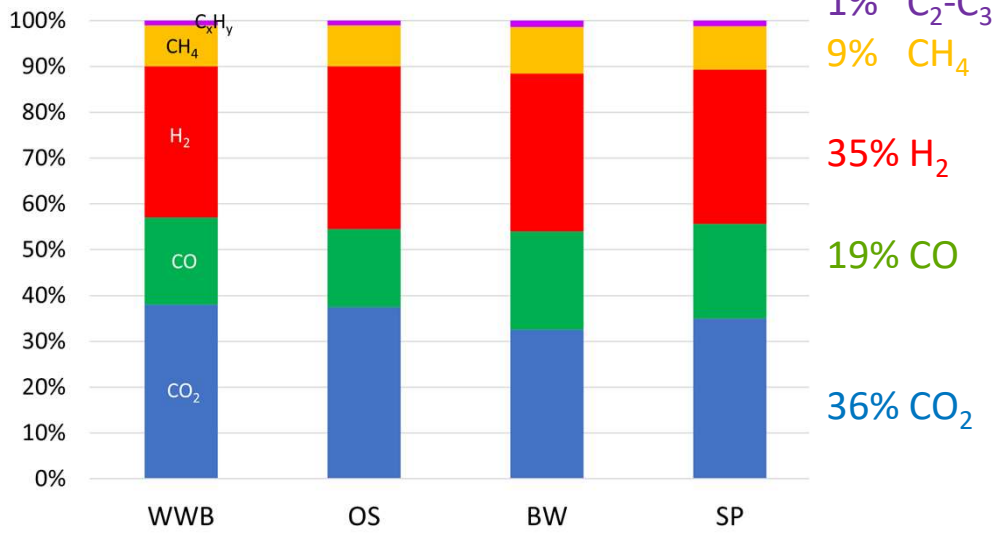
Influence of oxygen-to-fuel ratio (λ)

AUTOTHERMAL CONDITIONS



AUTOTHERMAL CONDITIONS



- Syngas yield (Y_g) decreased when increasing λ while hydrocarbon yield (Y_{HC}) was not affected
- Slight differences between the four biogenic residues
- The syngas produced depends more on λ than on the type of biogenic residue

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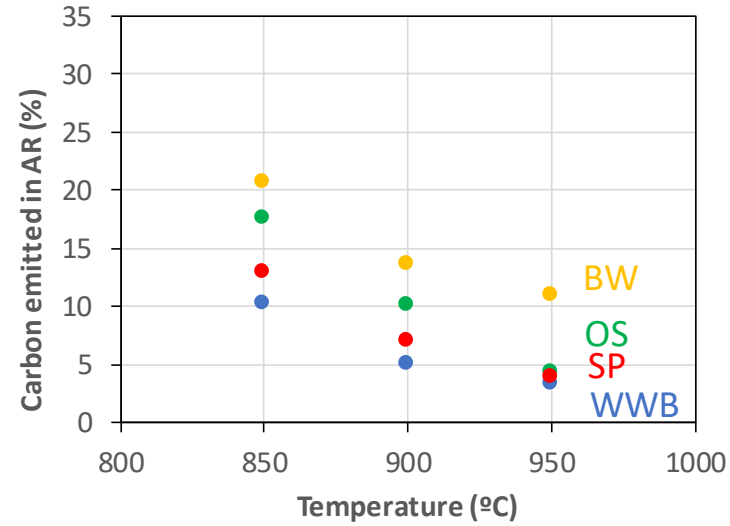
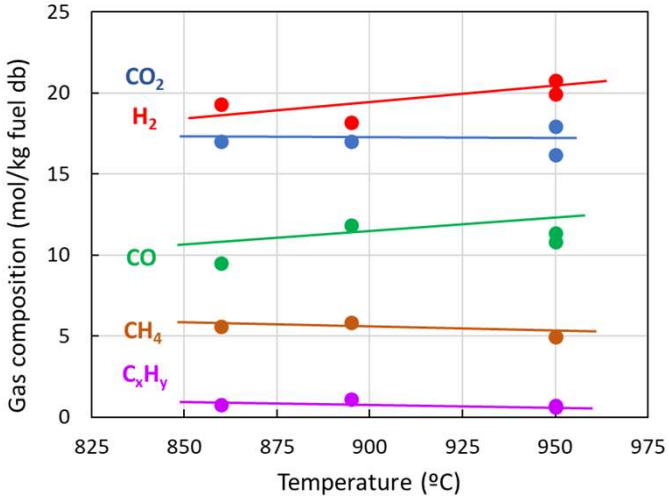
Influence of FR temperature

Air reactor



- Carbon emitted in AR decrease with increasing temperature

Fuel reactor



- Syngas composition weakly affected by temperature: governed primarily by λ
- CH_4 and the C_2–C_3 fraction remained high

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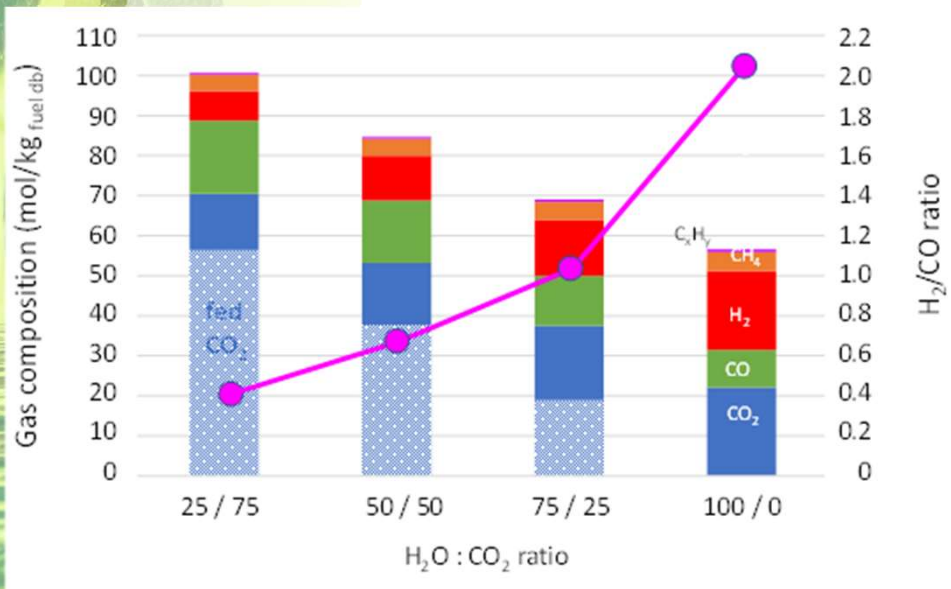
Influence of steam-to-CO_2 ratio (S/CO_2)

Olive Stone, T_{FR} = 950 ºC and λ ~ 0.3



- As the S/CO_2 ratio decreased, the amount of CO_2 generated decreased, whereas the CO produced grew moderately
- Only a small fraction of the additional CO_2 supplied was converted into CO via the Boudouard reaction, while most of the fed CO_2 left the fuel reactor unreacted
- The H_2 yield decreased as the steam content was reduced. Thus, the H_2/CO ratio increased with increasing steam fraction in the gasifying agent.

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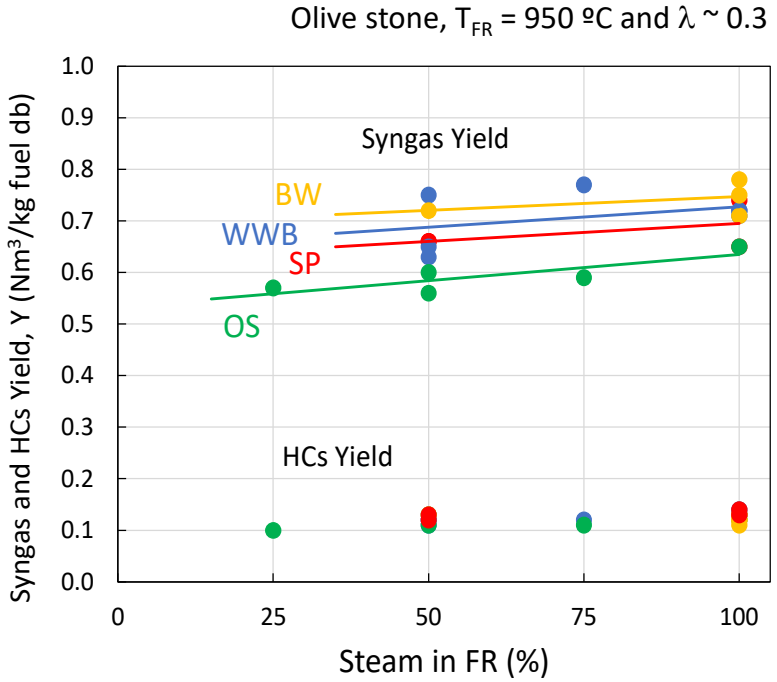
Influence of steam-to-CO_2 ratio (S/CO_2)



- Syngas yield improved slightly as the steam fraction increased
- Differences between biogenic residues: BW≈0.8 while OS≈0.65 Nm^3/kg biomass d.b.

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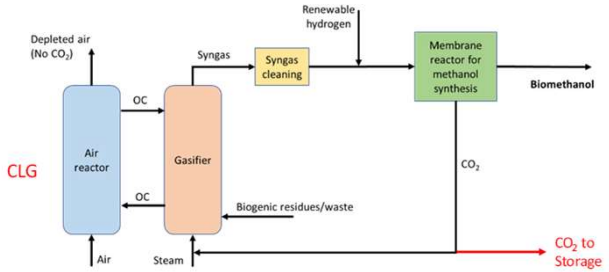
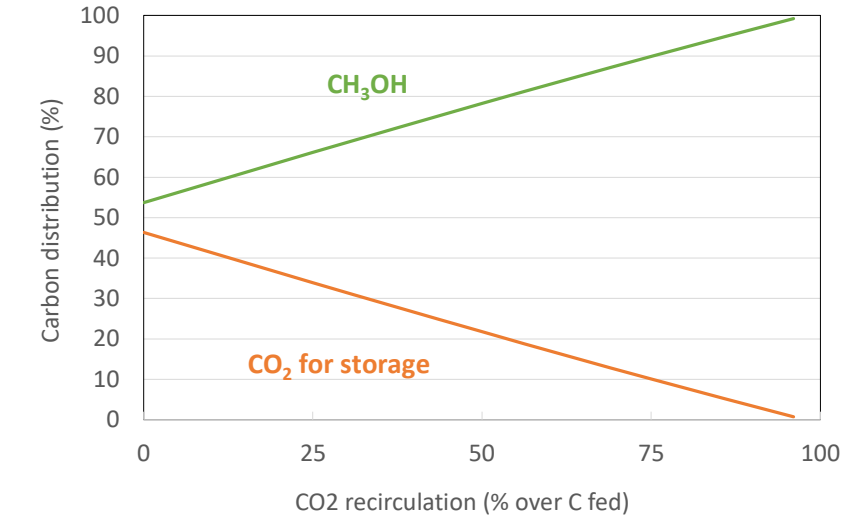
Recirculation and negative CO_2 emissions



λ=0.3. T_{FR}=950 ºC
Syngas at equilibrium
WWB, S/B=1



- CO_2 recirculation from the retentate stream in the membrane improves Carbon utilization
- CO_2 storage leading on negative emissions will be balanced with CH_3OH production

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Conclusions

- The oxygen-to-fuel ratio (λ) was the **most influential operating variable affecting the syngas** quality.
- At λ values corresponding to auto-thermal operation (λ ~ 0.30-0.35) at 950 °C, the syngas composition was similar for all four biogenic residues, consisting of **35 % H_2, 19 % CO, 36 % CO_2, 9 % CH_4 and 1 % C_2-C_3 (d.b.)**. A syngas yield of approximately **0.7 Nm^3/kg biomass (d.b.)** at 950 °C can be expected.
- The **gasifying agent used in CLG** (steam or CO_2) **affect both syngas composition and biomass conversion in the FR**.
- CO_2 recirculation from the membrane retentate stream improves overall Carbon utilization
- CO_2 storage, resulting in **negative emissions,** will be balanced against **CH_3OH production**

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Web

BiOMeGaFuel

LinkedIn

THANK YOU

QUESTIONS/COMMENTS

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Por si te preguntan algo de las membranas

Methanol synthesis via membrane reactors

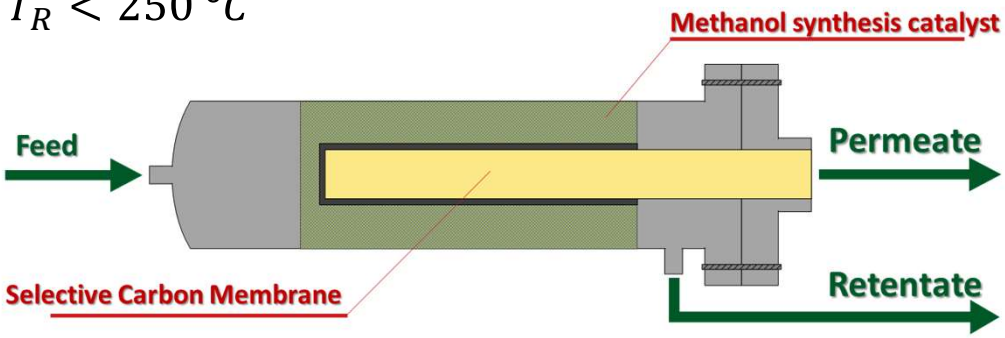
The methanol synthesis is an equilibrium system:

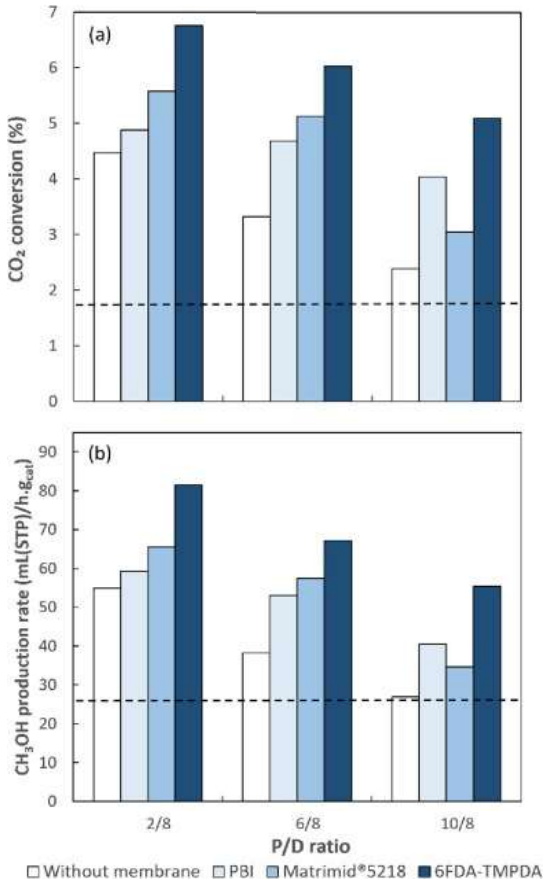
$$CO + 2\,H_2 \Leftrightarrow CH_3OH \qquad \Delta H = -90.7 \quad kJ/mol$$
$$CO_2 + H_2 \Leftrightarrow CO + H_2O \qquad \Delta H = 41.19 \quad kJ/mol$$
$$CO_2 + 3\,H_2 \Leftrightarrow CH_3OH + H_2O \qquad \Delta H = -49.51 \quad kJ/mol$$

Commercial $Cu/ZnO/Al_2O_3$ catalyst

$P_R < 40\ bar$

$T_R < 250\ °C$





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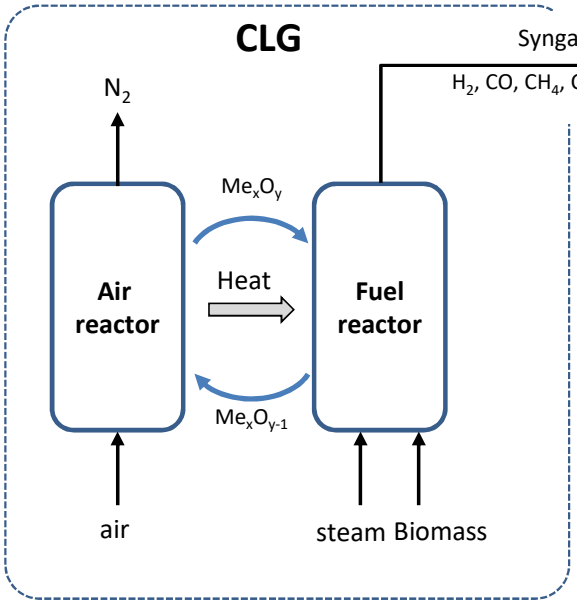
Chemical Looping Gasification

Biomass, wastes



SYNGAS

H_2
FT-diesel, gasoline
Methanol
DME, MTBE
chemicals

Oxygen-to-biomass ratio, λ

$$\lambda = \frac{\text{oxygen fed in the AR (mol/h)}}{\text{oxygen needed for full biomass combustion (mol/h)}}$$

$$S/B = \frac{\text{flow of steam (kg/h)}}{\text{flow of dry biomass (kg/h)}}$$

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