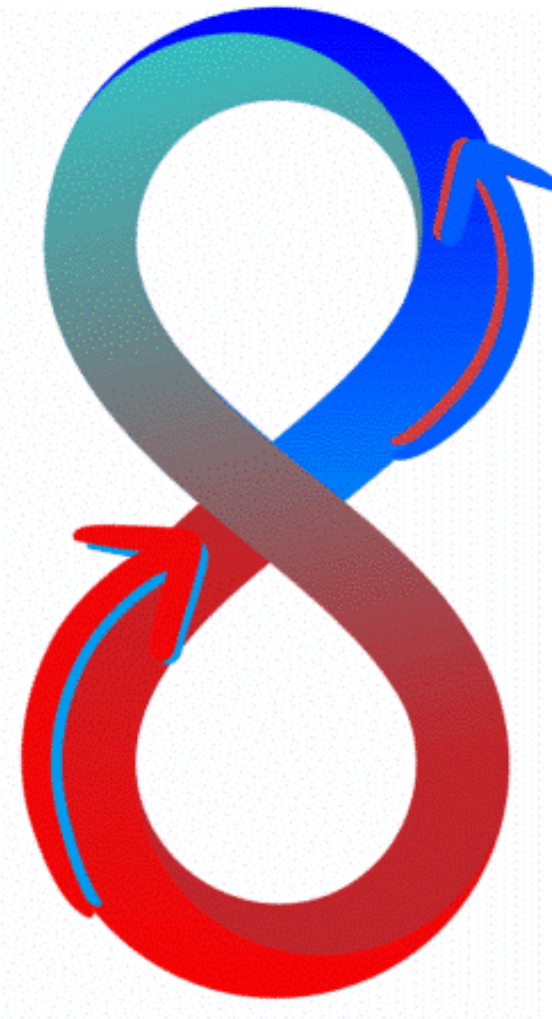


Syngas production from biogenic resources through Chemical Looping Gasification

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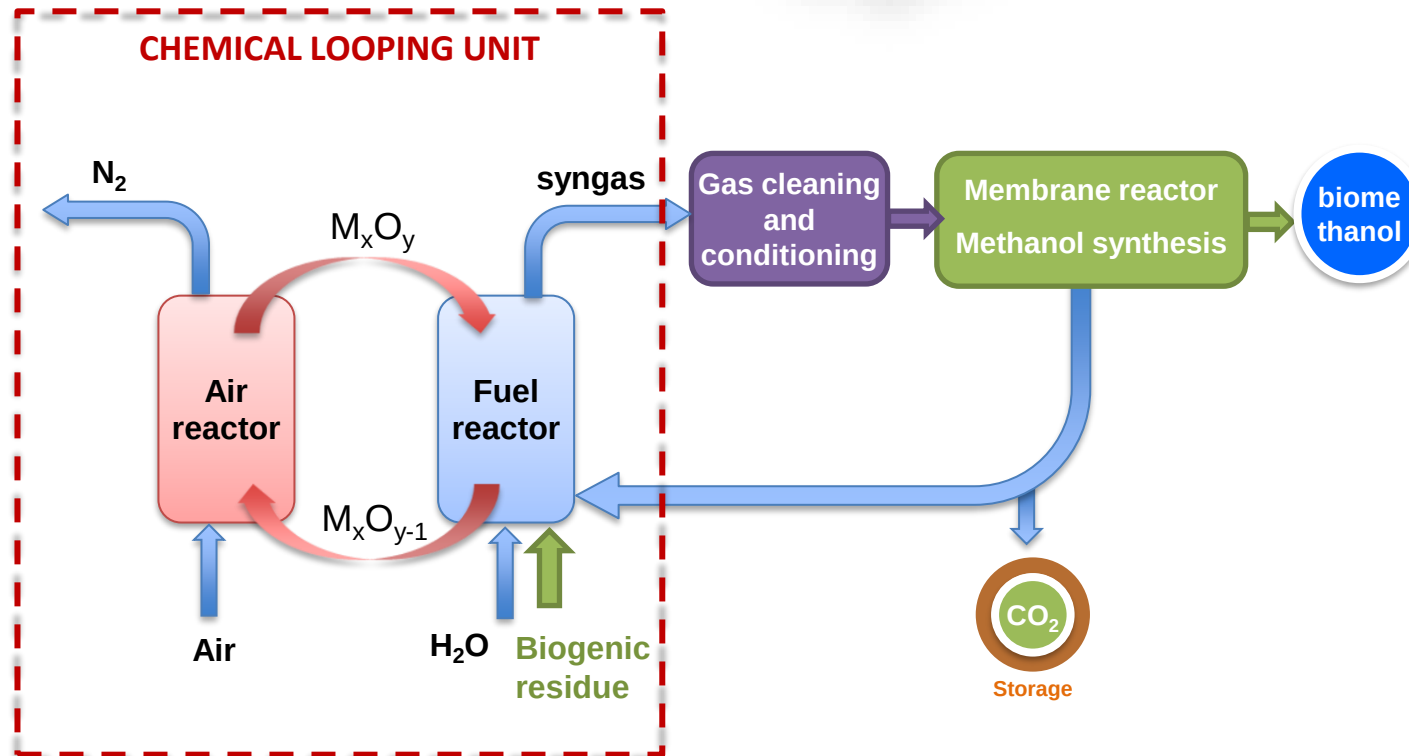


- **Context: BioMeGaFuel Project**
- **Objective**
- **Experimental**
- **Results**
- **Ongoing work**
- **Conclusions**



Bio Methanol Production via Chemical Looping Gasification
Coupled with Membrane Reactors

HORIZON-No. 101147737



BioMeGaFuel aims at developing innovative, efficient, and scalable pathway to **convert low-cost biogenic waste into biomethanol**

- ▶ Minimal carbon footprint
- ▶ Combining biomass **Chemical Looping**
- ▶ **Gasification** with membrane reactors



Bio Methanol Production via Chemical Looping Gasification
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BioMeGaFuel consortium involves partners from **5 countries**:

- **2 universities** (TUDA, TUE)



TECHNISCHE
UNIVERSITÄT
DARMSTADT

TU/e EINDHOVEN
UNIVERSITY OF
TECHNOLOGY

- **3 research institutes** (RISE, **CSIC**, IVL)



CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

@ivl
Swedish Environmental
Research Institute

- **4 companies** (Blue World Technologies, PERPETUAL NEXT, 1CUBE, GIDARA Energy)



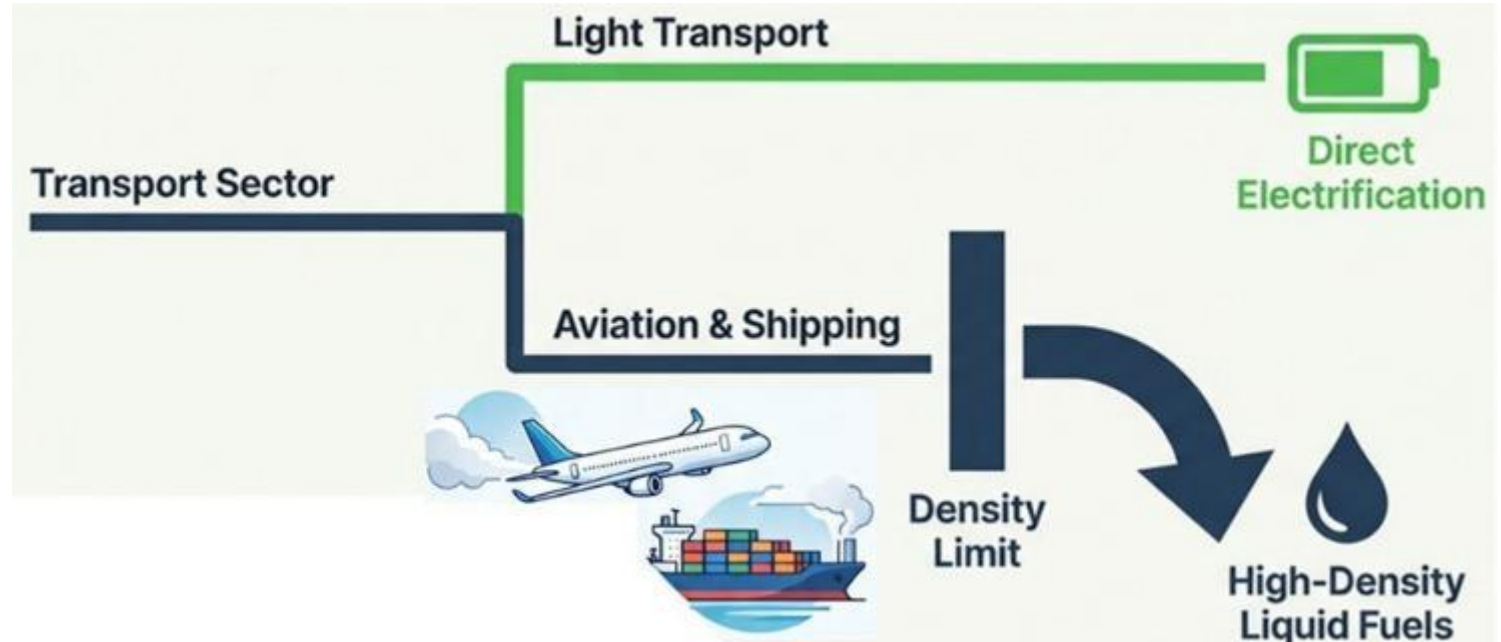
To comply with the goals set in the **Paris Agreement**, **fossil fuels** should be **replaced** by renewable alternatives

Why biomethanol?

Biomethanol is key low-carbon fuel to **decarbonize the heavy-duty road transport and marine shipping**.

Biomethanol is a **flexible fuel** used:

- Directly in IC engines
- Blended with conventional fuels
- To make fuel additives to boost engine performance



Challenges for biomethanol **deployment**:

- Methanol mainly produced from fossil resources
- Use of methanol remains in the chemical industry (limited availability for energy applications)

Why biogenic residues or wastes?

Renewable Energy
Directive III (RED III)

5.5%

Advanced biofuels
(Gen 2 & 3) mandatory
share of the transport
sector by 2030.

	Generation 1	Generation 2	Generation 3	Generation 4
Feedstock	 Sugarcane, maize, rapeseed.	 Non-edible farming/forestry residues and organic waste.	 Algae.	 Modified microorganisms (engineered for higher C capture).
Food Competition	High.	None (Valorizes discarded materials).	None (No farmland needed, fast growth).	None.
Readiness	Large-scale production.	Most realistic choice today, close to industrial use.	Early/Pilot.	Early stage of development.
Primary Drawback	 Relies on crops that could otherwise feed populations.	 Requires advanced thermochemical conversion.	 Growing and harvesting remains highly expensive.	 Unproven at industrial scale.

AI Generated

Biogenic residues and wastes in Europe



Agricultural Residues

The largest segment. Comprises cereals, oilseeds, and rice husks.



Forestry Residues

Major contributor. Includes logging harvests, tree maintenance, and wood processing.



Biogenic Waste

Smaller but critical stream. Covers wood/food waste, paper, municipal solid waste, sewage sludge, and manure.

Agricultural Leaders:

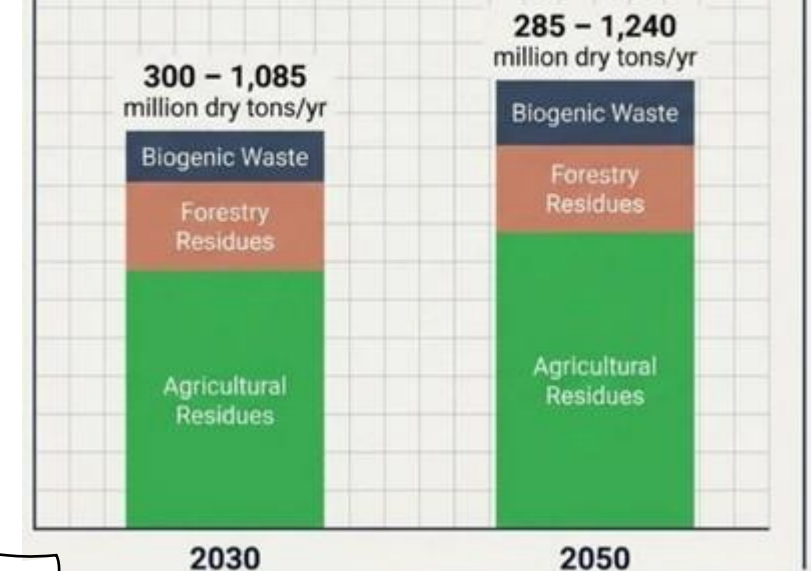
France, Germany, Poland, Spain, Romania, and Italy hold high shares of the continent's agricultural residue potential.



Forestry Leaders: Finland and Sweden dominate the sustainable forestry residue and wood processing potential.

AI Generated based on Concawe 2021

Volume Projections (Million Dry Tons/Year)



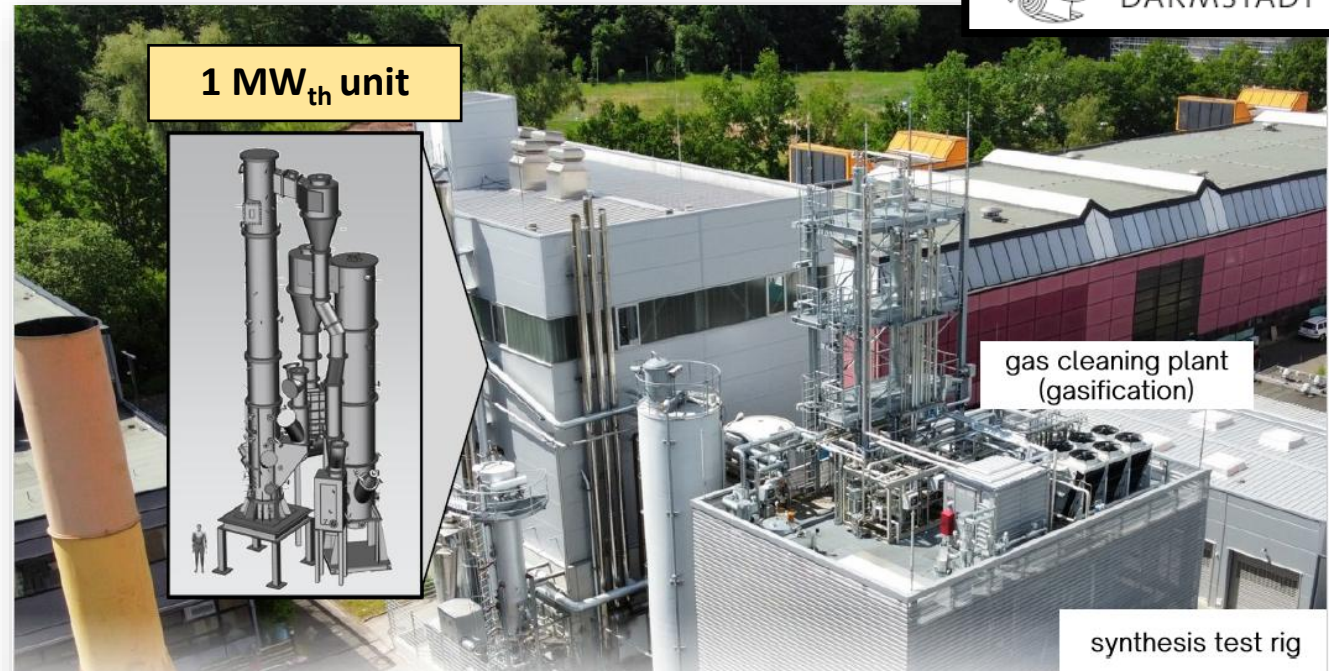
European landscape has a distributed network to sustain localized fuel production

Why Chemical Looping Gasification?

Delivers **high quality non-N₂ diluted syngas** without the need of ASU and with **reduced tar formation**.
CO₂ is concentrated in syngas, thus **Negative CO₂ emissions** can be reached if CCS



20 kW_{th} unit



1 MW_{th} unit

gas cleaning plant
(gasification)

synthesis test rig

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-CO₂ ratio used as the gasifying agent
- Providing a basis for optimizing CLG operation and feedstock selection for diverse syngas applications within the European bioeconomy

Selection of oxygen carrier and biogenic residues

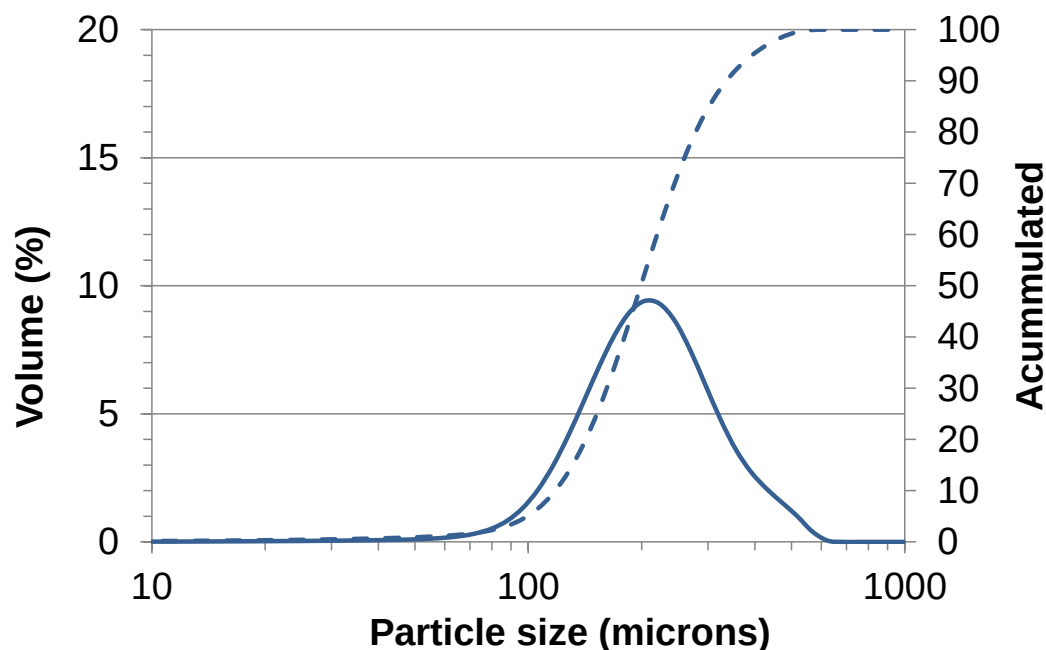


Fresh ilmenite from Titania, Norway.

Calcination: 950 °C in air for 2 h

Circulated 6 h at 800 °C 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
$R_{\text{O,ilm}}$ (%)	4.0
Porosity (%)	1.2
Crushing strength(N)	2.2
XRD (main species)	Fe_2TiO_5 , Fe_2O_3 , TiO_2

Selection of oxygen carrier and biogenic residues

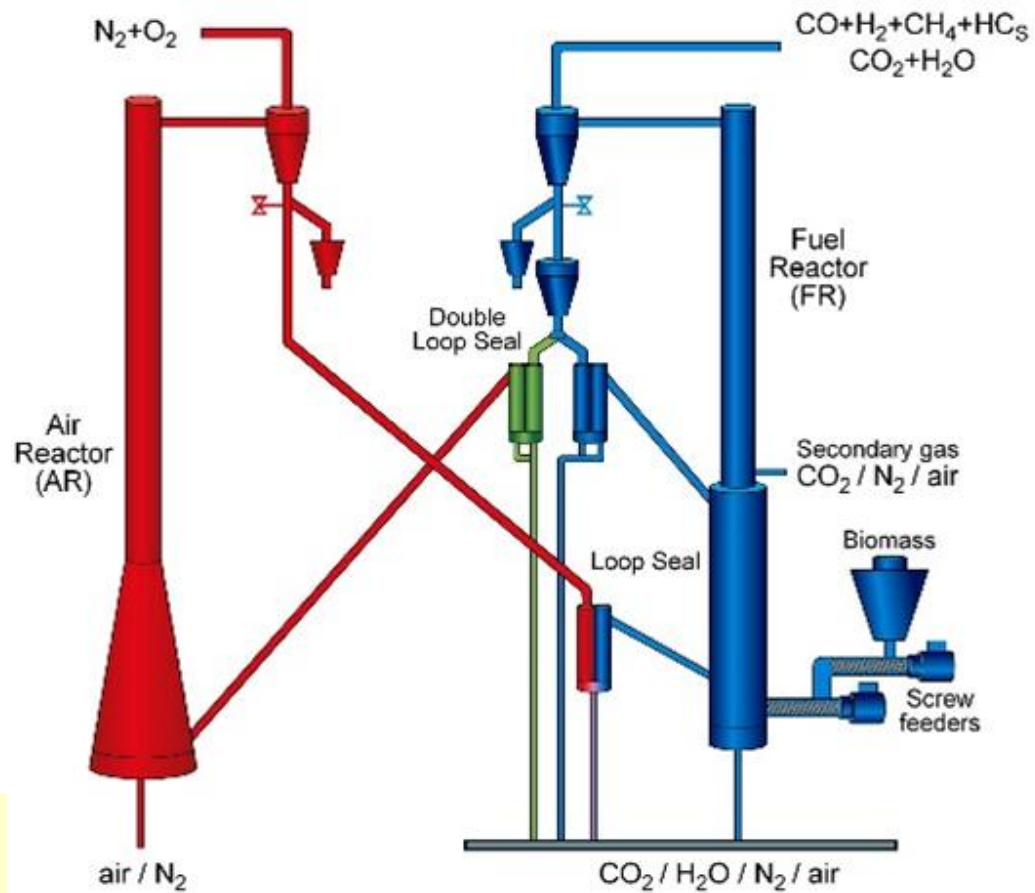
ANALYSIS (wt.%)				
	Waste Wood Type B (WWB)	Olive pits (OS)	Buckwheat husk (BW)	Spruce branches (SP)
Size (mm)	L: 10, Ø:6	0.5-3.2	L: 10, Ø:6	0.5-10
Moisture	6.8	7.3	9.7	8.0
Ash	1.7	0.3	2.0	2.5
Volatiles	74.2	74.9	66.4	72.1
Fixed carbon	17.3	17.4	21.8	17.5
C	46.3	46.3	45.0	46.7
H	5.5	5.5	5.2	5.4
N	1.1	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

The 20 kW_{th} unit at CSIC

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

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

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



FR temperature (T _{FR})
850 – 950 °C
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

Performance evaluation: Key Performance Indicators

BIOMASS CONVERSION

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

CARBON EMITTED IN AR

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

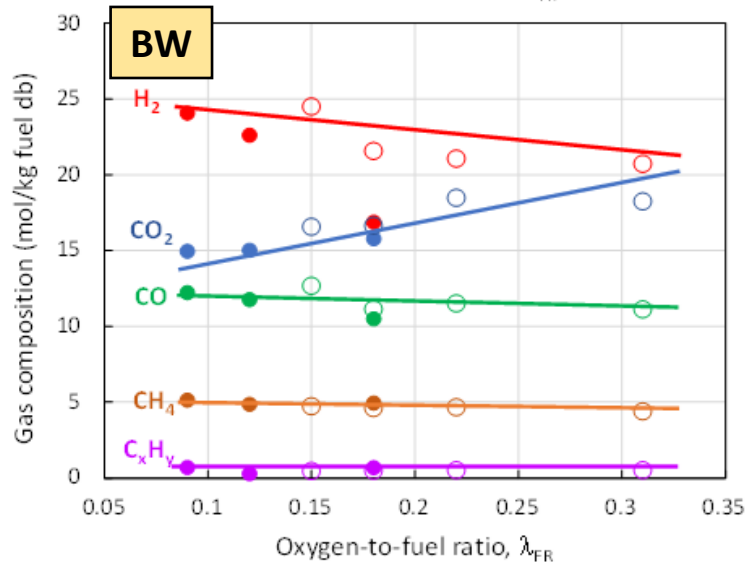
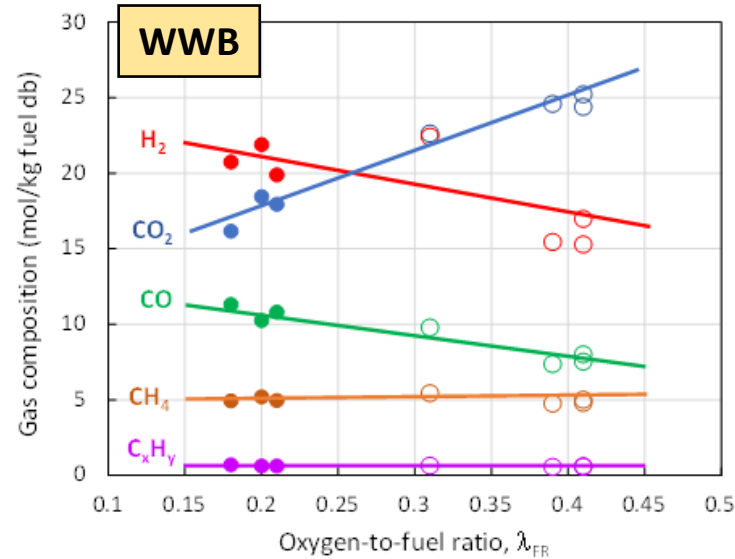
SYNGAS YIELD

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

HC YIELD

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

Influence of oxygen-to-fuel ratio (λ)_Composition



$T_{FR} = 950 \text{ }^{\circ}\text{C}$ and $S/\text{CO}_2 = 100/0$.

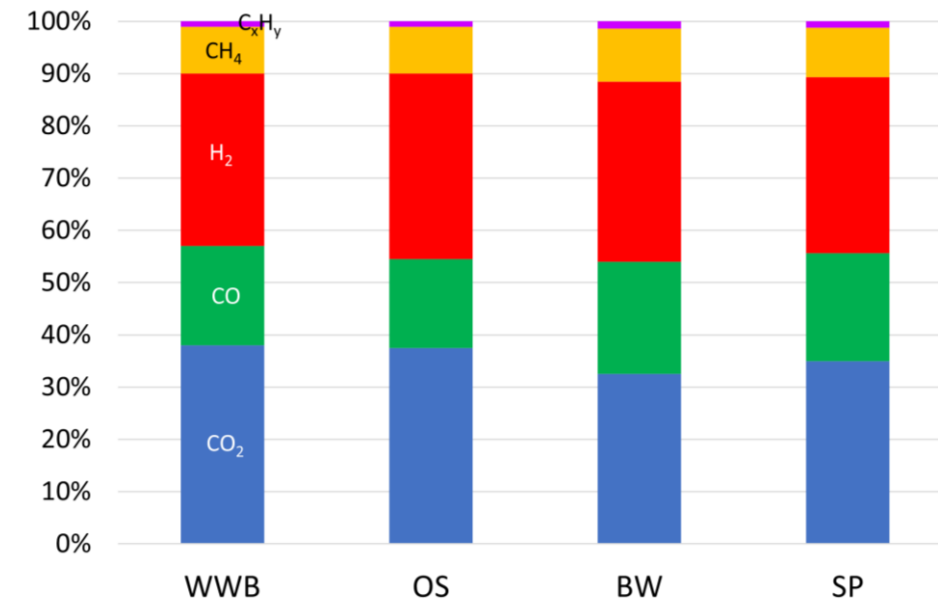
- An increase in λ produced an increase in CO_2 flow and a decrease in the H_2 and CO generated, being lower in the case of CO
- High amount of CH_4 and $\text{C}_2\text{-C}_3$ hydrocarbons

AUTOTHERMAL CONDITIONS

35% H_2 , 19% CO , 36% CO_2 ,
9% CH_4 , 1% $\text{C}_2\text{-C}_3$

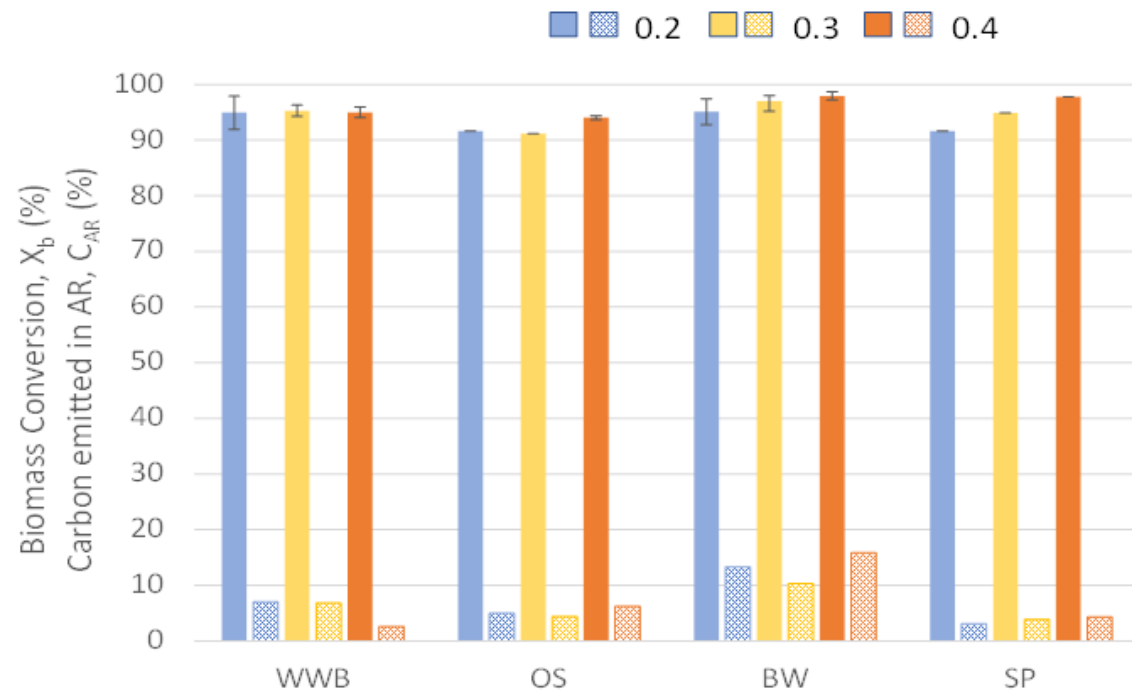
AUTOTHERMAL CONDITIONS

$\lambda = 0.30\text{-}0.35$



Steam 100% at $T_{FR} = 950^{\circ}\text{C}$

The syngas produced depends more on λ than on the type of biogenic residue

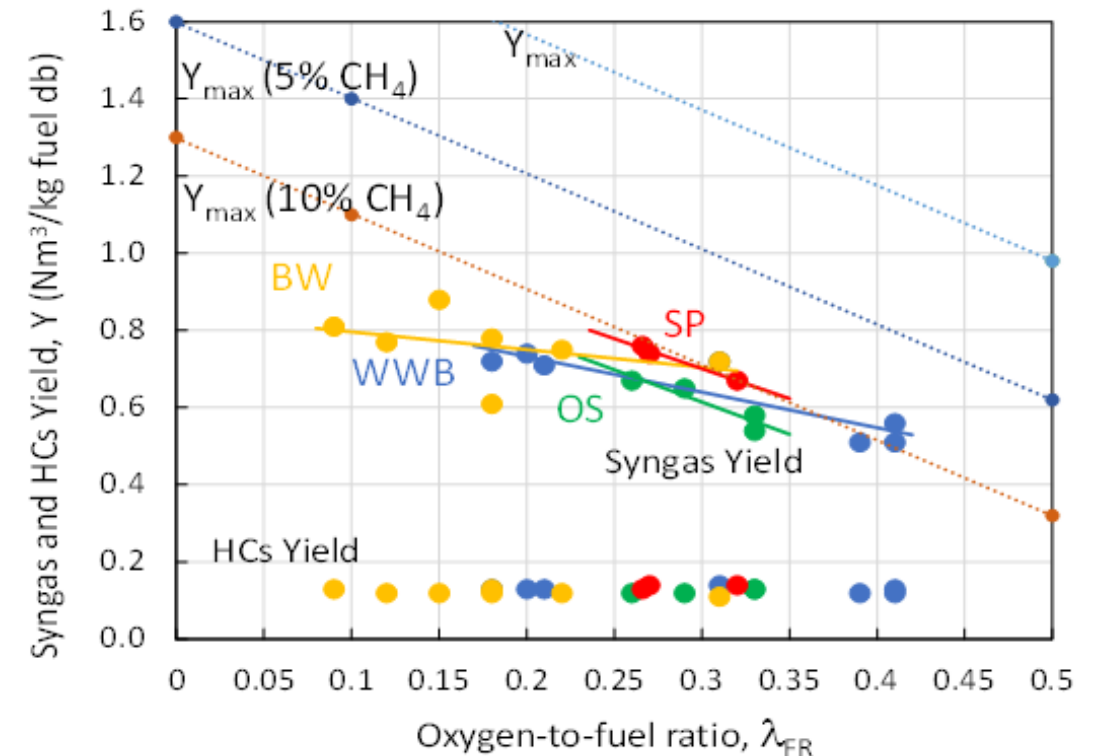


- Biomass conversion higher than 90% for all
- $C_{AR} < 5\%$ for spruce (SP) and olive stones (OS). Larger values for WWB and BW pellets due to their larger size

AUTOTHERMAL CONDITIONS

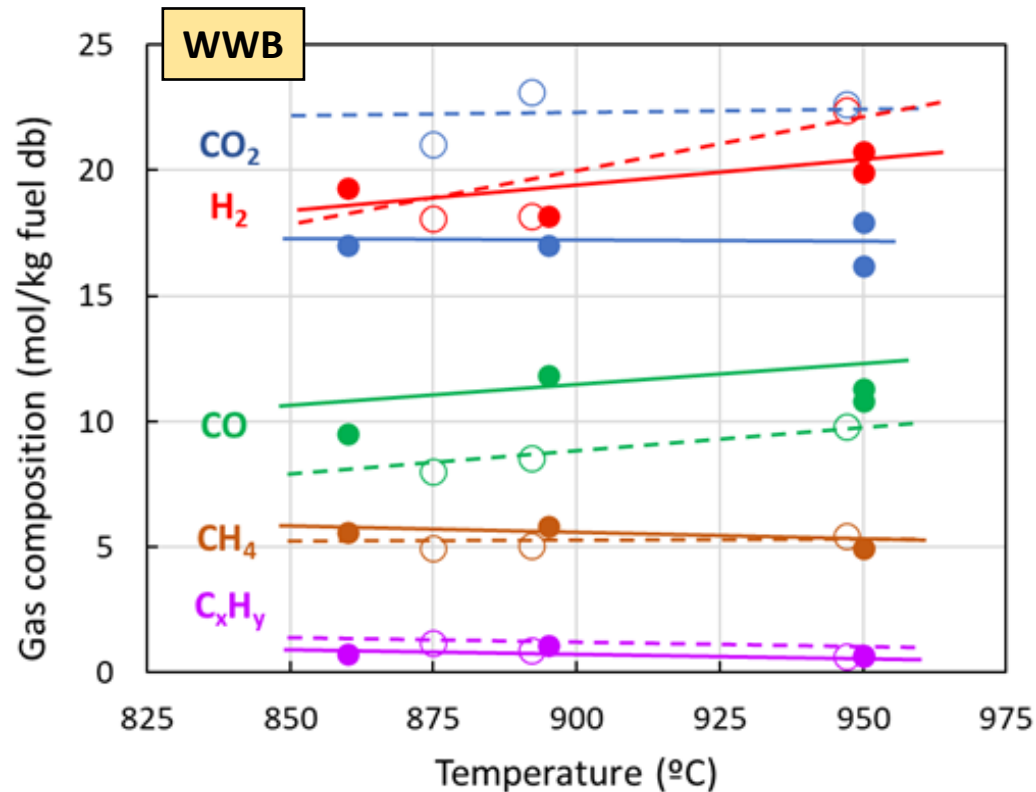
$$Y_g \cong 0.6-0.7 \text{ and } Y_{HC} \cong 0.15 \text{ Nm}^3/\text{kg biomass d.b.}$$

Influence of oxygen-to-fuel ratio (λ)_KPIs



- Syngas yield (Y_g) decreased when increasing λ while hydrocarbon yield (Y_{HC}) was not affected
- No differences for the four biogenic residues

Influence of temperature in FR_Composition



$\lambda \sim 0.3$ and $S/\text{CO}_2 = 100/0$.

Open symbols: pellets with 10 mm length

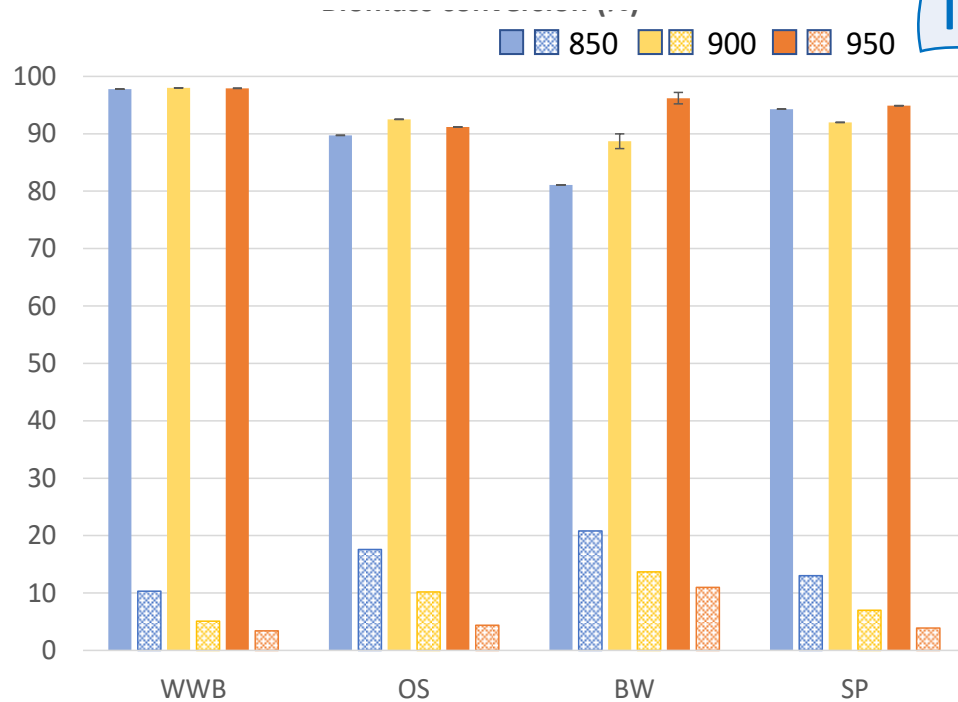
Filled symbols: pellets with 20–30 mm length

- Syngas composition weakly affected by temperature: governed primarily by λ
- H₂ is the dominant permanent gas
- CH₄ and the C₂–C₃ fraction remained constant with temperature

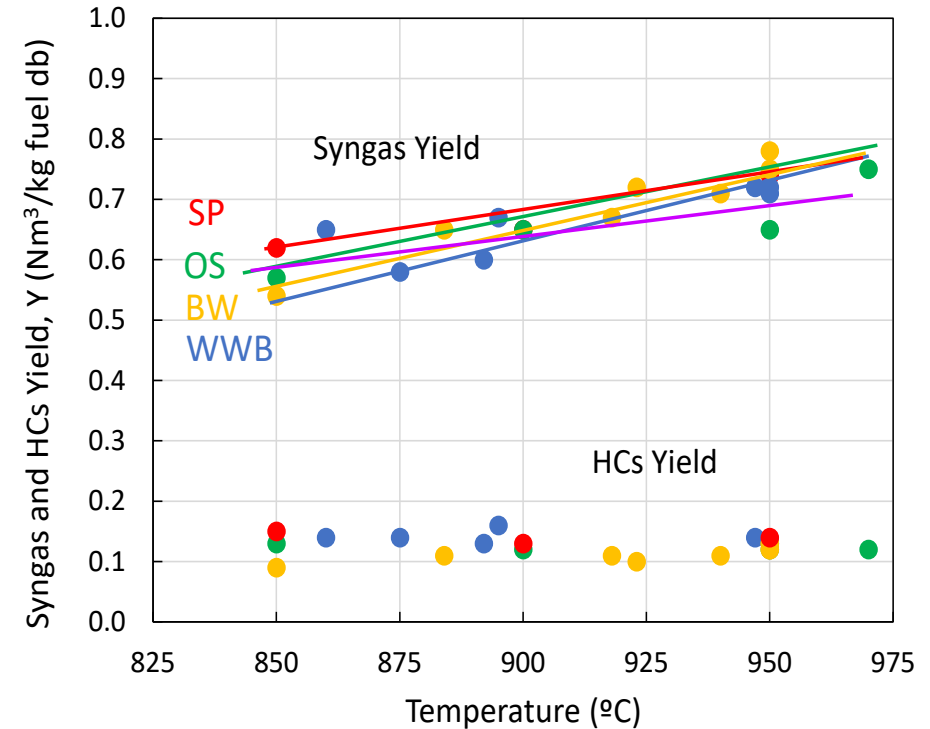
EFFECT OF PARTICLE SIZE

- Smaller biomass particles resulted in higher CO₂ concentrations and lower CO contents due to enhanced water-gas shift reaction, promoted by a more complete fuel conversion for the smaller particle size
- CH₄ and C₂–C₃ were hardly affected by the particle size of the pellets

Influence of Influence of temperature in FR_KPIs



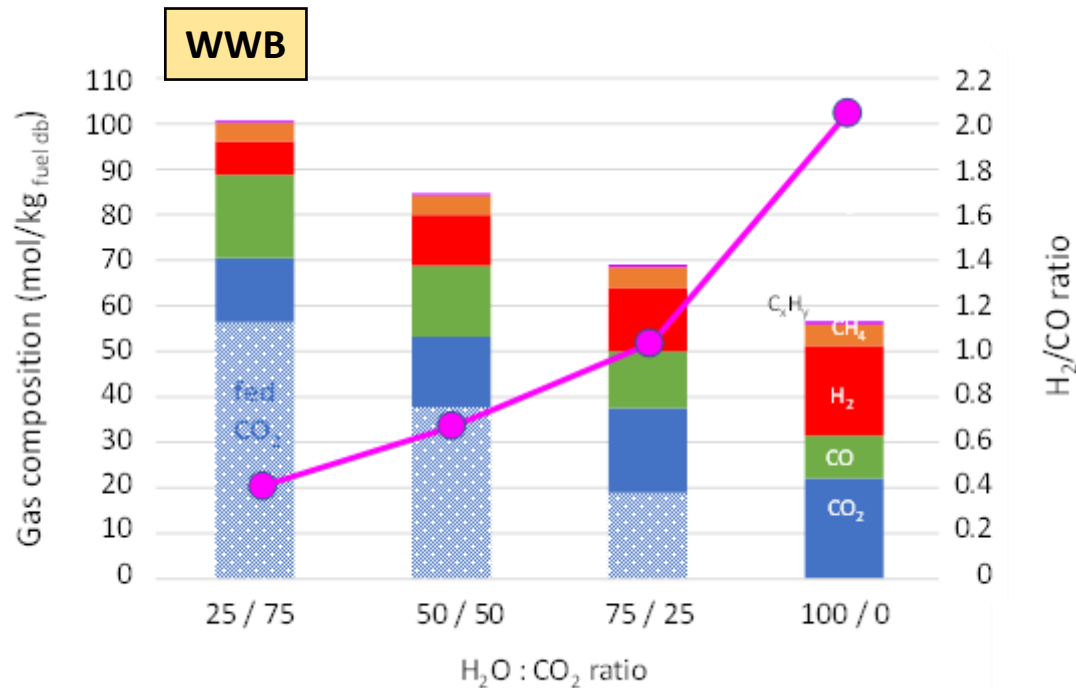
- Biomass conversion > 90% for almost all. Pronounced increase for buckwheat husk (BW)
- At 950 °C, $C_{AR} < 10\%$ for all biogenic residues



- Y_g increased with temperature with no relevant differences between biogenic residues

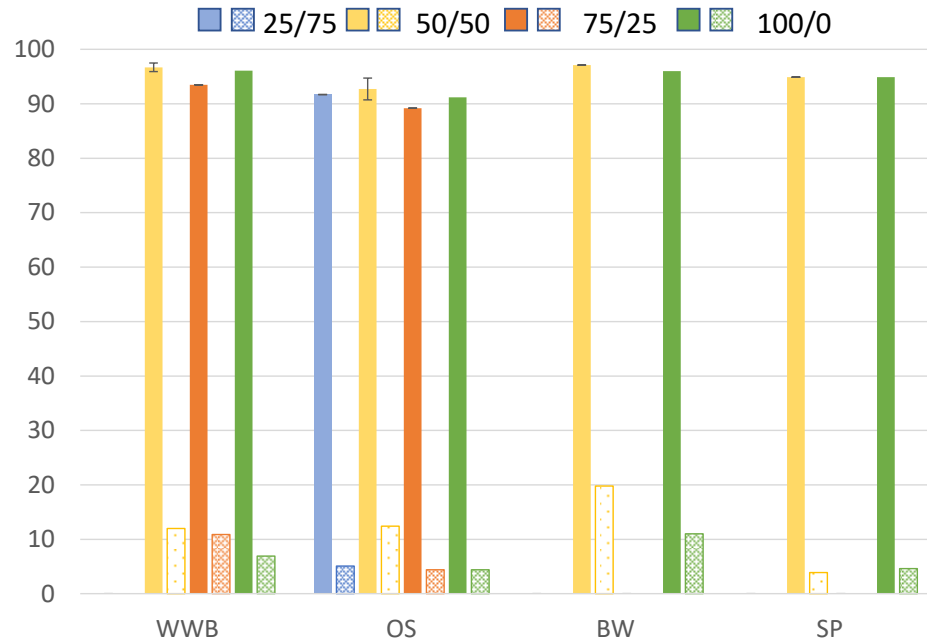
Regardless residue, the maximum $Y_g \sim 0.7 \text{ Nm}^3/\text{kg biomass d.b.}$ at 950°C

Influence of steam-to-CO₂ ratio (S/CO₂)_Composition

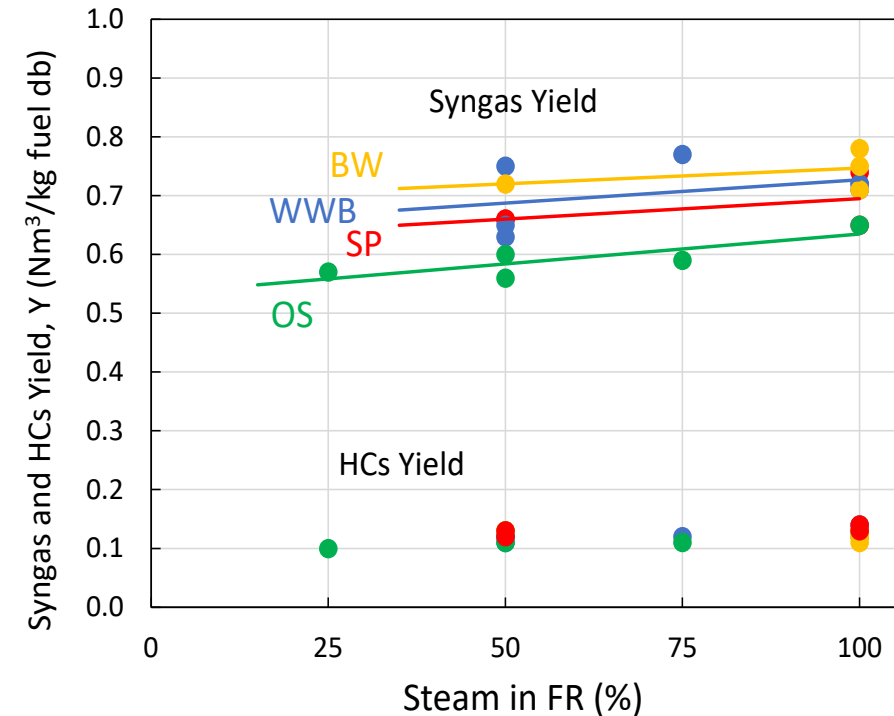


$T_{FR} = 950\text{ }^{\circ}\text{C}$ and $\lambda \sim 0.3$

- As the S/CO₂ ratio decreased, the amount of CO₂ generated decreased, whereas the CO produced grew moderately
- Only a small fraction of the additional CO₂ supplied was converted into CO via the Boudouard reaction, while most of the fed CO₂ left the fuel reactor unreacted
- The H₂ yield decreased as the steam content was reduced. Thus, the H₂/CO ratio increased with increasing steam fraction in the gasifying agent.



Influence of steam-to-CO₂ ratio (S/CO₂)_KPIs



- C_{AR} decrease with increasing S/CO₂ ratio, due to the higher reactivity of steam-char gasification than CO₂-char gasification
- Steam is preferred to maximise conversion, while co-feeding CO₂ is mainly of interest as a way of adjusting the H₂/CO ratio

- Y_g improved slightly as the steam fraction increased
- Differences between biogenic residues: BW≈0.8 while OS≈0.65 Nm³/kg biomass d.b.).

The choice of gasifying agent depends on the intended application

- ❑ Evaluation of the influence of the **oxygen-to-fuel ratio** (λ), fuel reactor **temperature** and **S/CO₂** ratio on tar formation with the four biogenic residues
- ❑ Analysis of the **NO_x formation in the fuel reactor**
- ❑ Investigation of possible **oxygen carrier-biomass ash interactions** during CLG experiments

- ❑ The oxygen-to-fuel ratio (λ) was the **most influential operating variable affecting the syngas** quality, more than the temperature in the fuel reactor. At λ values for auto-thermal operation ($\lambda \sim 0.30$ - 0.35) at $950\text{ }^{\circ}\text{C}$, the syngas composition was similar for the four biogenic residues, **35 % H_2 , 19 % CO , 36 % CO_2 , 9 % CH_4 and 1 % $\text{C}_2\text{-C}_3$ (d.b.)**. A syngas yield of approximately **$0.7\text{ Nm}^3/\text{kg biomass}$ (d.b.)** at $950\text{ }^{\circ}\text{C}$ can be expected.
- ❑ Particle size shows influence, since **smaller biomass particles led to a more oxidised syngas** composition.
- ❑ The choice of **gasifying agent** (steam or CO_2) **affect both syngas composition and biomass conversion in the FR**. Higher reactivity of steam-char gasification than CO_2 -char gasification.
- ❑ The selection of **operating conditions should be guided by the intended end-use of the syngas**. Steam is recommended when **maximising conversion in the FR and hydrogen production is the primary objective**, whereas **CO_2 co-feeding** may be considered for **adjusting syngas composition**, particularly in systems where captured CO_2 is readily available

Thanks for your attention!



info <https://www.icb.csic.es/grupo/grupo-de-combustion-y-gasificacion/>

Contact tmendiara@icb.csic.es



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