Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas

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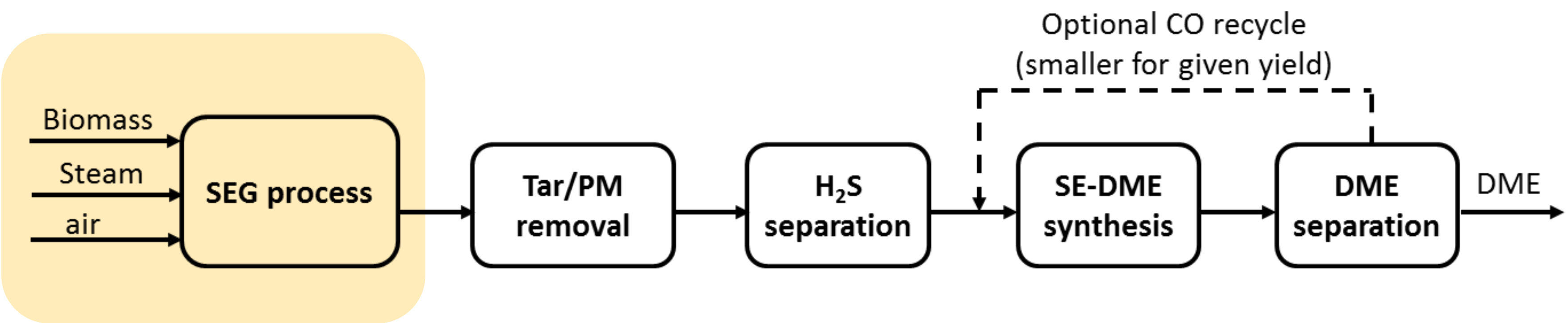
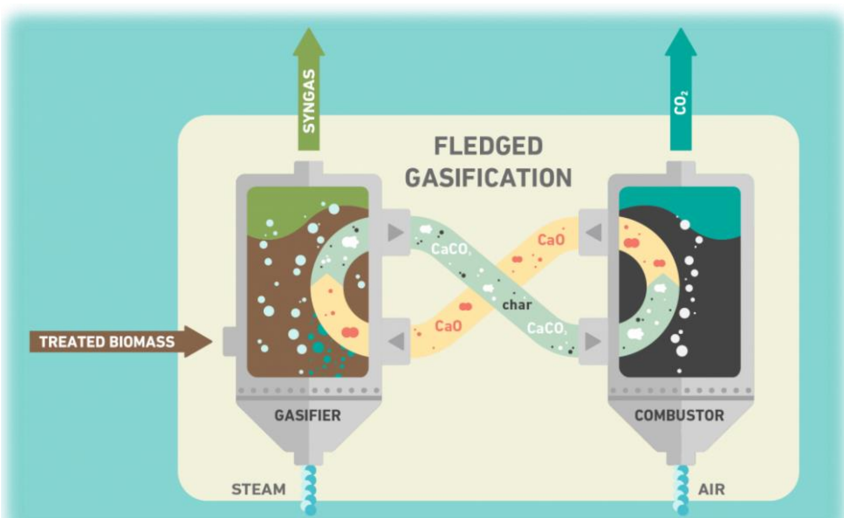
- OBJECTIVE FLEDGED project: **Develop a highly intensified and flexible process for DME production from biomass and validate it under industrially relevant environments** (i.e. Technology Readiness Level 5 (TRL))





- **Indirect gasification** in a **dual fluidized bed** system using CaO as bed material
- **Energy needed for gasification** supplied by **CaO carbonation** (→ $CaCO_3$) and by **circulating solids**
- **Unconverted char** leaving the gasifier supplies the **energy needed in the combustor**
- The presence of CaO **simplifies the syngas cleaning and purification section**

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FUNDAMENTAL RESEARCH ON GASIFICATION OF DIFFERENT BIOMASSES AND DIFFERENT NATURAL SORBENTS

✓ **Assessment of the enhanced gasification process in a bubbling fluidized bed reactor**

- Test the **different biomasses under different conditions of temperature, sorbent/fuel ratio and steam/carbon ratio**.
- Influence of **type of sorbent** and the **activity** of the limestone (number of cycles)

Sorption enhanced gasification tests using grape seeds as biomass have been performed, analyzing the effect of the S/C ratio, the sorbent-to-biomass ratio and the activity of the sorbent on the syngas composition

○ Biomass: Grape seeds

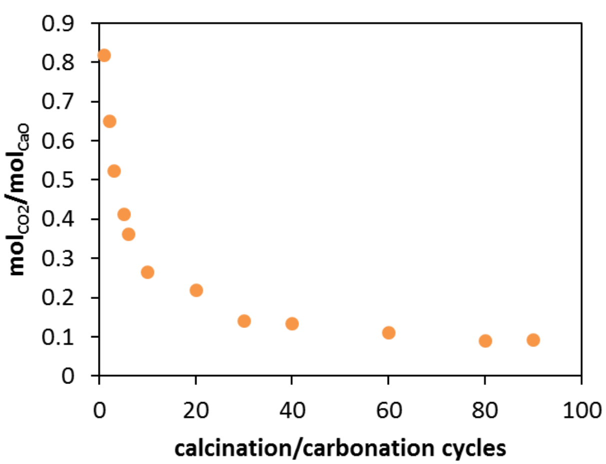
4.5-6.8 mm

Ultimate analysis [%wt.]		Proximate analysis [%wt.]	
C	53.92	Moisture	6.30
H	6.58	Volatile matter	65.12
N	2.20	Ash	4.30
S	0.12	Fixed carbon	24.28
O	32.35		
Cl	0.06	LHV [MJ/kg]	20.51

- Homogenous biomass
- High LHV (compared with PW or A1 pellets)
- Relatively low Ash and S contents (residual biomass)

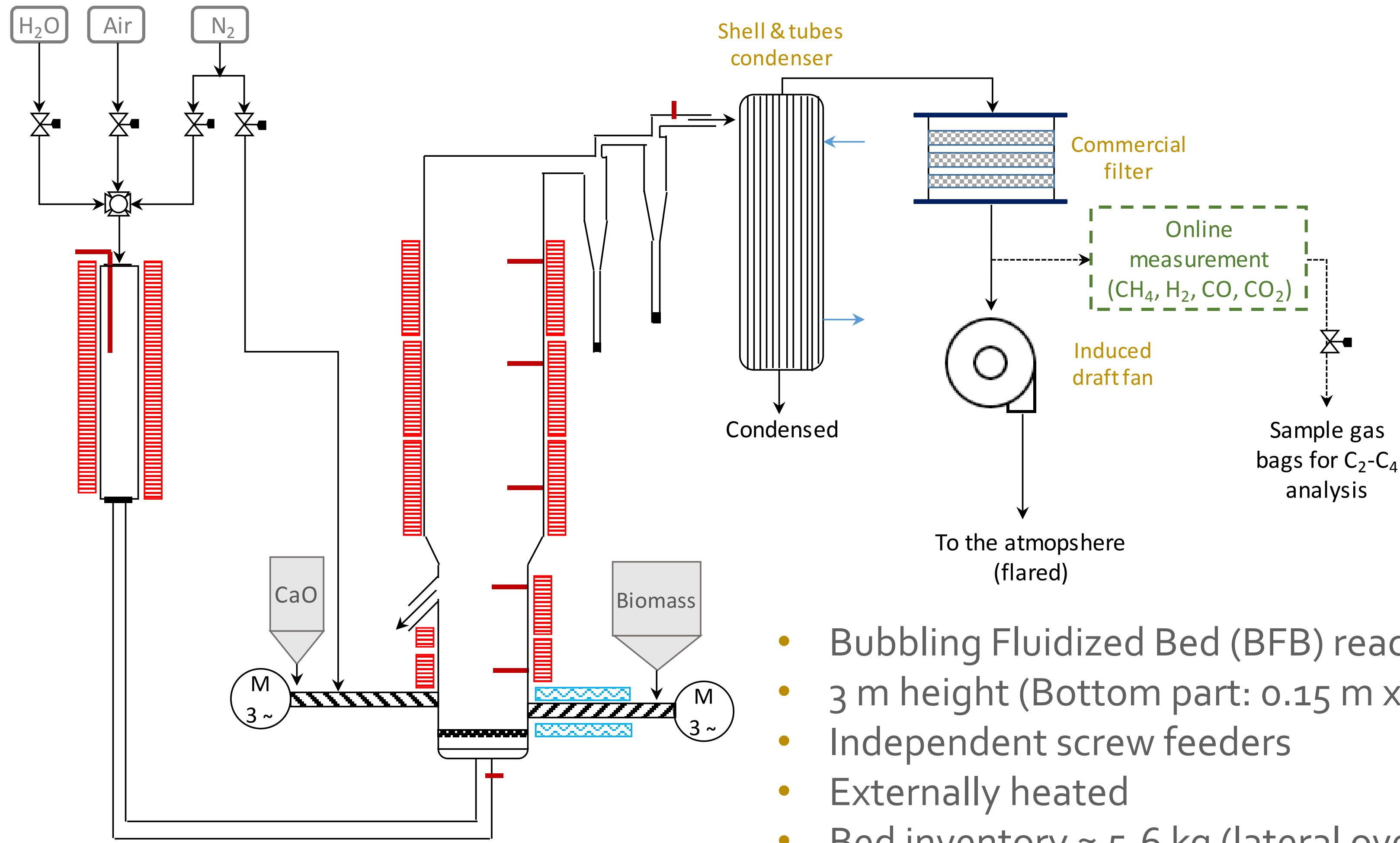
○ CO2 sorbent: Calcined limestone

	Calcined limestone
CaO [%wt]	98.25
Al_2O_3 [%wt]	0.145
Fe_2O_3 [%wt]	0.002
K_2O [%wt]	<0.001
MgO [%wt]	0.183
Na_2O [%wt]	<0.001
SiO_2 [%wt]	0.132
Porosity [-]	0.52
Surface area [m²/g]	8.8
Solid density [kg/m³]	3139



- High purity limestone
- Mean particle diameter: 450 microns
- Typical CO2 sorption decay of natural Ca-based sorbents

Sorption enhanced gasification (SEG) tests
Experimental facility



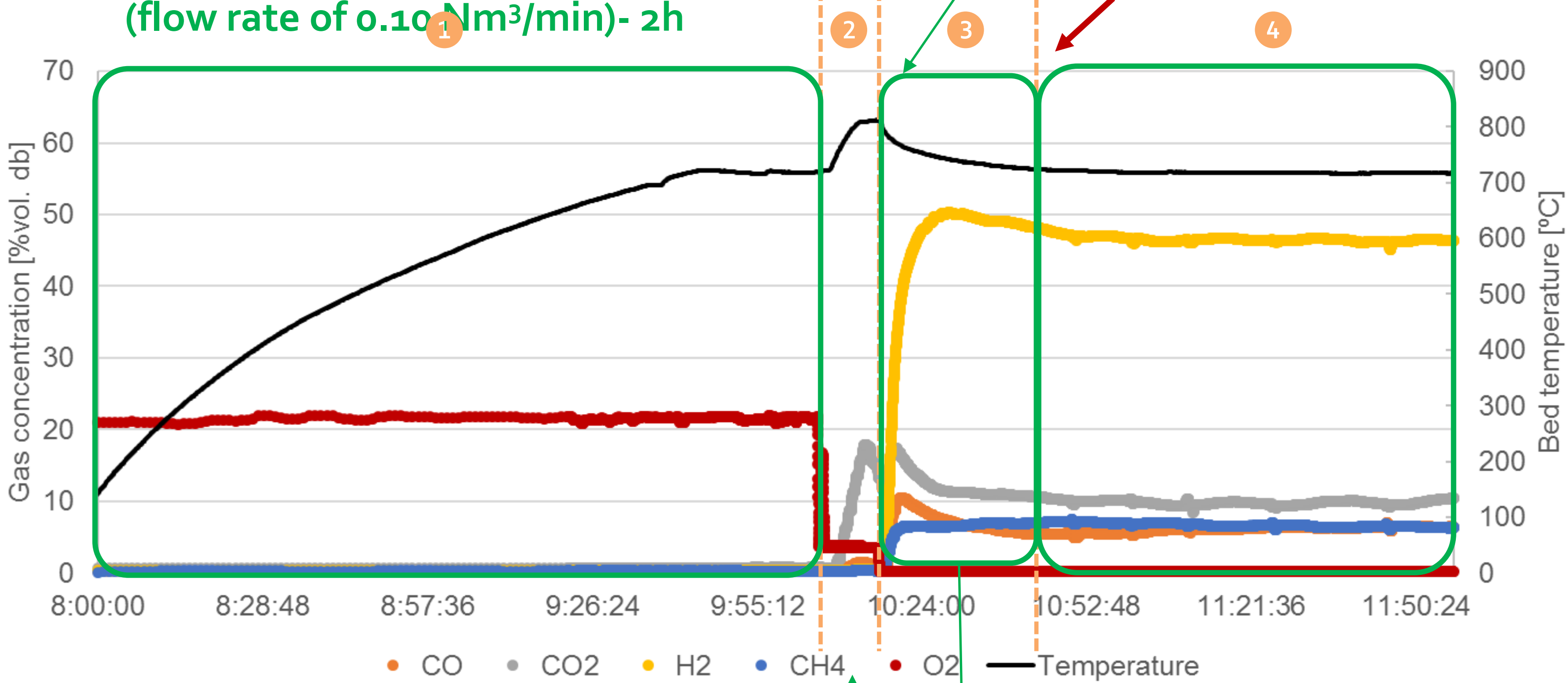
- Bubbling Fluidized Bed (BFB) reactor
- 3 m height (Bottom part: 0.15 m x 1 m)
- Independent screw feeders
- Externally heated
- Bed inventory ≈ 5-6 kg (lateral overflow)
- N2 flow rate fed to the evaporator (heater) and to the CaO screw feeder

Sorption enhanced gasification (SEG) tests
Experimental routine

Steady-state reached for the gas and bed temperature
(BEGINNING OF GAS AND SOLID SAMPLING)

Change to experiment conditions

Electric heating in air up to ≈ 700ºC
(flow rate of 0.10 Nm³/min)- 2h



Stabilization of temperature and gases

Feed of biomass for speeding the heating up to 820-850ºC while feeding CaO to fill the bed

Sorption enhanced gasification (SEG) tests
Experimental conditions

Ca/C ratio \ S/C ratio	1	1.5
0.55		
0.5		
0.45		
0.4		
0.3		

- Different Ca/C ratios (0.3-0.55) and S/C ratios (1 and 1.5) tested
- Stabilization temperature between 707 and 755°C
- Effect of CO_2 carrying capacity of the sorbent used tested

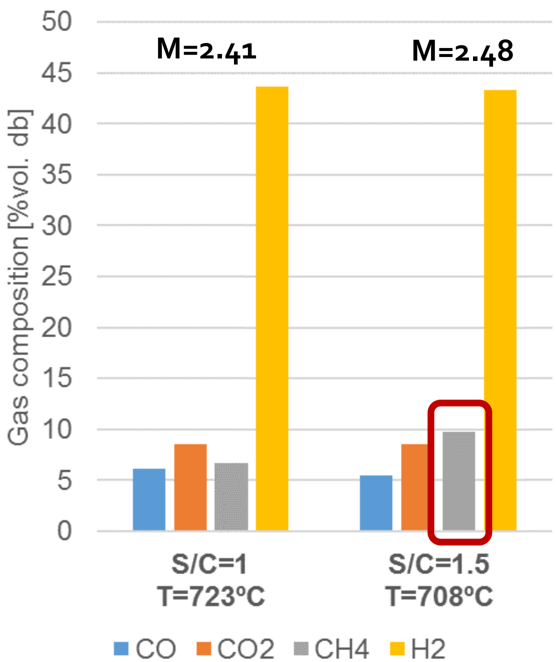
Char conversion in the BFB gasifier:

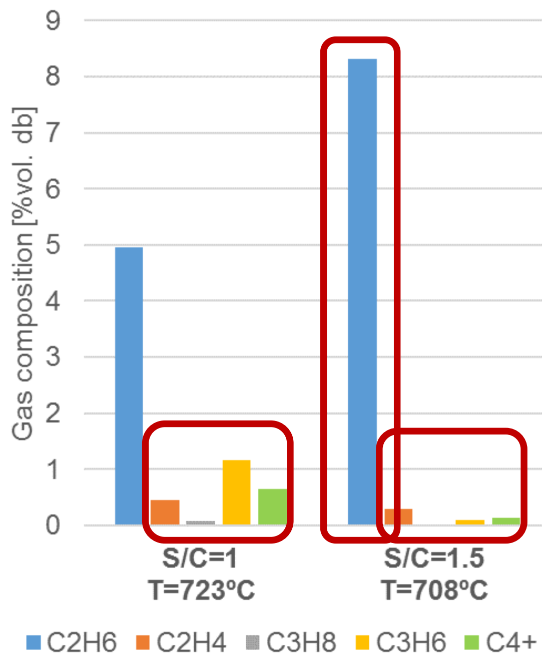
$$X_{CHAR} = 1 - \frac{m_{C,s\ overflow}}{m_{FC,biomass}}$$

Char particles residence time:

$$\tau_{CHAR} = \frac{m_{char,SS}}{\dot{m}_{biomass} \cdot (y_{FC} + y_{ash})}$$

✓ Effect of S/C ratio (Ca/C ratio constant)





Ca/C ratio	0.53-0.55

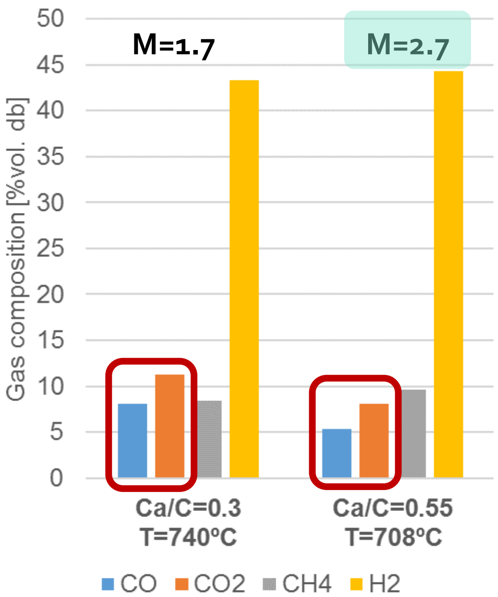
S/C	Gas yield (db) [Nm³/min]	X_{CHAR} [%]	τ_{CHAR} [min]
1	0.050	41-42	34
1.5	0.055	37	35

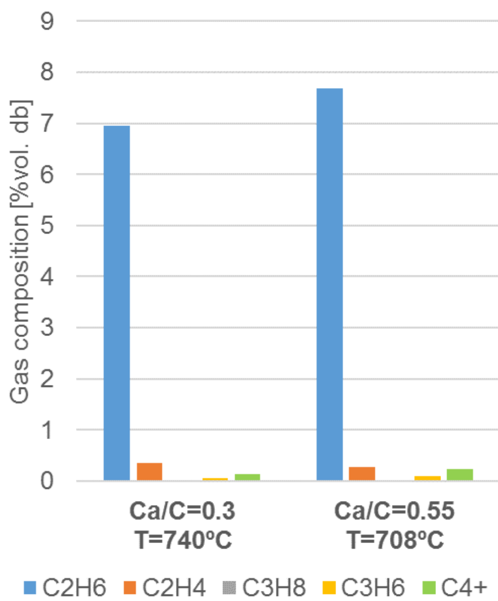
M module: $$M = \frac{H_2 - CO_2}{CO + CO_2}$$

- Amount of C3+ and unsaturated C2 reduced <0.53%vol. with S/C ratio of 1.5 (≈2.4%vol. for S/C=1)
- **C3+ and C_2H_4 cracked into C_2H_6 and CH_4, resulting into a larger gas yield**
- Solid residence time for char particles has not changed, **differences in conversion due to temperature**

Sorption enhanced gasification (SEG) tests
Results discussion

✓ Effect of Ca/C ratio (S/C ratio constant)





S/C ratio	1.5

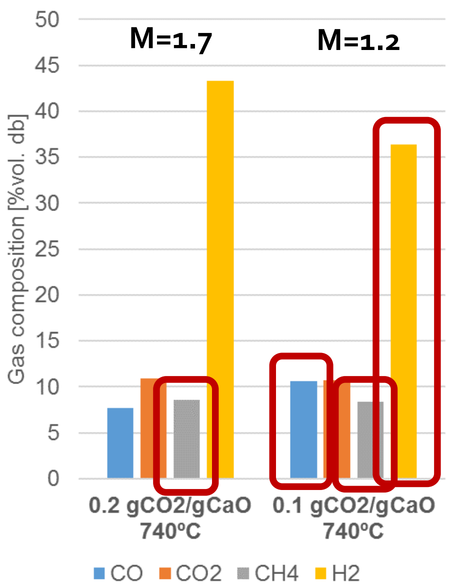
Ca/C	Gas yield (db) [Nm³/min]	X_{CHAR} [%]	τ_{CHAR} [min]	X_{CaO} [%]
0.3	0.065	41	50	22-23
0.55	0.055	37	35	27

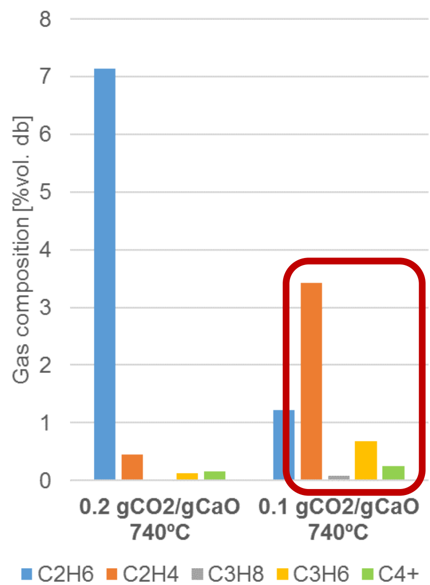
M module:
$$M = \frac{H_2 - CO_2}{CO + CO_2}$$

- No effect on C3+ and unsaturated C2 (<0.59%vol.) since S/C ratio is high
- CH_4 (and C_2H_6) is **slightly higher for Ca/C=0.55** due to the **lower stabilization temperature** when Ca/C increases
- **Larger M module for Ca/C=0.5 (lower temperature): linked to the amount of CO2 separated**
- **Lower temperature and larger excess of CaO improve CO2 separation** and reduce CO2 in the syngas (→ less CO content since WGS reaction is pushed)

✓ Effect of CO_2 sorbent activity (S/C and Ca/C ratios constant)

S/C ratio	1.5
Ca/C ratio	0.3

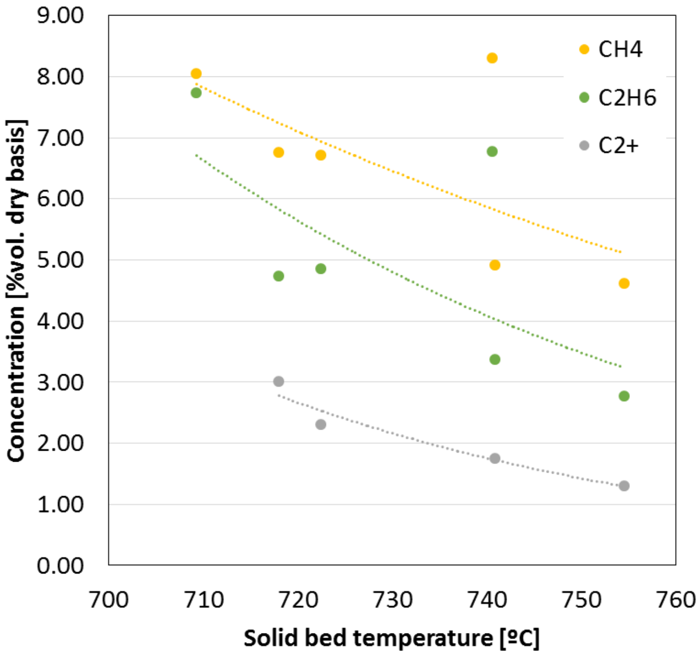




g_{CO_2}/g_{CaO}	Gas yield (db) [Nm^3/min]	X_{CHAR} [%]	τ_{CHAR} [min]	X_{CaO} [%]
0.2	0.065	41	50	22-23
0.1	0.056	40	48	15

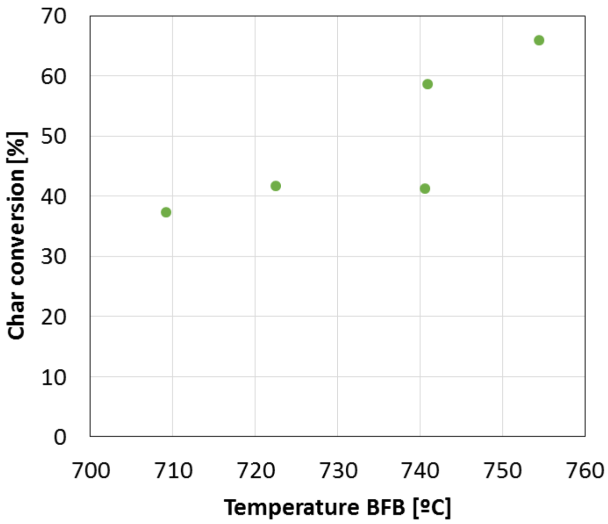
- **Less CO_2 is separated from the gas phase** (less activity of the CaO) → **lower amount of H_2 and higher CO**
- **CH_4 concentration is kept constant at 8.5%vol. (db)** (stabilization temperature is the same)
- **Amount of C3+ and unsaturated C2 increased for deactivated CaO** (4.4%vol. vs 0.7%vol.) → less H_2 produced (less cracking into saturated C2 and CH_4)
- Increased gas yield for more active CO2 sorbent since the amount of lighter C+ and H2 is raised

✓ Factors influencing the efficiency of the biomass-to-biofuel process



- Important to reduce the CH_4 and C2+ concentrations (inerts→ reduce yield and decrease the global efficiency)
- Dependence of HCs content on temperature → higher temperature decreases HCs concentration (except for C2+ and S/C=1.5, not depicted in figure)
- Limit on HCs reduction → need of conditioning steps before the synthetic fuel production process (i.e. reforming stage)

- Char conversion in the gasifier influenced by the temperature (CaO excess and τ barely affect)
- Efficiency of the SEG has an optimum: increasing char conversion boosts the efficiency but if there is not enough unconverted char in the combustor/calciner, additional biomass is needed (↓ efficiency)



- ✓ The **effect of the steam-to-carbon, CO_2 sorbent-to-biomass and the sorbent CO_2 carrying capacity have been assessed** for the sorption enhanced gasification of grape seeds
- ✓ S/C ratios of 1.5 needed for reducing C_2H_4 and C3+ concentrations below 0.6%vol. (db), which will impact the downstream fuel production process
- ✓ CH_4 and C_2H_6 concentrations have shown dependence with temperature (i.e. decreases with increasing temperature). CH_4 contents as low as 4.5 %vol. (db) at around 755ºC have been obtained
- ✓ A wide range of M modules has been obtained (M=1.7-2.7) , suitable for producing different types of biofuels (i.e., M=2 for DME or M=3 for SNG)

FUTURE WORK

- ✓ Tar and S- compounds analysis to be tuned-up (analysis under different operating conditions in the next campaign)
- ✓ Higher S/C and wider range of temperatures to be tested
- ✓ Other biomasses to be studied

Thanks for you attention

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