77° CONGRESSO NAZIONALE ATI

LA SFIDA DEL NUOVO MODELLO ENERGETICO NAZIONALE TRA DECARBONIZZAZIONE, COMUNITA' ENERGETICHE E DIVERSIFICAZIONE DELLE FONTI

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Biomass oxy-CO_2 gasification process for bio-methane production: an experimental and numerical activity

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Introduction and Research motivations

- Air gasification of biomass is a well-known thermochemical process able to convert the biomass into a mixture of gases (syngas), mainly composed of CO, H_2, CO_2, CH_4 and N_2, plus small quantities of other hydrocarbon species;
- Depending on its composition, the producer gas can be conveniently transformed into chemicals, fuels or energy (both heat and power);
- **The present study aims at investigating the feasibility to utilise the oxy-CO_2 gasification approach in order to obtain a nitrogen free syngas, which can be subsequently converted into Synthetic Natural Gas (SNG)**;
- CO_2 is needed in combination with O_2 to mitigate its reactivity, which can lead to excessive reaction temperatures, and also to increase the percentage of CO/H_2 in the syngas;

EXPERIMENTAL ACTIVITY

Experimental gasification plant located at the biomass research area of the University of Pisa:

- Oxy-CO_2 gasification campaign of woody biomass.

NUMERICAL ACTIVITY

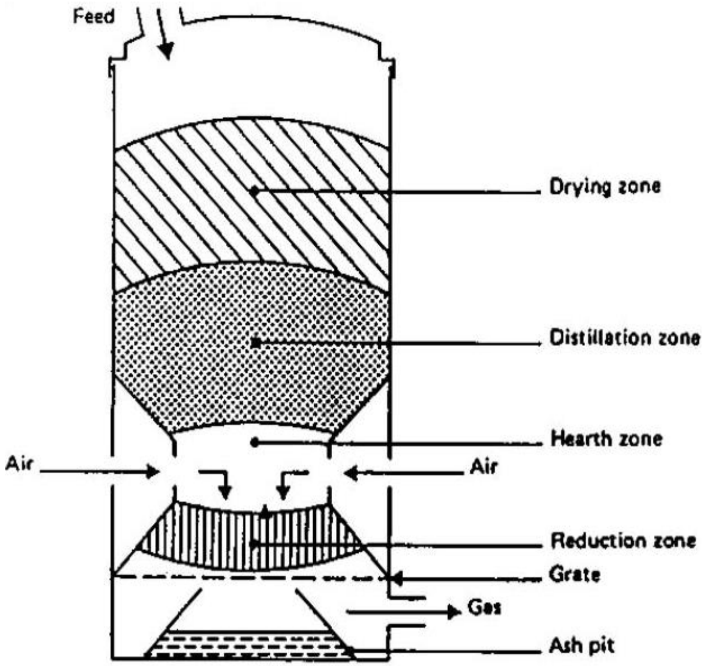
Development in Aspen Plus® environment of:

- Oxy-CO_2 gasification model;
- Methanation model.

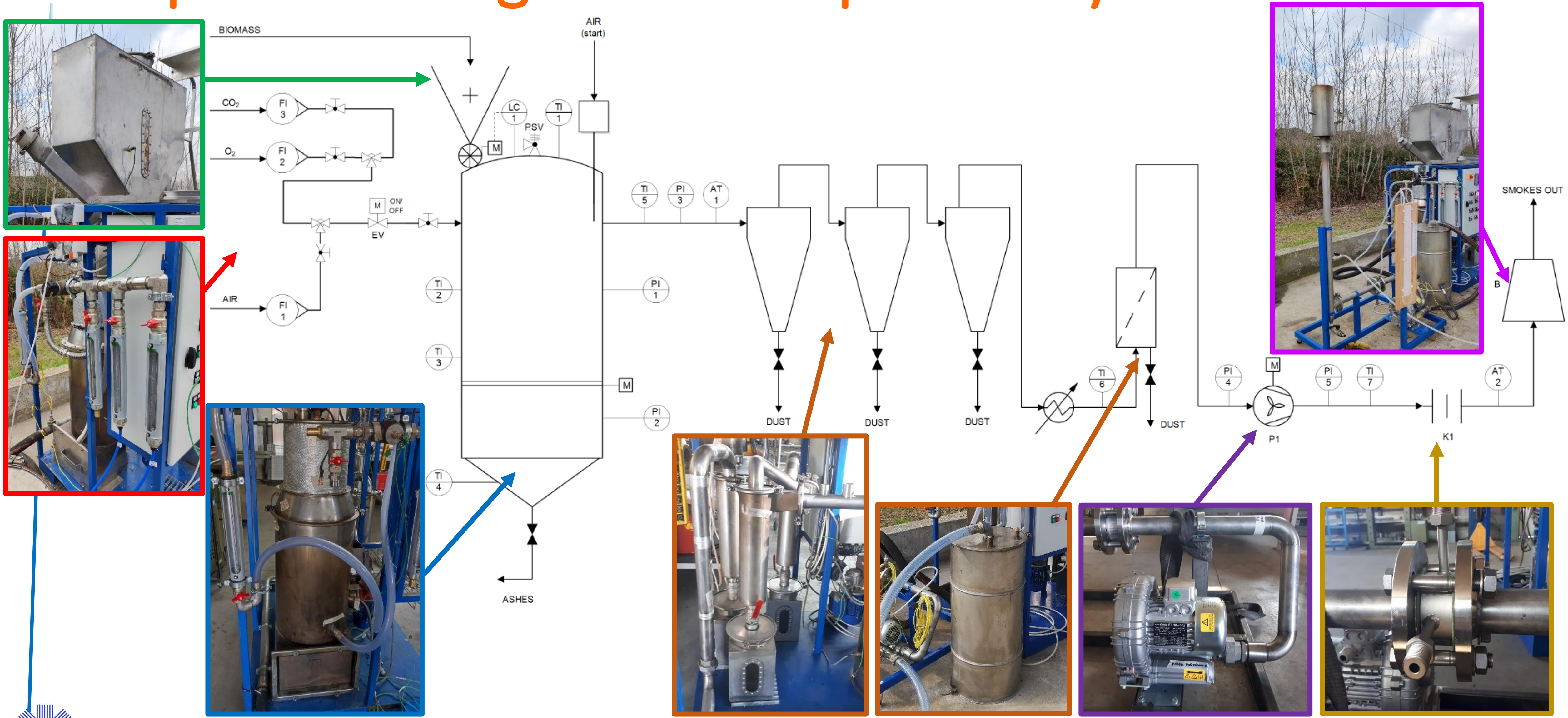
- **The present research has been carried out in the framework of Project LIFE AUGIA "*Sewage oxy-gasification for chemicals production*" (LIFE19 ENV/IT/000669).**

Experimental gasification plant

- Small-scale: max thermal power of roughly 100 kW;
- Fixed-bed gasifier (downdraft);
- Max biomass consumption: 20 kg/h;
- The original plant, conceived for air gasification, had to be adapted for the oxy-gasification experimental activities;
- Technical/mechanical modifications in terms of feeding system layout, piping and gasifying agents distribution system inside the gasifier, this last to obtain more homogeneous conditions of reaction;
- Sealing gaskets for high temperatures;
- Well instrumented (flow meters and temperature/pressure sensors).



Experimental gasification plant: Layout



Biomass characterization activity

Analytical parameters of woody biomass

- moisture content;
- volatile matter (VM) and fixed carbon (FC);
- ash content;
- elemental content of carbon (C), hydrogen (H), oxygen (O) and nitrogen (N);
- heating value (HV).

FEEDSTOCK	Proximate Analysis				Ultimate Analysis				LHV
	Moisture (wt %, ar)	VM (wt %, dry)	FC (wt %, dry)	Ash (wt %, dry)	C (wt %, dry)	H (wt %, dry)	N (wt %, dry)	O (wt %, dry)	LHV (MJ/kg, dry)
Fir pellet	6.83	84.14	15.38	0.47	49.88	6.05	0.07	43.53	18.78

Preliminary experimental activities

Check list tests

- plant control logic;
- correct running of all the sensors/devices;
- recording system;
- cold leak;
- start-up;
- hot leak.

START-UP METHOD

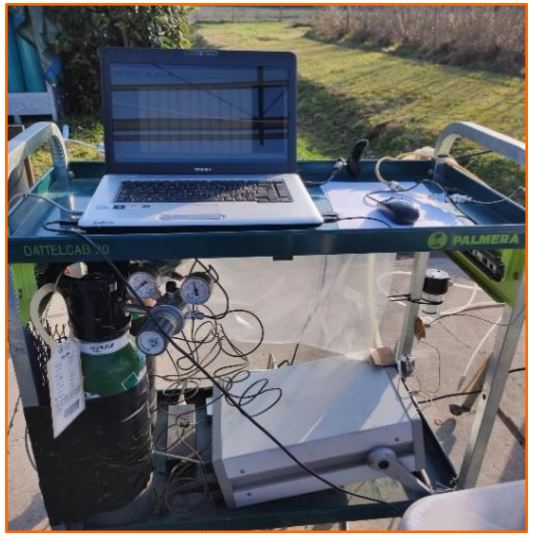
Start:
- cold;
- ignition with air.

After roughly 1h:
- stable operating condition;
- 800-900°C in the reaction zone.

Switch to **oxy-CO_2 gasification**:
- stop air inlet;
- open gradually O_2;
- introduce also CO_2 to mithigate the temperatures.

Experimental activities: oxy - CO_2 gasification

INPUT



Different operating conditions in terms of:

- CO_2/O_2 flow rate ratio;
- CO_2/Biomass mass flow rate ratio;
- Gasifyng agent flow rate.

OUTPUT

- Pressure and temperature values were monitored and recorded;
- Syngas composition was monitored using an Agilent 3000 micro-GC;
- Syngas volume flow rate;
- Mean values for all the measured parameters were calculated for each operative condition.

$$ER = \frac{Actual\ O_2}{Stoich.\ O_2}$$

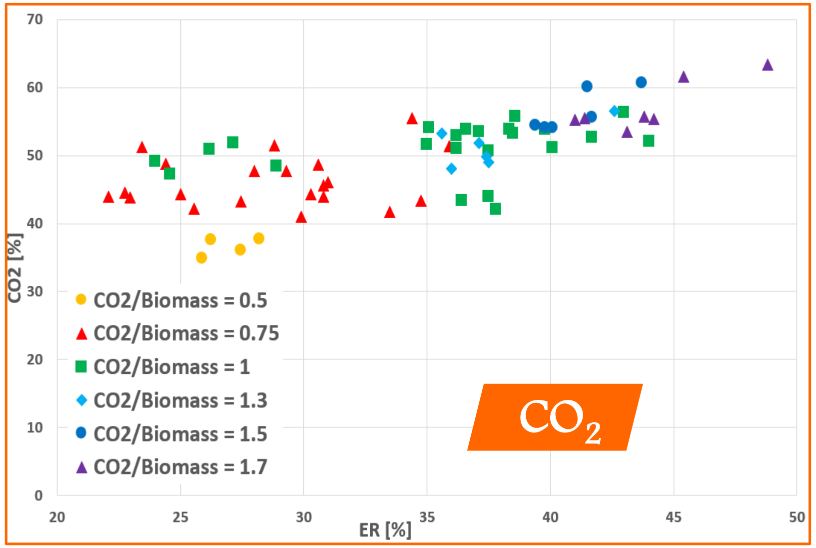
Biomass consumption

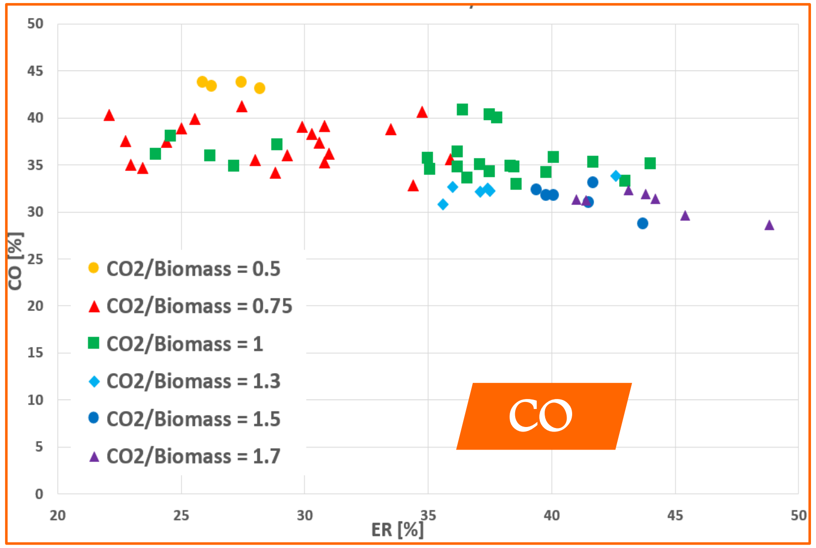
$$CGE = \frac{Th.Power\ Syngas}{Th.Power\ Biomass}$$

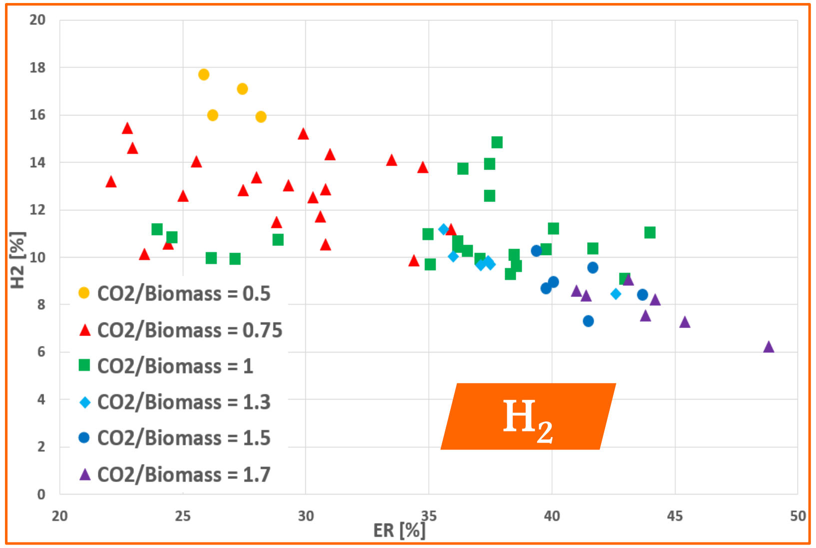
Experimental activities: oxy - CO_2 gasification

OUTPUT RESULTS

Syngas Composition





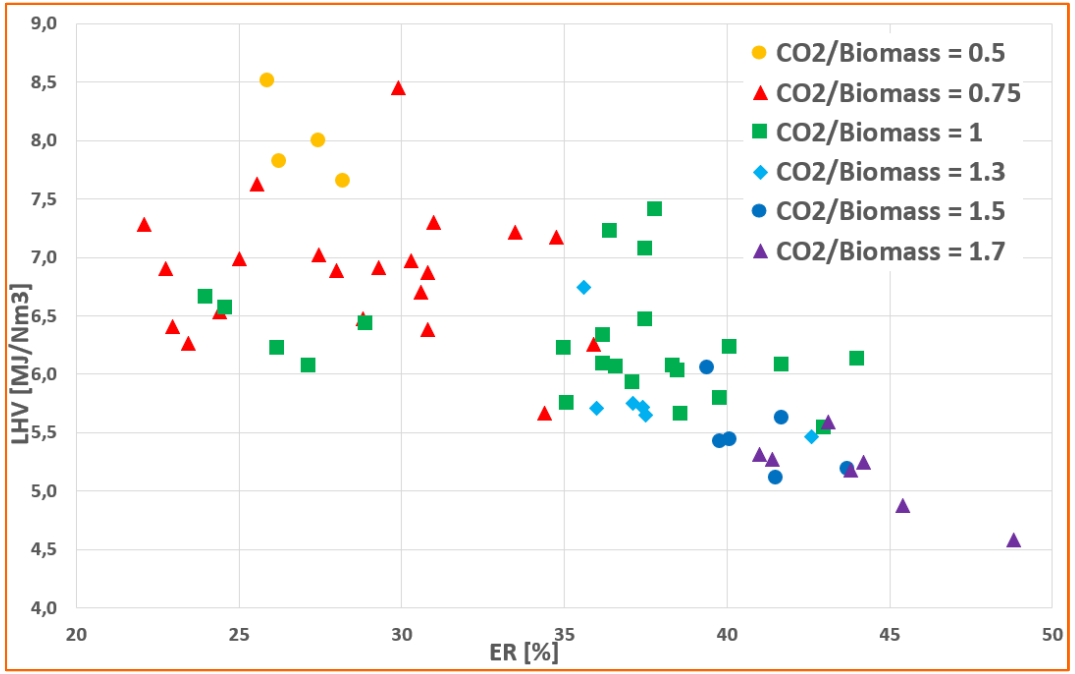


- Equivalence ratio significantly affects the syngas composition:
  CO_2 exhibits an increasing trend as ER increases, while CO and H_2 exhibit a decreasing one;
- The substitution of air with a O_2/CO_2 mixture increases considerably the molar fraction of CO and H_2 in the syngas.

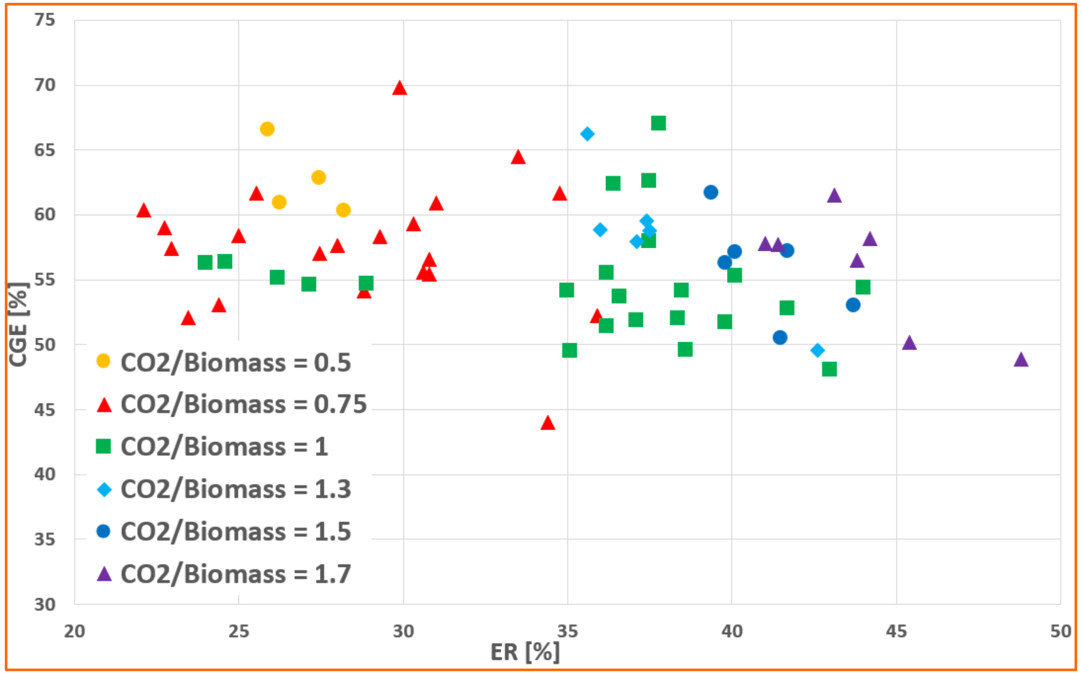
Experimental activities: oxy - CO_2 gasification

OUTPUT RESULTS

Syngas LHV



CGE



- The LHV of the produced syngas decreases with an increase in ER: beneficial effect of lower ER values;
- Satisfying values of the CGE were obtained.

Gasification modelling activity: Description

The gasifier has been simulated using different blocks:

- **DRYING**
- **PYROLYSIS**

} 2 RYield + 2 SEP

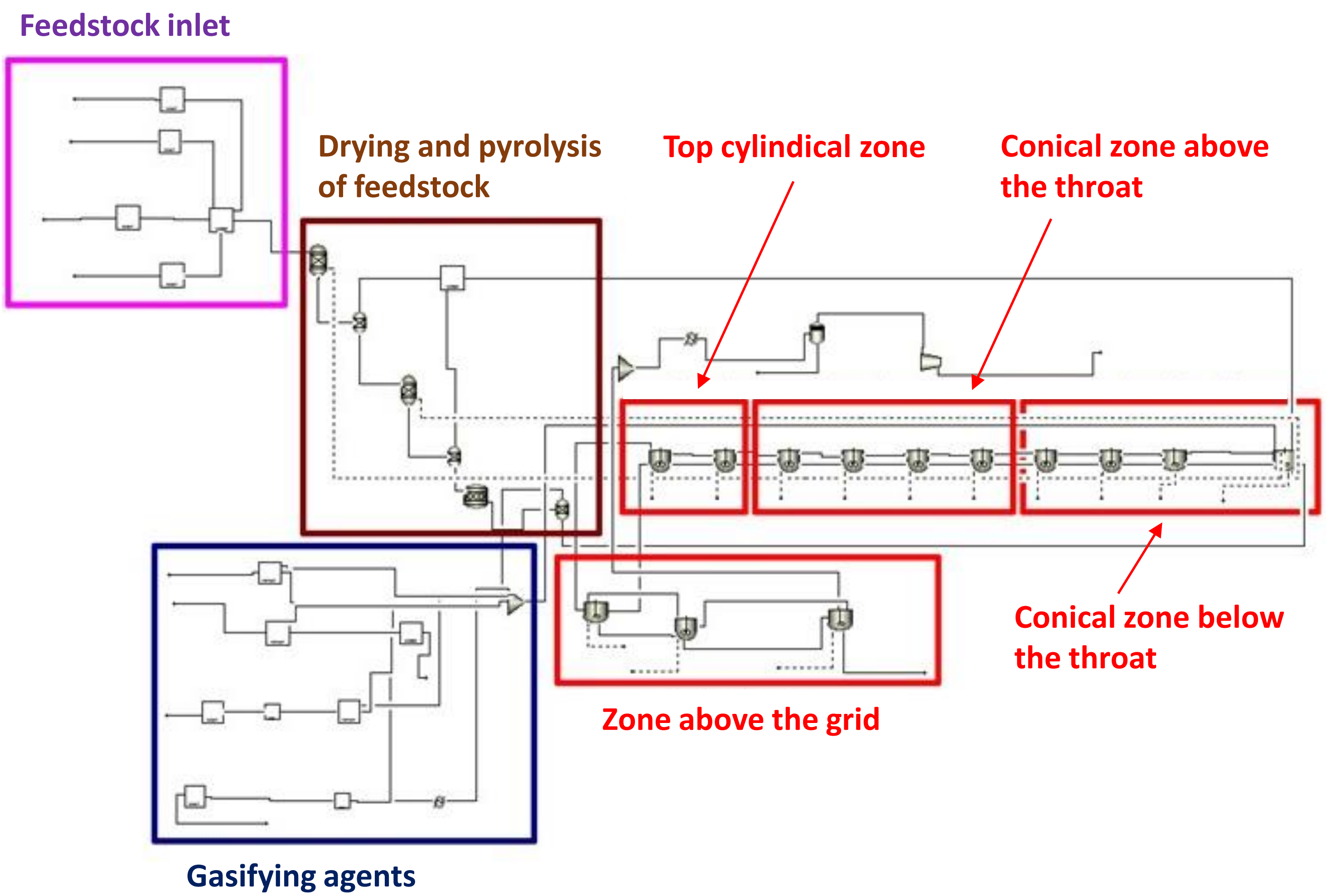
- **OXIDATION**
- **GASIFICATION**

} 13 RCSTR

PSEUDO – KINETIC MODEL

Importance of:

- Geometry;
- Reactions.



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PSEUDO – KINETIC MODEL

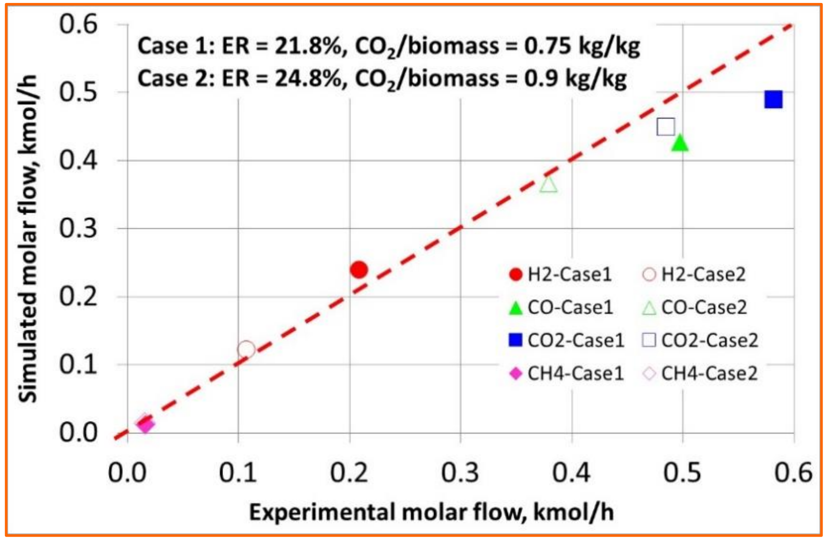
Importance of:

- Geometry;
- Reactions

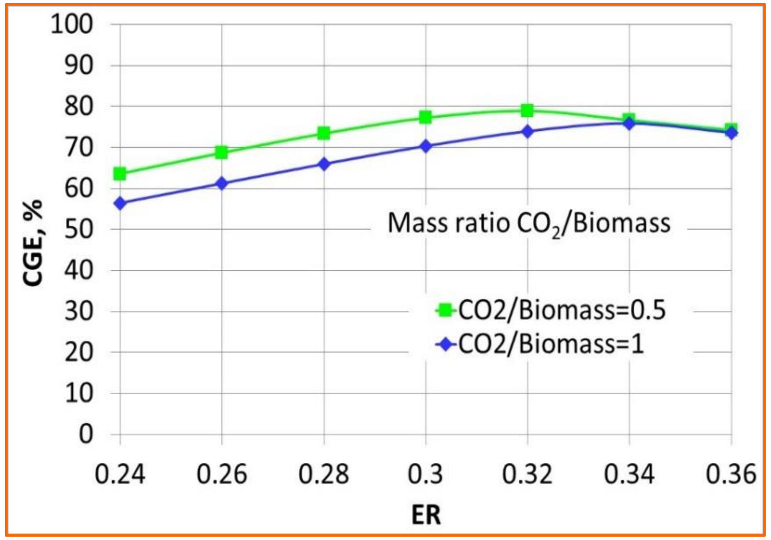
Heterogeneous reactions		
R_1	$C_{(s)} + (\alpha+2)/(2\alpha+2)\ O_{2(g)} \rightarrow \alpha/(\alpha+1)\ CO_{(g)} + 1/(\alpha+1)\ CO_{2(g)}$ $+(110.53\ \alpha + 393.5)/(\alpha+1)$ kJ/mol	*Char Combustion*
R_2	$C_{(s)} + CO_{2(g)} \rightarrow 2\ CO_{(g)}$ - 172 kJ/mol	*Boudouard*
R_3	$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$ - 131 kJ/mol	*Water-gas*
R_4	$C_{(s)} + 2\ H_{2(g)} \rightarrow CH_{4(g)}$ + 75 kJ/mol	*Methanation*
Homogeneous reactions		
R_5	$CO_{(g)} + 0.5\ O_{2(g)} \rightarrow CO_{2(g)}$ + 283 kJ/mol	*CO combustion*
R_6	$H_{2(g)} + 0.5\ O_{2(g)} \rightarrow H_2O_{(g)}$ +242 kJ/mol	*H_2 combustion*
R_7	$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$ + 41 kJ/mol	*Water gas shift*
R_8	$CH_{4(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3\ H_{2(g)}$ - 206 kJ/mol	*Steam-methane reforming*
R_9	$CH_{4(g)} + 1.5O_{2(g)} \rightarrow CO_{(g)} + 2H_2O_{(g)}$ + 517 kJ/mol	*Methane partial- oxidation*
R_{10}	$C_6H_{6(g)} + 7.5\ O_{2(g)} \rightarrow 6\ CO_{2(g)} + 3\ H_2O_{(g)}$ + 3169 kJ/mol	*Oxidation of benzene*
R_{11}	$CH_{4(g)} + 2\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)}$ +804 kJ/mol	*Methane oxidation*

Gasification modelling activity: Validation & Results

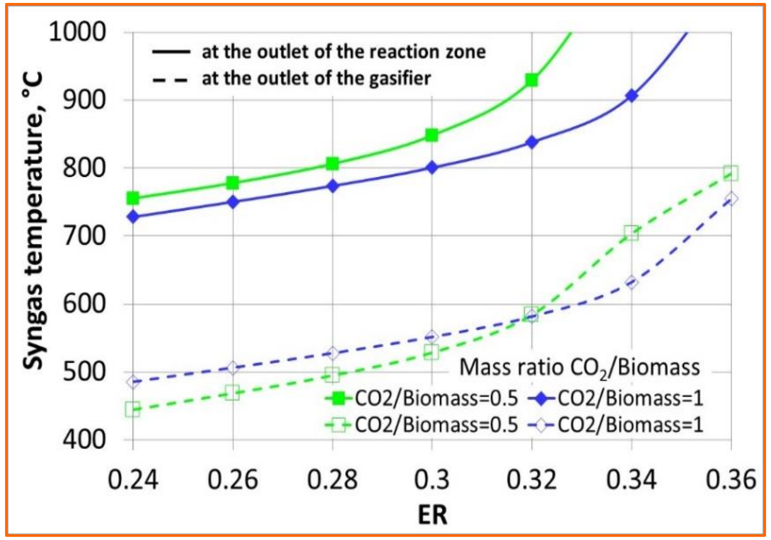
Validation



CGE



Syngas Temperature

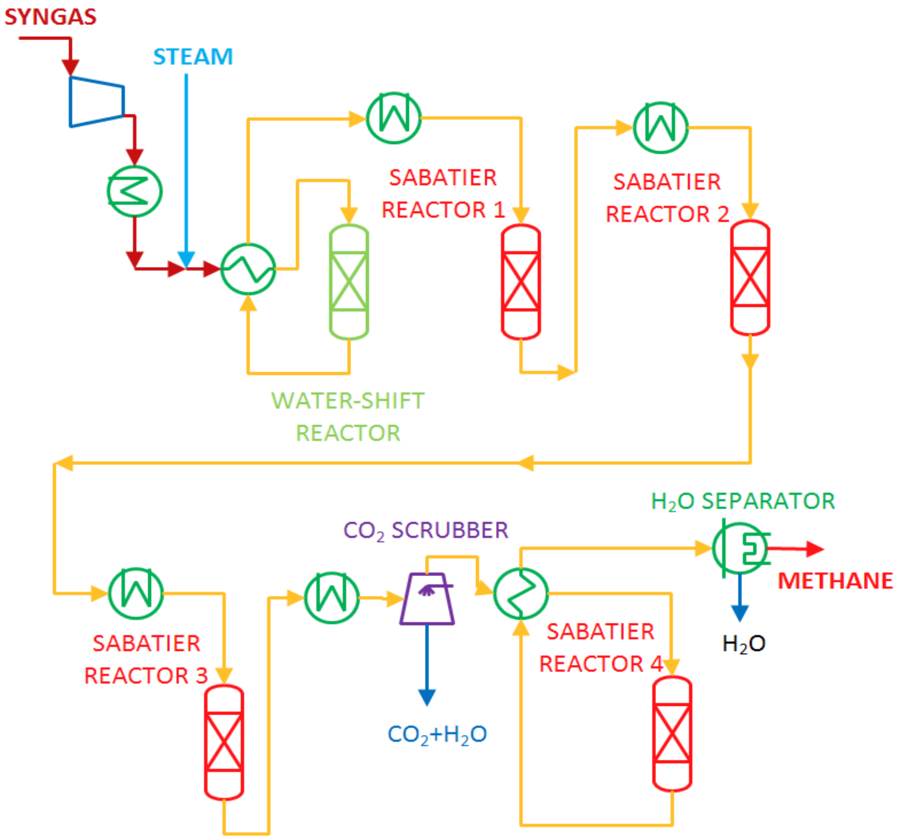


- Using two experimental conditions, a tuning of the model has been carried out in order to limit its estimation error of the molar flow of the main syngas components (H_2, CO, CO_2 and CH_4);
- Best performances of the gasifier can be obtained when a lower amount of CO_2 is used;
- The maximum of the CGE is reached for higher values of ER increasing the CO_2;
- The quantity of CO_2 largely affects the dilution of the syngas and therefore its temperature: it is important for structural limits of the materials.

Methanation modelling activity: Description

The syngas from the gasification system can feed a methanation plant to produce CH_4 enriched stream.

Aspen Plant Layout



Main reactions

Water-shift reactor:

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2\,(g)} + H_{2\,(g)}$$

Sabatier reactor:

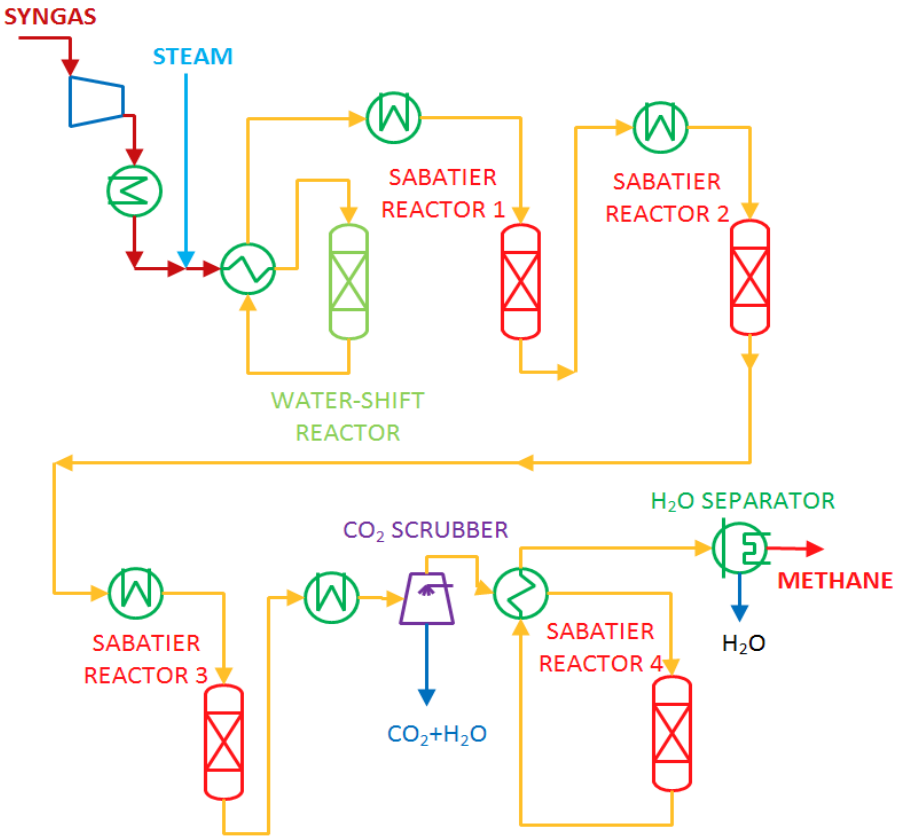
$$CO_{2\,(g)} + 4\,H_{2\,(g)} \leftrightarrow CH_{4\,(g)} + 2\,H_2O_{(g)}$$

- Four reactors with intermediate heating removal systems;
- Activated metallic catalysts (Nickel).

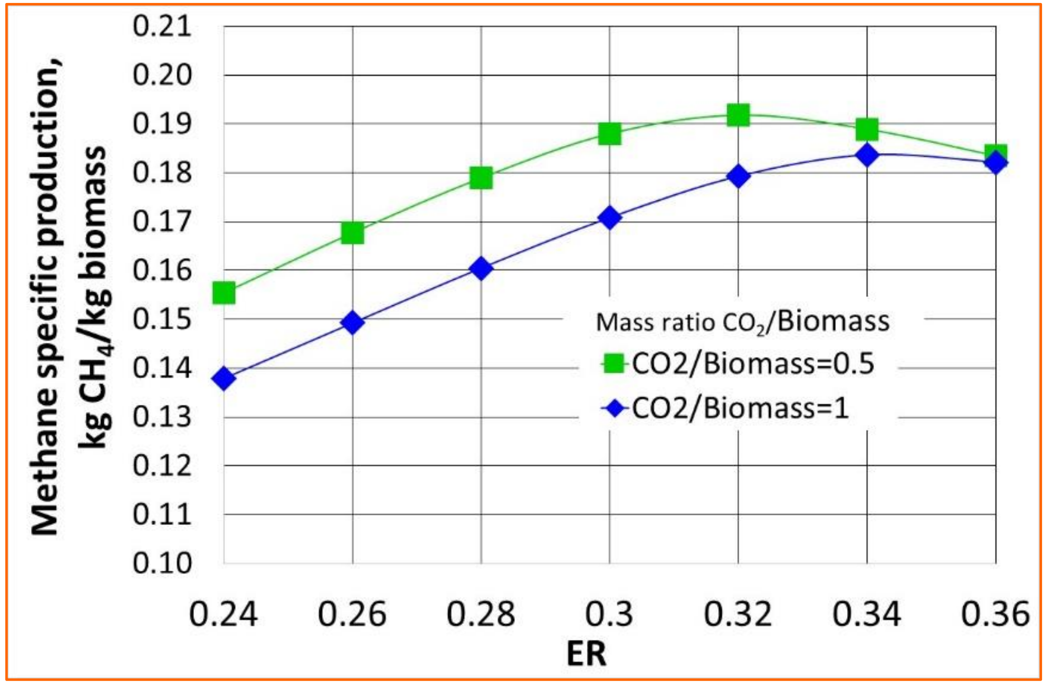
Methanation modelling activity: Results

The syngas from the gasification system can feed a methanation plant to produce CH_4 enriched stream.

Aspen Plant Layout



Results



- The specific production of CH_4 has a trend which is similar to the CGE;
- Best performances of the gasifier can be obtained when a lower amount of CO_2 is used.

Conclusions

- Feasibility of the oxy-CO_2 biomass gasification approach;
- Satisfying experimental results: LHV ~ 7 MJ/Nm^3 and CGE_{max} ~ 70% ;
- Numerical gasification results: high performances when the CO_2 amount is lowered in accordance with the temperature limits due to the structural integrity of the equipment;
- Optimal condition: ER ~ 32%;
- Numerical methanation results: best performances when the CO_2 amount is lowered and ER not so high;
- Max production of methane: ~ 20 kg_{CH4} / 100 $kg_{biomass}$;
- Under the economic point of view, oxy-CO_2 gasification can be interesting if utilised in combination with elettrolitic plants and CO_2-capture system.

Future Activities

- Execution of tests using steam as gasifying agent, substituting partially or completely the CO_2 ;
- Co-gasification of woody biomass with waste matrices (agro-industrial wastes, sewage sludges, ..).

THANKS FOR YOUR ATTENTION

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