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# Modelling and assessment of a sorption enhanced gasification system coupled with hydrothermal carbonization, hot gas cleaning, and plasma to produce pure H<sub>2</sub> from biomass

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## HIGHLIGHTS

- A global simulation model for SEG, HTC, HGC and plasma for H<sub>2</sub> production was developed.
- The carbon footprint of the global plant is 2.3 kg CO<sub>2</sub>/kg H<sub>2</sub>.
- The hydrogen yield referred to the whole plant is 250 g<sub>H2</sub>/kg<sub>BIOMASS</sub>.

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## ABSTRACT

Concerns about energy security, energy prices and climate change led scientific research towards sustainable solutions to fossil fuel as renewable energy sources coupled to hydrogen as energy vector and carbon capture and conversion technologies. Among the technologies investigated in the last decades, biomass gasification acquired great interest owing to the possibility to obtain low cost and CO<sub>2</sub> negative emission hydrogen production from a large variety of everywhere available organic wastes. Upstream and downstream treatment were then studied in order to maximize hydrogen yield, reduce the content of organic and inorganic contaminants under the admissible levels for the technologies which are coupled with, capture, and convert carbon dioxide. However, studies which analyse a whole process made of all those technologies is still missing. In order to fill this lack, the present paper investigated the coexistence of Hydrothermal Carbonization (HTC), Sorption Enhance Gasification (SEG), Hot Gas Cleaning (HGC), and CO<sub>2</sub> conversion by Dielectric Barrier Discharge (DBD) plasma reactor for H<sub>2</sub> production from biomass waste by means of Aspen Plus software. The proposed model aimed to identify and optimise the performance of the plant by varying operating parameters (such as temperature, CaO/biomass ratio, separation efficiency, etc.). The carbon footprint of the global plant is 2.3 kg CO<sub>2</sub>/kg H<sub>2</sub>, lower than the latest limit value imposed by the European Commission to

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consider hydrogen as “clean”, that was set to 3 kg CO<sub>2</sub>/kg H<sub>2</sub>. The hydrogen yield referred to the whole plant is 250 g<sub>H<sub>2</sub></sub>/kg<sub>BIOMASS</sub>.

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## Introduction

In recent decades, fossil fuels have lost their attractiveness as energy source due to global warming and climate change issues, but also because of the urgent need for countries to have their own energy sources.

A reliable alternative to fossil fuels is biomass, a renewable feedstock that is available in large quantities worldwide. In terms of environmental protection concerns, biomass is considered a favourable fuel based on its net carbon balance, as the amount of carbon dioxide produced during the combustion process is virtually used for the production of oxygen during photosynthesis. In this context, the use of organic waste generated by industrial, agro-forestry and municipal activities constitutes a low-cost and sustainable strategy that avoids competition between food and fuels, while reusing and valorising polluting wastes [1–5].

An encouraging way to apply biomass for the production of heat, electricity and other biofuels is through gasification, which has proven to be an efficient and environmental-friendly method of obtaining energy from a large variety of organic wastes [6,7].

Gasification is a thermochemical process for gaseous fuel production involving the partial oxidation of a solid feedstock. In this process, chemical energy of solid is converted into chemical and thermal energy of produced gas [6]. The most relevant advantages of this technology applied to biomass can be listed as [8,9]:

- potential for high electrical efficiencies (compared to conventional small-scale biomass-fired power plants that show an electrical efficiency from around 20% in the 5–20 MWe range up to 35% in the 20–40 MWe range);
- great prospects in fuel synthesis;
- wide market potential (application to a wide range of biomass feedstocks).

Biomass gasification produces a gaseous stream (syngas), which is essentially composed of hydrogen, carbon monoxide, carbon dioxide, water vapour and methane, although undesired organic (tar) and inorganic (mainly hydrogen sulphide and hydrogen chloride) by-products may also be present. Syngas is therefore the first step in the production of hydrogen, a very advantageous energy carrier suitable for the production of electrical and thermal energy without carbon dioxide emissions. Hydrogen is highly efficient since its Lower Heating Value (LHV) is close to 120 MJ/kg (about 3 times higher than that of hydrocarbon fuels [10]) and can be used in sectors as diverse as methanol and ammonia production, internal combustion engine and fuel cell. The latter represents a very

efficient way of converting hydrogen into electricity, ensuring very high efficiency and clean exhaust gases [11].

Biomass displays a number of disadvantages to be used as feedstock in direct gasification, such as high moisture and ash contents, hydrophilic character, poor grindability, low energy density, and heterogeneity. Hydrothermal carbonization (HTC) is becoming a promising technology for upgrading wet biomass, without a drying step prior to gasification [12,13]. HTC of biomass or organic waste consists of the thermochemical transformation in the presence of water of carbon structures by combining temperatures in the range of 180–250 °C and the respective autogenous vapour pressure. Under these conditions, the water acts as a reagent and biomass undergoes reactions similar to those of biochar production, but less activation energy is required. In addition, the lower dielectric constant of sub-critical water favours the decomposition of biopolymers at lower temperatures and the solubilisation of organic compounds. The initial carbon in the raw materials is mostly retained in a carbon enriched-solid, the so-called hydrochar. The liquid by-product is an aqueous stream containing valuable organic and inorganic compounds and the gases generated do not usually exceed 5 wt% [13–16].

Then, capture carbon dioxide (CO<sub>2</sub>) from syngas before its using is very important, especially because CO<sub>2</sub> is the first responsible for greenhouse gas emissions (~82%), which contributes significantly to global warming and climate change issues [17–19]. Sorption-enhanced gasification (SEG) is therefore a highly recommended capture method for purifying syngas and enriching it in hydrogen; this technology is carried out by coupling a CaO-based sorbent to adsorb CO<sub>2</sub>. The gasifier operates at temperatures between 630 and 750 °C to favour this process. Under these conditions, the hydrogen content in the output syngas stream can reach 70% mol (dry basis) [20].

In recent years, besides capture processes, CO<sub>2</sub> conversion processes have acquiring great interest. Those processes are less studied than capture processes, but they seem very promising. It is possible to list three main methods for CO<sub>2</sub> conversion: catalyst, electrolysis, and non-thermal plasma. The latter is the most promising since it has the great advantage to work close to room temperature and atmospheric pressure, moreover it does not need of high electricity consumption that are instead typical of catalyst, electrolysis, which also have the advantageous to operate a high temperature [17,21,22]. Plasma is composed of many reactive species (electrons, ions, radicals, and natural gas molecules) and its responsible for the conversion of CO<sub>2</sub> into CO and O<sub>2</sub> with higher reaction rates and faster reaching of steady state compared to other conversion processes [23]. Plasma is commonly generated by supplying electrical power and, until now, most of the current electrical power is from non-

renewable fossil fuel, which means it enters an amount of CO<sub>2</sub> into the atmosphere. So, in order to make the process sustainable, it is necessary to replace the electrical power from fossil fuels source to renewable source. In this way, plasma technology fed up with renewable energy can be a promising chemical energy storage localised or distributed system during peak grid times [23,24]. Among non-thermal plasma technologies, the most promising reactor seems to be the dielectric barrier discharge (DBD) [25–29], which has an easy design, low operational costs and can be easily integrated with catalyst and also easily upscaled [30,31]. The main disadvantageous of DBD reactor is the limited energy efficiency which is below 20% [32], and this is due to the high energy of electrons produced by the electric field that is not a favourable condition for CO<sub>2</sub> conversion. Nevertheless, recent studies pointed out that it is possible to overcome this issue if some modifications to the plasma system are taken into account, such as integrating a catalyst [33,34]. Zeng and Tu [35] studied the DBD reactor performances and they showed that when alumina, copper or manganese catalyst were added there was an increase of CO<sub>2</sub> conversion up to 4%.

Next, to remove organic and inorganic impurities, hot gas cleaning (HGT) processes (e.g., filter candle and sorbent reactor) have proven to be the most successful [36]. Bed gasifier sorbents and catalytic filter candles represent a good combination to reduce tar compounds as well as to decrease the gasification temperature [36]. Calcined dolomite is the most commonly used sorbent in in-bed gasifiers due to its low cost and wide availability. Calcined dolomite adsorbs tar up to 80% [37]. In contrast, catalytic filter candles convert tar into syngas via reforming reactions. The candles are located in the freeboard of the gasifier, working at a temperature close to that of the gasification process.

Sorbent reactors for the removal of inorganic pollutants can be indicated as the last step of the HGT. Depending on the type of pollutant, it is possible to choose the most suitable sorbent taking into account that it must display high adsorption capacity, fast adsorption kinetics, high equilibrium constant, ability to tolerate high temperatures and regeneration capacity, while maintaining efficient sorption [38]. Generally, hydrogen sulphide is the predominant inorganic compound in biomass-derived syngas and experiments in the literature suggest that zinc-based sorbent successfully removes H<sub>2</sub>S [39–42].

All the above mentioned technologies have been individually studied over the past decades, but there is not available in literature a single study of a global plant which combines all of them. The investigation of a biomass gasification system which includes HTC, SEG, DBD plasma and HGC is very related to the EU Strategic Energy Technology Plan (SET Plan) [43], answering to the biomass general challenges “to improve the performance of the biomass conversion to intermediate bio-energy carriers analogous to coal, oil and gaseous fossil energy carriers and thus create the crude energy feedstock basis that could be further refined to final bioenergy products or directly used for high efficient heat and power generation”. Moreover, the investigation of a such combined plant is also fully aligned with SPIRE PPP roadmap [44] and to the focus area “Connecting

economic and environmental gains-the Circular Economy”, with the objectives to convert residues and to investigate technologies for CO<sub>2</sub> transformation into energy storage molecules (e.g. calcium based sorbents are relatively abundant cheap materials with several outlet markets: iron, steel, aggregates and cement industries), helping to the circular economy, industry decarbonization as well as a more sustainable world and economy based on more efficient, secure and clean energies.

For the reasons explained above, the present research paper developed a simulative model of a biomass gasification system coupled with HTC, SEG, DBD plasma and HGC, since modelling is a well-known tool to investigate plant behaviour in order to optimise its performance by varying operating parameters (such as temperature, steam/biomass ratio, etc.).

As already underlined, until now in literature there are not models which take into account all those units working together, but of course in the last decades researchers have developed and optimized the single unit operations. So, the present paper started with the already achieved knowledge found in literature about the building of the single model units, improving them and developing a coupled system of HTC, SEG, DBD plasma and HGC units. In this way it is possible to understand how the single unit influences each other and how to optimise them in the overall perspective of the whole plant.

About HTC modelling, in recent years a few simulations on HTC have been carried out using Aspen Plus and most of them were techno-economic models. Two works are worth mentioning:

- ❖ the steady-state model developed by McGaughy and Reza [45], who simulated the HTC with a Gibbs reactor, using as input experimental data and forcing the output of carbon content and solid yield according to those experimental results;
- ❖ the steady-state model developed by Akbari et al. [46], who simulated the HTC with a yield reactor, setting as input the yield of the different phases.

Both models do not take into account the kinetic reactions and suffer from oversimplification; however, given the limited source of kinetic data available, these models still provide a reliable basis for investigating the HTC process [25,26].

The simulation of the SEG process using Aspen Plus has been investigated by several authors and the common way to carry out the simulation is by means of an equilibrium model based on free energy minimisation taking into account the gasifier and the calcination reactors both simulated as Gibbs reactor, using CaO as sorbent for in situ CO<sub>2</sub> removal [47,48], showing a 10% increase in H<sub>2</sub> yield at 650 °C and with a CaO/biomass ratio close to 2.

Non-thermal plasma processes can be simplified through the thermodynamic equilibrium modelling. By comparing results coming from a kinetic and thermodynamic equilibrium simulation, it is possible to point out that the majority species are in good agreement, but the minority ones are not [49]. Kinetic models are specific to a single application and

difficult to extend due to the lack of an adequate number of trials since the plasma process has not been deeply investigated yet [50]. So, as first raw results it is fine to provide a thermodynamic equilibrium simulation by means of stoichiometric reactors and separators in Aspen Plus.

HGC has also been approached by several simulations [51–53]. In previous work, Marcantonio et al. [36] have modelled an innovative simulation using Aspen Plus composed of three reactors: a sorbent reactor feeding by catalyst that represents the in-bed gasifier sorbent, a stoichiometric reactor corresponding to the bundle of ceramic filter candles and a stoichiometric reactor feeding by ZnO for hydrogen sulphide removal.

The model investigated in the present paper aimed to identify and optimise the plant performances by varying operating parameters (such as temperature, CaO/biomass ratio, separation efficiency, etc.) and also taking into account the carbon footprint and the hydrogen yield of the global plant.

## Materials and methods

### Feedstocks

For the selection of the biomass waste to use in the gasification process the following criteria were taken into account: feedstock availability on a significant scale (t/year); high LHV; density comparable with the one of the bed; uniform size and shape; low content in sulphur, chlorine and ash [3].

The selected biomass was a representative batch of end-of-life wood supplied by the consortium for solid waste management of Asturias-Spain (COGERSA [54]).

The cheese factory “La Borbolla” [55], located in Asturias-Spain, provided the necessary amount of residual whey as a substitute for water.

Chemical and physics characteristics of the biomass wastes used are reported in paragraph 3.1 *Experimental results*.

### Pre-treatment of biomass waste by HTC

Hydrothermal carbonization was carried out in a 2 m<sup>3</sup> capacity reactor integrated in the COGERSA biorefinery nod. The system was heated with superheated steam (28 bar and 350 °C) generated in the incineration plant of sanitary waste. Out-of-use wood and whey are used as biomass and medium, respectively. Whey is a polluting by-product of the dairy industry that is generated in massive quantities [56]. It consists mainly of water, and some sugars, proteins, and fats, as well as a minor proportion of minerals. Due to its high moisture content, it is not useable as such for fuel production, but it can act as an alternative reaction medium in the HTC process. This combined approach allows the simultaneous recovery of two organic residues, while avoiding water consumption.

Out-of-use wood (30 kg) and whey (1:4 wt ratio, taking into account the biomass moisture) were processed under automated control at 195 °C and autogenous pressure of 13 bar for 3 h. The resulting hydrochar was pressed under 300 bar until

its moisture content was reduced to around 60 wt% and, finally, dried at 35 °C.

In order to obtain sufficiently representative samples of hydrochar, three HTC runs were carried out.

### Characterization of feedstocks and HTC solid product

Proximate and ultimate analyses as well as calorific value determination were accomplished. Moisture and ash content were evaluated following the standard ASTM D7582–15, whereas the percentage of volatile matter was assessed according to ISO18123. The fixed carbon was calculated by subtracting the percentages of moisture, ash, and volatile matter from 100%. The elemental analysis was accomplished by dry combustion in a LECO TruSpec Micro analyser for C, H, N, and S, and oxygen was estimated by the difference from the mass balance (100-Ash-C-H-N-S). The Lower Heating Value and Higher Heating Value (HHV) were assessed using an IKA-WEEME C4000 adiabatic bomb calorimeter.

### HTC plant simulation

The HTC has been modelled according to the following restrictions [57]:

- reaction kinetics effects are neglected;
- the thermodynamic of the HTC reactions are simplified using data coming from experimental pilot plant and reported in Table 4, setting the proximate and ultimate analysis of the two biomasses as input and imposing the ultimate analysis of hydrochar as output;
- mass transport and fluid-dynamics phenomena are not considered.

The Aspen Plus modelling of the HTC has been done using a RYield reactor, in which the yield of the outlet products is defined as input data basing on experimental data, following the approach of Akbari et al. [46].

The simulations of HTC process are carried out at 200 °C (the experimental T was 195 °C) and 13 bar with whey to biomass ratio 4.

### SEG plant simulation

The simulation of the SEG process by means of Aspen Plus is based on mass-energy preservation and chemical equilibrium. The following main assumptions have been made:

- process is steady-state and isothermal [58];
- volatile products principally consist of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O [59];
- char is 100% carbon [60];
- all gases behave ideally;
- pressure drops and heat losses are neglected.

The gasifier is simulated as Gibbs reactor by means of the restricted chemical equilibrium defining the reactions occurring. The temperature of the gasification process is 630 °C. The gasifier is fed by CaO for the *in-situ* CO<sub>2</sub> adsorption. The



**Table 1 – Gasification reactions [47,61].**

Reaction	Reaction name	Heat of reaction	Reaction number
Heterogeneous reaction			
$C + 0.5 O_2 \rightarrow CO$	Char partial combustion	$(-111 \text{ MJ kmol}^{-1})$	(R1)
$C + H_2O \leftrightarrow CO + H_2$	Water-gas	$(+172 \text{ MJ kmol}^{-1})$	(R2)
$2 CO \leftrightarrow CO_2 + C$	Boudouard	$(+172 \text{ MJ kmol}^{-1})$	(R3)
Homogeneous reactions			
$H_2 + 0.5 O_2 \rightarrow H_2O$	$H_2$ partial combustion	$(-283 \text{ MJ kmol}^{-1})$	(R4)
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water gas-shift	$(-41 \text{ MJ kmol}^{-1})$	(R5)
$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam-methane reforming	$(+206 \text{ MJ kmol}^{-1})$	(R6)
$CaO + CO_2 \leftrightarrow CaCO_3$	Carbonation	$(+179 \text{ MJ kmol}^{-1})$	(R7)

**Table 2 – Conversion rate (%) of tar and inorganic compounds reacting with dolomite [36].**

Benzene	50
Naphthalene	82
Toluene	80
Hydrogen sulphide	85

**Table 3 – Conversion rate of components that react in CANDLE [62].**

	S/B = 0.5
Methane	90
Benzene	95
Toluene	92
Naphthalene	90

oxidising agent is steam at steam to biomass (S/B) ratio 0.6. The CaO to biomass ratio is 2 [48]. The reactions occurring within the reactor are listed in Table 1.

Then,  $CaCO_3$  which comes out the gasifier is regenerated in the calcination reactor. The calcination reactor works at 950 °C and it is simulated as a Gibbs reactor setting the reaction:



#### DBD reactor simulation

As mentioned in the Introduction section, the most precise way to model a non-thermal plasma process is through kinetic approach, but this way is difficult due to the lack of kinetic constants and rate coefficients in literature. Since results from kinetic and thermodynamic equilibrium simulation showed that the majority species are in good agreement [49], it

is reasonable to develop a thermodynamic equilibrium model able to give a first indicative raw results. In order to do that, a stoichiometric reactor and two separator blocks were used.

The reaction happened inside the stoichiometric reactor is:



Where the fractional conversion of  $CO_2$  was set at 25% according to Ref. [53].

Then, the two separator blocks are for:

- $O_2$  separation, with an ideally separation efficiency of 100% is assumed;
- Splitting of CO and  $CO_2$ .

#### HGC plant simulation

The proposed HGC process is composed of:

- In-bed use of calcined dolomite;
- Catalytic filter candles in the freeboard of gasifier;
- Adsorption of  $H_2S$  at 450 °C using ZnO as sorbent.

Under the assumption of neglecting by-products formed by the reaction of components with calcined dolomite, the conversion rates reported in Table 2 are used in the simulation. These conversion rates coming from literature experiments carried out in the temperature range 750–850 °C and atmospheric pressure.

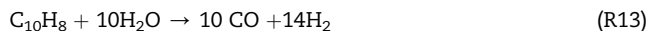
Tar components considered in the present work are toluene ( $C_7H_8$ ), benzene ( $C_6H_6$ ) and naphthalene ( $C_{10}H_8$ ).

The reactions that occur into the block CANDLE of Aspen Plus simulation are:

**Table 4 – Characteristics of the biomass wastes and the HTC solid product.**

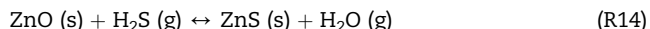
Sample	Proximate analysis (wt% dry basis)				Ultimate analysis (wt% dry basis)					Calorific value (MJ/kg)	
	Moisture (%)	Ash	Volatile Matter	Fixed carbon	C	H	N	S	O	HHV	LHV
Out-of-use wood	11.7 <sup>a</sup>	3.1	77.6	19.3	50.4	5.8	2.9	0.2	37.6	19.7	18.6
Whey	94.2 <sup>a</sup>	11.7	68.1	20.2	40.5	5.5	2.5	0.2	39.6	15.9	14.8
Hydrochar	4.6	4.9	71.2	23.9	51.9	5.5	2.1	0.1	35.5	20.5	19.3

<sup>a</sup> As received.



The conversion rates reported in Table 3 is used in the stoichiometric reactor CANDLE. These conversion rates come from lab-scale gasification tests, which were experimentally validated for S/B = 0.5 [62].

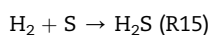
Reaction occurs into the equilibrium reactor “H2SREMOV” is:



Zinc oxide sorbent to H<sub>2</sub>S ratio is set to 2.5 [36].

### Description of Aspen Plus flowsheet

Aspen Plus flowsheet of the developed model is shown in Fig. 1. Stream BIO-WOOD represents the non-conventional biomass feedstock out-of-use wood with constant flow rate ( $m_{\text{bio}}$ ) set to 180 kg/h (1 MW<sub>th</sub> input size, considering HHV). Stream WHEY represents the biomass waste used as medium and mixed with the out-of-use wood (whey to biomass ratio 4) in the mixer MIX0. The mixed stream BIO goes to the pump, called PUMP in Fig. 1, which pressurized the mixture up to 14 bar. Then, the so pressurized stream goes into the HTC, that is set at 200 °C. HTC is simulated as RYield reactor (see section 2.4). The output stream goes into a separator called DRYER that separates the moisture content. At this point, the stream enters to a RStoic reactor called RSTOIC which simulates the production of H<sub>2</sub>S through the following reaction:



The fractional conversion considered for S is 1 [63]. The resulting stream enters a separator (SEP), which splits it into three sub-streams: volatile compounds (VOLATILE), carbonaceous solid (CHAR) and a mix of H<sub>2</sub>S and HCl (INORG). VOLATILE is then split into the VOL and H2 streams. The former is mixed with steam and sent to the gasifier. H2 mixed with the S3 stream needs to simulate the tar production occurring in a RYield reactor (TARPROD); in fact, due to the limitation of the

equilibrium conditions tar formation cannot be simulated in the gasifier reactor. The yield of the produced tar is taken from experimental data quoted in the literature [36]: 60% C<sub>6</sub>H<sub>6</sub>, 20% C<sub>7</sub>H<sub>8</sub> and 20% C<sub>10</sub>H<sub>8</sub>. The S3 stream represents the unreacted char, while the TOGASIF and TOCOMB streams correspond to the char reacted in the gasifier and in the combustor, respectively. The unreacted char was set as 11% of biomass inlet (dry) according to Ref. [64]. MIX2 is a mixture of the RAWSYNG, INORG and TAR streams; the S6 stream is the real output of the gasifier. This is followed by an RGibbs reactor (BEDREACT) simulating the use of calcined dolomite in the bed, an RStoic reactor (CANDLE) approaching the catalytic reaction of the filter and a REquil reactor (H2SREMOV) simulating the removal of H<sub>2</sub>S (section 2.6).

The combustion chamber is simulated as an RStoic, called COMB. The sorption-enhanced gasification consists of a gasifier (GASIF) and a calcination reactor (CALCER), both simulated as RGibbs reactors, as indicated in section 2.5 above.

The CAOFRESH stream feeds the gasifier with solid CaO at a ratio CaO/biomass = 2. CYCLONE is a cyclone that separates the solid part (hydrochar and CaCO<sub>3</sub>) from the volatile matter. The hydrochar and CaCO<sub>3</sub> contained in the “CACO3+CH” stream goes to the CALCER calcination reactor where the CaO is regenerated and through a second cyclone (CYCLONE2) split while the CO<sub>2</sub> is separated and captured. The CaO separated can be recirculated in the gasifier, but since the simulation is in steady state it is not possible to evaluate it. The captured CO<sub>2</sub> is sent to a RStoic reactor which simulates the DBD plasma reactor according to reaction (R9) and then two separator blocks following, the first for O<sub>2</sub> separation and the latter to split CO and CO<sub>2</sub>. The so separated CO<sub>2</sub> can be recirculated into the DBD reactor.

## Results and discussion

### Experimental results

Proximate and ultimate analysis and the calorific value of the biomass wastes used as feedstocks and the resulting solid (hydrochar) from the HTC pre-treatment are shown in Table 4.

Following the general pattern reported for hydrothermal treatment of woody biomass at 180–200 °C [65–67], out-of-use

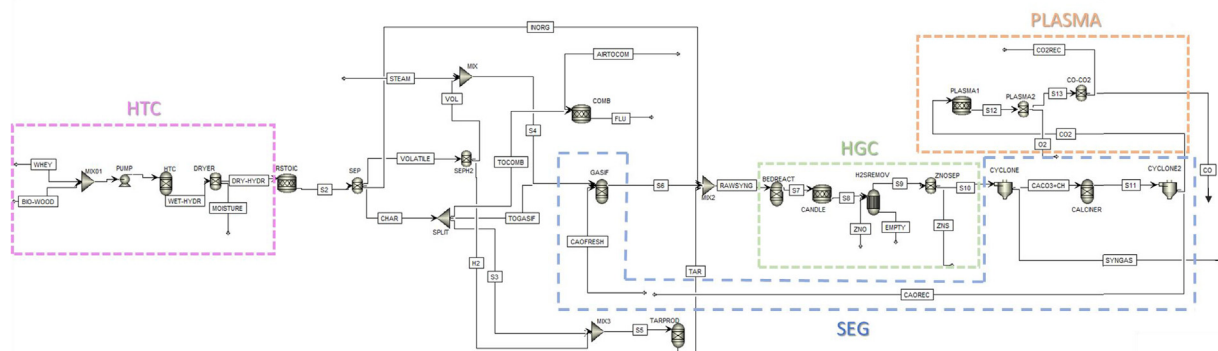


Fig. 1 – Aspen Plus flowsheet of the developed model.

wood waste yields 75.6 wt% of hydrochar with respect to the original feedstock (dry basis). This HTC solid is enriched in fixed carbon, while the oxygen and volatile matter content is reduced. The ash percentage is increased due to the contribution from inorganic impurities of whey, but the value still remains below 5 wt%. The slight decrease in O/C (from 0.56 to 0.51) and H/C (from 1.38 to 1.27) ratio indicates a mild carbonization process that converts wood residue into a stable peat-like solid [68] with LHV of 19.3 MJ/kg.

### Evaluation of the effect of HTC pre-treatment of biomass

The approach carried out by means of Aspen Plus software provides insights into the impact of HTC pre-treatment on the syngas composition out of the gasifier. Two scenarios have been compared: the case with HTC and dewatering and the case without HTC and dewatering. The results of the comparison are shown in Table 5.

It appears that the increase in carbon content generated by the HTC pre-treatment (Table 4) influences the content of CO and CO<sub>2</sub>. Indeed, the higher availability of char favours for the water gas (R2) and the Boduard reaction (R3), determining an increase in CO and CO<sub>2</sub> content respectively. Also, the O/C must be taken into account, in fact this ratio is lower when HTC is used, favouring the incomplete char oxidation, and resulting in the increasing of CO concentration. In literature similar trends were observed by Refs. [69,70].

Then, about the trend of methane concentration: the under or over prediction of CH<sub>4</sub> is an ordinary issue in equilibrium models [71]. Indeed, in reality the conversion methane is kinetically limited, that means the moles of carbon and hydrogen converted in methane are controlled by non-equilibrium factors, so it is not possible to obtain a good prediction by means of simulative models that are based on equilibrium [72].

The case without HTC and dewatering obtained a higher fraction of H<sub>2</sub> (about 34% more) compared to the case with HTC and dewatering. This negative effect of HTC and dewatering on syngas production is due to the large number of organic matters that are removed as an HTC liquid. By means of Aspen Plus simulation, modelling the HTC process as a RYield according to experimental data, it is not possible to identify this liquid stream and to investigate its reuse, but in the real case it is possible to use the liquid for methane production through anaerobic digestion or for recovering of valuable chemicals [73]. The scenario with HTC and dewatering has the worse CO<sub>2eq</sub> emission (6.88 tonnes) compared with the case without (1.14 tonnes), since the syngas produced

is more in the case with HTC (biomass whey is summed to out-of-use biomass). Before concluding that HTC only negatively affects syngas composition, an energy efficiency analysis was carried on. Investigating the cold gas efficiency of the gasification process (calculated as shown in (1)) with and without HTC and dewatering it was found that the use of HTC and dewatering increases the cold gas efficiency by about 8%, going from 58% to 63%.

$$\mu_{CG} = \frac{M_{syn} \cdot LHV_{syn}}{M_{biomass} \cdot LHV_{biomass}} \quad (1)$$

Where  $M_{syn}$  and  $M_{biomass}$  are the mass of the produced syngas and the original biomass respectively;  $LHV_{syn}$  and  $LHV_{biomass}$  are the LHV of the produced syngas and the original biomass respectively.

### SEG performance evaluation

In order to evaluate the effectiveness of SEG model coupled with HTC, the output syngas has been compared in two cases (see Table 6): without SEG, only using a gasifier simulated as RGibbs working at 630 °C and with SEG, following the operative conditions introduced in paragraph 2.3 SEG plant simulation.

Removing CO<sub>2</sub> as solid CaCO<sub>3</sub> shifts the water gas-shift (R5) equilibrium to convert more carbonaceous gas into hydrogen. The under or the over prediction of CH<sub>4</sub> is an ordinary issue in the simulative modelling since tar is not considered in the equilibrium models and it is simulated apart from the gasifier block [71].

In order to validate the developed model of SEG, output results from SEG, without HTC influence, have been compared against a range of literature experimental data coming from:

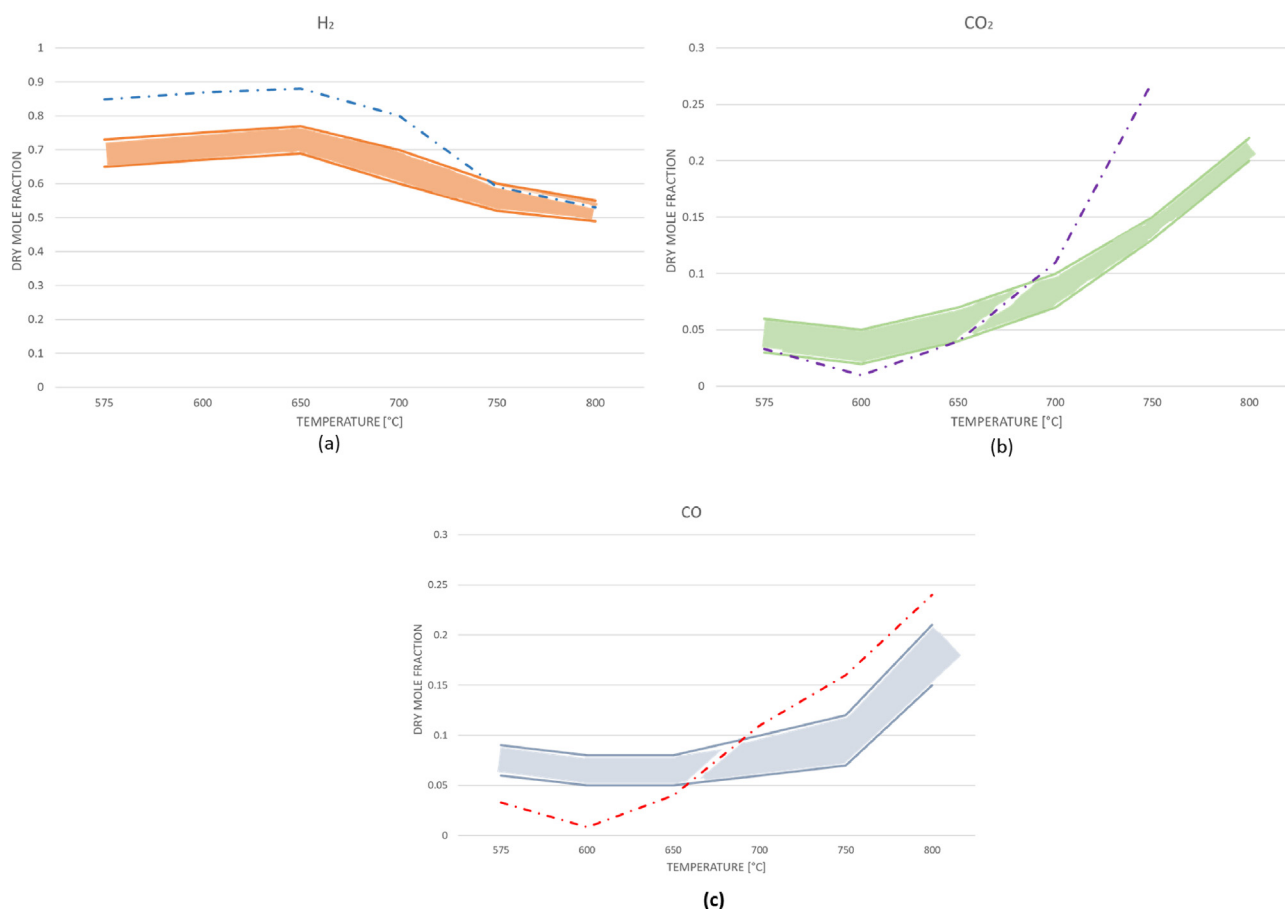
- Schmid et al. [74], who realized a 100 kW SEG with a dual fluidised bed gasifier using CaO as bed material. Alternative biomass feedstock was considered: soft wood, bark and lignite, steam to biomass was in the range 0.5–1 and gasifier temperature was investigated in the range 550–800 °C.
- Hawthorne et al. [75], who investigate a 200 kW SEG with a dual fluidised bed gasifier using Swabian limestone, which is almost made of CaO, as bed material. Biomass used was

**Table 5 – Comparison of syngas composition out of SEG with and without HTC process.**

	Stream RAWSYNG (without HTC)	Stream RAWSYNG (with HTC)
H <sub>2</sub> (%dry mole fraction)	88.12	57.64
CO (%dry mole fraction)	1.80	14.08
CO <sub>2</sub> (%dry mole fraction)	1.01	9.81
CH <sub>4</sub> (%dry mole fraction)	2.91	8.81
H <sub>2</sub> yield (g <sub>H2</sub> /kg <sub>BIOMASS</sub> )	83	150

**Table 6 – Comparison of syngas composition with and without SEG process, coupled with HTC.**

	Stream DRYSYNG (without SEG)	Stream DRYSYNG (with SEG)
H <sub>2</sub> (%dry mole fraction)	45.72	57.64
CO (%dry mole fraction)	21.78	14.08
CO <sub>2</sub> (%dry mole fraction)	22.21	9.89
CH <sub>4</sub> (%dry mole fraction)	5.1	8.81
H <sub>2</sub> yield (g <sub>H2</sub> /kg <sub>BIOMASS</sub> )	140	150



**Fig. 2 – (a)–(c) - Range of the main product gas composition from Refs. [74–76] varying gasification temperature. Experimental data coming from literature are inside the range covered by the coloured area, while simulative results coming from the developed model presented in this paper are indicated as dashed line.**

wood pellets. Gasification temperature was evaluated in the range 550–800 °C.

- Fuchs et al. [76], who analysed a 100 kW SEG with a dual fluidised bed gasifier using CaO as bed material. Biomass investigated in the experiment was: soft wood, rice husk, bark, and lignite. Gasifier temperature was investigated in the range 550–800 °C.

In Fig. 2 (a)–(c) is reported the range of the main product gas composition from Refs. [74–76] varying gasification temperature. Experimental data coming from literature are inside the range covered by the coloured area, while simulative results coming from the developed model presented in this paper are

indicated as dashed line. The higher H<sub>2</sub> production from simulative results shown in Fig. 2 (a) is due to the thermodynamic equilibrium model which overestimate the values. However, the trend of hydrogen concentration varying temperature is in good agreement with experimental data and over 650 °C clearly showed a significant decrease. The trend of CO<sub>2</sub> from simulative model is pretty close to experimental data up to 700 °C then there is a higher increase probably due to the ideality of the model which not considered all the by-products. The trend of CO from simulative model is inside the range of experimental data between 650 and 700 °C, and even if a bit far from the experimental data the simulative trend is still in agreement with real values. Methane was not

**Table 7 – Comparison of H<sub>2</sub> yields from different biomass conversion processes.**

Technology	Biomass	Reactor	S/B	Temperature (°C)	H <sub>2</sub> yield (g <sub>H2</sub> /kg <sub>BIOMASS</sub> )	Ref.
Steam gasification	Wood sawdust		0.17–0.51	630–830	98–101	[78]
Steam gasification	Palm oil	Fixed bed	0.6	800	121	[79]
Steam gasification	Mixed sawdust		0.5–1.5	730–1200	80–130	[80]
Steam gasification	Pellet wood	Fluidised bed	1.7	850	128	[77]
Steam gasification	Miscanthus X giganteus	Fluidised bed	1	800	73	[81]
Pyrolysis/reforming	Pine wood/pyrolysis volatiles	Spouted bed/fluidised bed	1.7	500/600	110	[82]
Bio-oil reforming	Raw bio-oil	Fluidised bed	10	700	102	[83]



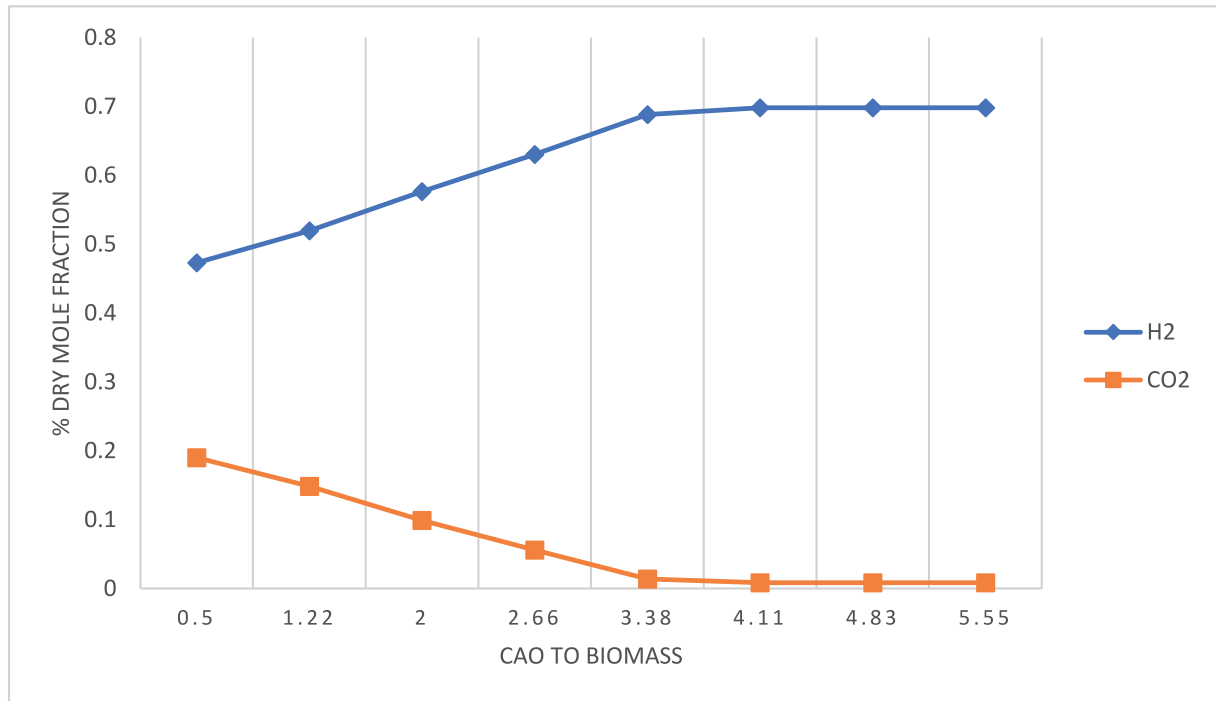
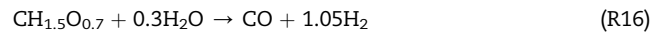


Fig. 3 – Effect of CaO to biomass ratio on H<sub>2</sub> production and CO<sub>2</sub> production at constant 630 °C and S/B = 0.6.

included in the validation because it is not a significant comparison since the neglect of tar in the equilibrium model of the gasifier determines an under or over prediction of CH<sub>4</sub> that is far from reality as already discussed above.

As shown in Table 6, the hydrogen yield increases from 140 g<sub>H<sub>2</sub></sub>/kg<sub>BIOMASS</sub> without SEG to 150 g<sub>H<sub>2</sub></sub>/kg<sub>BIOMASS</sub> with SEG. In order to do a more significant comparison, the theoretical hydrogen yield obtainable gasifying the biomass described by its ultimate and proximate analysis in Table 1 was calculated as follow. According to the major elements, the biofuel can be

written as CH<sub>1.5</sub>O<sub>0.7</sub> and assuming to use steam as gasifying agent, the following chemical reactions occurs [77]:



If the fuel reacts with a hydrogen bearing species, the hydrogen yield potential can be increased near to the 6% maximum imposed by fuel composition [77]. Under those

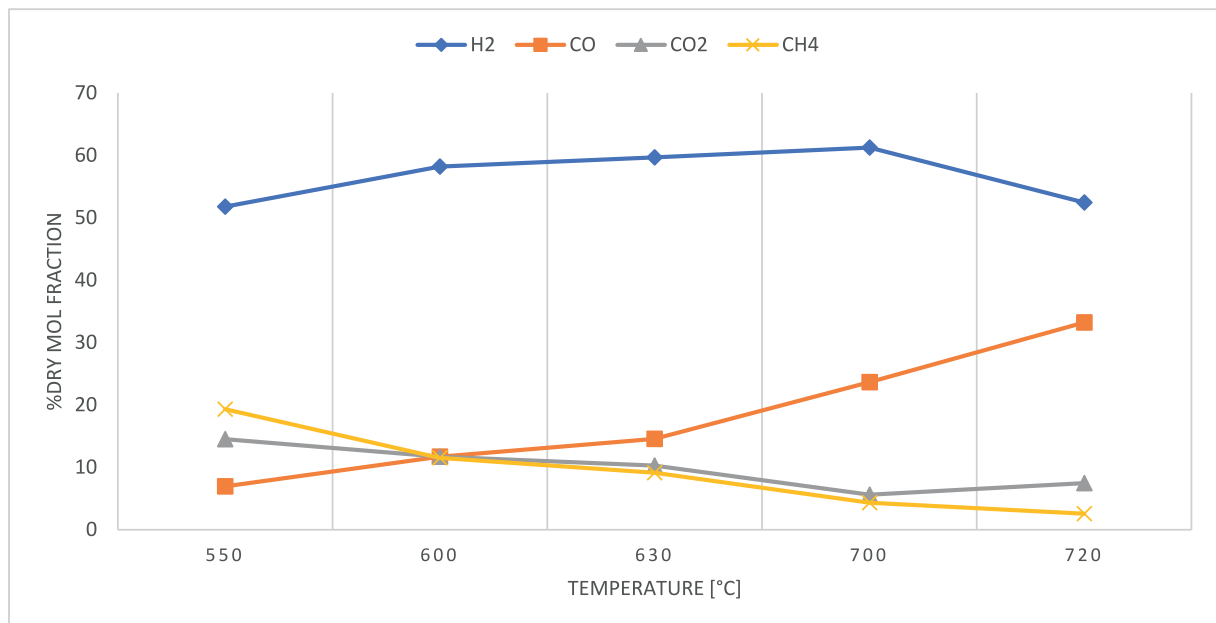


Fig. 4 – Effect of temperature on SEG performances.

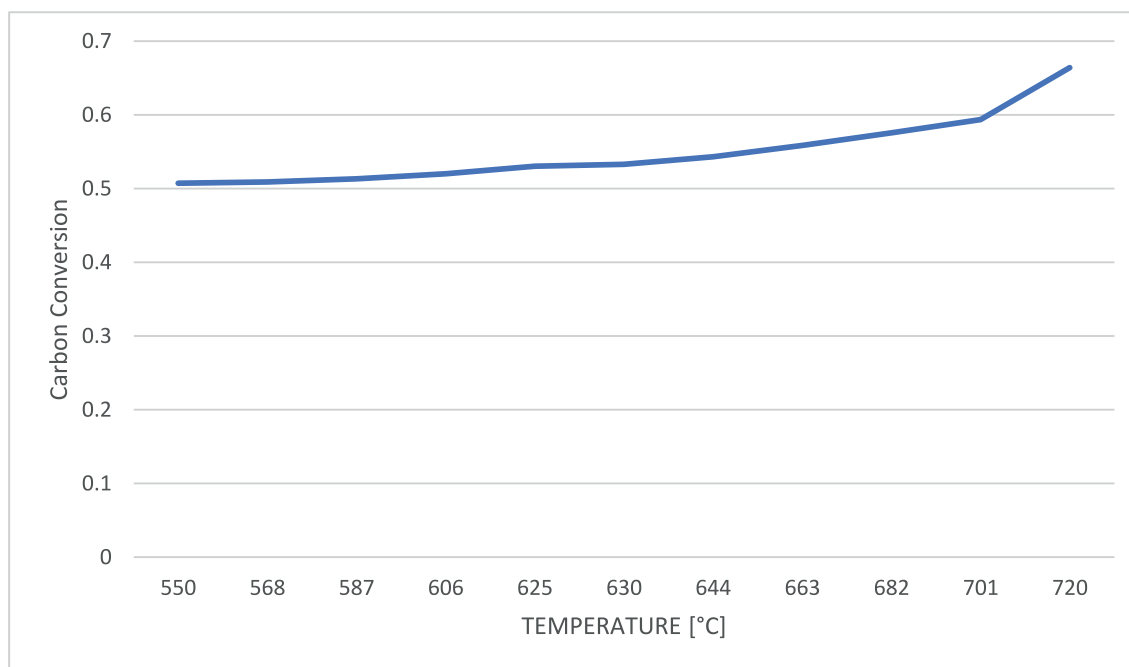


Fig. 5 – Influence of gasifier temperature on carbon conversion.

assumptions, the theoretical maximum yield of  $165 \text{ g}_{\text{H}_2}/\text{kg}_{\text{BIOMASS}}$  is calculated. Of course, the theoretical maximum yield cannot be reached but ideally, and the simulative results obtained are very high and promising in comparison with the theoretical case, showing that the process under investigation is feasible and profitable. Moreover, in Table 7 it is shown a list of  $\text{H}_2$  yield from literature experiments. The experimental results of  $\text{H}_2$  yield in the S/B range 0.17–1.7 and in the temperature range 630–1220 °C are lower than the simulative results achieved in the present model, underlining the potential of the proposed system.

Considering again the SEG unit coupled with HTC, the effect of varying CaO to biomass ratio on  $\text{H}_2$  production and  $\text{CO}_2$  production is shown in Fig. 3.

CaO enhances the production of  $\text{H}_2$  while adsorbing  $\text{CO}_2$  following reaction (R7) and then shifting the chemical equilibrium of reaction (R5) consuming more CO to produce more  $\text{H}_2$ . Similar trends have found in literature [48]. As shown in Fig. 3, the trend of  $\text{H}_2$  and  $\text{CO}_2$  reaches a plateau when CaO to biomass ratio overcomes 4; so, accordingly to the desired output of  $\text{H}_2$  and  $\text{CO}_2$ , the best range for CaO to biomass ratio is from 2 up to 3.

The effect of temperature on SEG performances has evaluated and showed in Fig. 4. The sensitivity analysis clearly indicated that over 700 °C unfavourable conditions happen:  $\text{H}_2$  production decreases and  $\text{CO}_2$  production increases.

The influence of temperature on carbon conversion inside the gasifier was investigated, as shown in Fig. 5.

#### HGC performance evaluation

The syngas composition after each step of HGC has been investigated and reported in Table 8. It has been assumed to neglect by-products formed by the reaction of components with ZnO in the sorbent reactor H2SREMOV.

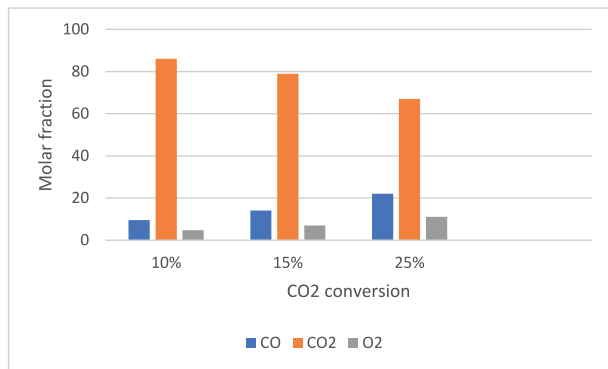
The HGC process increases the hydrogen production of 17%, going from 57.64% dry mole fraction out SEG to 69.34% dry mole fraction out the last step of HGC.

The hydrogen yield referred to the whole plant is  $250 \text{ g}_{\text{H}_2}/\text{kg}_{\text{BIOMASS}}$ .

Moreover, the model of HGC proposed allows to reduce the level of  $\text{H}_2\text{S}$  and tar under the critical level associated to the most common syngas applications (such as not only ICE and gas turbine that have higher levels but also, ammonia and

Table 8 – Syngas composition after each step of HGC.

	Stream RAWSYNG (out of SEG process)	Stream S7 (out BEDREACT)	Stream S8 (out CANDLE)	Stream 9 (out H2SREMOV)
$\text{H}_2$ (%dry mole fraction)	57.64	61.90	69.34	69.34
CO (%dry mole fraction)	14.08	15.47	22.34	22.34
$\text{CO}_2$ (%dry mole fraction)	9.89	10.71	7.28	7.28
$\text{CH}_4$ (%dry mole fraction)	8.81	9.52	0.65	0.65
$\text{H}_2\text{S}$ (ppm)	1238	199	160	0.047
$\text{C}_6\text{H}_6$ ( $\text{g}/\text{Nm}^3$ )	70.60	34.41	0.21	0.21
$\text{C}_7\text{H}_8$ ( $\text{g}/\text{Nm}^3$ )	27.80	5.95	2.19	2.19
$\text{C}_{10}\text{H}_8$ ( $\text{g}/\text{Nm}^3$ )	38.62	7.45	0.59	0.59



**Fig. 6** – CO<sub>2</sub>, CO and O<sub>2</sub> trend out of stoichiometric plasma reactor for CO<sub>2</sub> conversion of 10%, 15% and 25%.

methanol synthesis and SOFC that have lower levels as less than 1 ppm for H<sub>2</sub>S and less than 1 g/Nm<sup>3</sup> for tar [36]).

Then, it was evaluated the carbon footprint of the global plant, this value is 2.3 kg CO<sub>2</sub>/kg H<sub>2</sub> and it is lower than the latest limit value imposed by the European Commission to consider hydrogen as “clean”, that was set to 3 kg CO<sub>2</sub>/kg H<sub>2</sub> [84].

#### DBD reactor performance evaluation

The stream of CO<sub>2</sub> coming from SEG process has a mass rate of 280 kg/h and when it entered into the stoichiometric reactor (called PLASMA1 in the flowsheet of Fig. 1) it is split in CO and O<sub>2</sub> according to reaction R8. The highest fractional conversion of CO<sub>2</sub> which can be achieved in a DBD reactor is 25% [53] and this value was set in the simulation. Then, Fig. 6 shows the resulting molar fraction of CO and O<sub>2</sub> for a CO<sub>2</sub> conversion of 10%, 15% and 25%.

Considering a fractional conversion of 25% for CO<sub>2</sub>, the resulting stream of O<sub>2</sub> and CO, after met the separator blocks, is 25 kg/h and 45 kg/h respectively. The stream of CO may be used for methanol synthesis.

## Conclusions

The present research investigated the coexistence of HTC, SEG, DBD plasma and HGC through a simulative approach by means of Aspen Plus software. This study took the literature knowledge of the single unit to improve them and to evaluate their function together in order to demonstrate the feasibility of the plant. Indeed, until now there is not a simulative comprehensive study which included all those units. The proposed model aimed to optimise the performance of the plant by varying operating parameters (such as temperature, CaO/biomass ratio, separation efficiency, etc.). The investigation highlighted that coupling HTC pre-treatment with SEG process negatively influences the syngas composition, decreasing H<sub>2</sub> and increasing CO and CO<sub>2</sub> due to the higher availability of char which favours the water gas (R2) and the Boduard reaction (R3). Also, the CO<sub>2eq</sub> emission is investigated, revealing that the scenario with HTC and dewatering

has the worse CO<sub>2eq</sub> emission (6.88 tonnes) compared with the case without (1.14 tonnes). Then, an energy efficiency analysis was carried through the calculation of cold gas efficiency which revealed that the use of HTC and dewatering increases the cold gas efficiency of SEG by about 8%, going from 58% to 63%. This means that HTC pre-treatment can be included or not depending on what is the aim of the plant, each case must be evaluated in order to understand if a worse syngas composition may be compensated by an increase of energy efficiency (with a consequent reduction of electricity consumption).

SEG process was then analysed, and it was found that the SEG increased the hydrogen yield of 5% compared with the case without SEG. Moreover, SEG increased the concentration of hydrogen about 20% due to the removal of CO<sub>2</sub> as solid CaCO<sub>3</sub> which shifts the water gas-shift (R5) equilibrium to convert more carbonaceous gas into hydrogen. The output results from SEG simulative unit were validated against experimental data showing a good agreement. A sensitivity analysis was carried out in order to evaluate the optimum CaO to biomass ratio and it was demonstrated that over 3.5 there was not increase of H<sub>2</sub> which reached a plateau. So, the optimum CaO to biomass ratio is in the range 2–3. Another sensitivity analysis was then carried out to investigate the effect of temperature on SEG performances. The investigation indicated that over 700 °C unfavourable conditions happen: H<sub>2</sub> production decreases and CO<sub>2</sub> production increases. The proposed HGC model was found to absolve the requisites required for the most common syngas applications (such as SOFC, ammonia production, methanol synthesis, gas turbine, etc.) which are less than 1 ppm for H<sub>2</sub>S and less than 1 g/Nm<sup>3</sup> for tar. Then, the plasma reactor allowed to convert the CO<sub>2</sub> captured by SEG into O<sub>2</sub> and CO. Considering a fractional conversion of 25% for CO<sub>2</sub> and considering an ideal efficiency of 100% for the membrane separator which split O<sub>2</sub> and CO, it is possible to obtain 45 kg/h of CO that can be used for other applications, such as methanol synthesis. This value is a major value, due to the assumption of ideally behaviour of membranes and due to the thermodynamic equilibrium model, which is less precises than kinetic approach. The carbon footprint of the global plant is 2.3 kg CO<sub>2</sub>/kg H<sub>2</sub>, lower than the latest limit value imposed by the European Commission to consider hydrogen as “clean”, that was set to 3 kg CO<sub>2</sub>/kg H<sub>2</sub>. The hydrogen yield referred to the whole plant is 250 g<sub>H2</sub>/kg<sub>BIOMASS</sub>.

Even if this study gave interesting insights about the overall view of a plant which included HTC, SEG, DBD plasma and HGC, in the future more implementations must be done. Such as changing the thermodynamic model of DBD reactor to a kinetic one and also adding an energy analysis of the whole plant.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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