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Abstract: Extensive use of fossil fuels have led to envisage their foreseeable depletion, thus opening the way to the use of alternative fuels as biomass. Among thermo-chemical treatments of biomass, gasification is particularly attractive for its release of syngas (or producer gas), suitable of being used in various combustion systems, including internal combustion engines. In principle, biomass contaminants and heavy hydrocarbons can be removed during syngas cleaning, before the actual combustion process, thus leading to an overall cleaner conversion process. At present, demonstrating operational feasibility and effectiveness of gasification technologies and proving long term sustainability, also through the enhancement of fuel flexibility, are recognized as key elements for the development and market diffusion of biomass energy systems. In fact, although gasification has been known for a long time, its control has long requested serious efforts by researchers and manufacturers. Nowadays, new perspectives are imaginable thanks to the use of simulation tools that may reveal particularly useful to improve gasification efficiency and increase the quality of the producer gas.

In recent years, several numerical models have been indeed proposed to characterise and predict such a complex process, where drying, pyrolysis, gasification and combustion take place simultaneously. This article presents a general overview of gasification models available, with emphasis on those based on the stoichiometric method. Although this last may seem too restrictive under some circumstances, equilibrium models are useful to predict the maximum yield attainable by a reagent system, since they reproduce an ideal gasification performance. Due to their simplicity and the reduced computational time, these models are suitable of being employed in a first stage of an analysis or within optimization procedures, where the influence of a number of parameters has to be investigated or a choice of the optimal biomass to be treated for a certain scope is to be made.

Response to Reviewers: Reviewer #5: This is a useful and well done paper. It is in the technical scope of this journal. However, there may be some issues with materials from other sources--that have to be addressed by the authors. The similarity index is high--about 45%--which would raise some alerts. The authors should scan their paper to ensure there are not issues with possible copying. Even if referenced in a review--direct copying is not allowed. Specifically, there seem to be issues with: (1) Thesis, University of Pisa "Sviluppo di Sistemi Sperimentali e Strumenti Modellistici per lo Studio della Gassificazione delle Biomasse" with some 1340 words from this thesis published in 2010 (copyright); (2) R. Karamarkovic, "Energy and energy analysis of biomass gasification in different temperatures," published in Energy (about 440 words); (3) Some 300 words from "Optimal Tuning of a Thermo-Chemical Equilibrium Model for Downdraft Biomass Gasifiers" by Costa, LaVilletta and Massarotti, CHEMICAL ENGINEERING TRANSACTIONS, 43, pp. 439- (2015), and several other sources. Although referencing is sometimes thought to be OK--one has to be careful about this. Re-writing some of the materials that the author finds as "similar" will help avoid issues later in having to possibly retract this very good paper. This is a caution so that the paper can proceed without issues.

Response to Reviewer #5 comment No. 1: Similar parts of the articles cited, have been changed.

# Modelling approaches to biomass gasification: a review with emphasis on the stoichiometric method

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## Abstract

Worldwide escalating energy consumption of recent years, due to the earth population growth and the spreading of industrialization, has resulted in an increased concern about the environmental impact of energy conversion systems. Heavy exploitation and extensive use of fossil fuels have indeed also led to envisage their foreseeable depletion, thus opening the way to the use of alternative fuels as biomass. Among thermochemical treatments of biomass, gasification is particularly attractive for its release of syngas (or producer gas), suitable of being used in various combustion systems, including internal combustion engines. In principle, biomass contaminants and heavy hydrocarbons can be removed during syngas cleaning, before the actual combustion process, thus leading to an overall cleaner conversion process. At present, demonstrating operational feasibility and effectiveness of gasification technologies and proving long term sustainability, also through the enhancement of fuel flexibility, are recognized as key elements for the development and market diffusion of biomass energy systems. In fact, although gasification has been known for a long time, its control has long requested serious efforts by researchers and manufacturers. Nowadays, new perspectives are imaginable thanks to the use of simulation tools that may reveal particularly useful to improve gasification efficiency and increase the quality of the producer gas.

In recent years, several numerical models have been indeed proposed to characterise and predict such a complex process, where drying, pyrolysis, gasification and combustion take place simultaneously. This article presents a general overview of gasification models available, with emphasis on those based on the stoichiometric method. Although this last may seem too restrictive under some circumstances, equilibrium models are useful to predict the maximum yield attainable by a reagent system, since they reproduce an ideal gasification performance. Due to their simplicity and the reduced computational time, these models are suitable of being employed in a first stage of an analysis or within optimization procedures, where the influence of a number of parameters has to be investigated or a choice of the optimal biomass to be treated for a certain scope is to be made.

## 1. Introduction

The worldwide continuous growth of the energy demand set against the simultaneous fossil fuels depletion and the widespread concern about the environmental impact of energy conversion systems, well recognized as the main cause of the Green House Gases (GHG) emissions, have progressively brought to light the role of Renewable Energy Sources (RESs).

Use of renewable energy in the EU has grown strongly in the recent years. This has surely been prompted by the “*Strategy on Climate Change for 2020 and Beyond*” (and related Directives), namely by the EU commitment to achieve by 2020 the so-called 20-20-20 objectives of 20% reduction of GHGs emissions, increase of share of renewable energy to 20% and increase of energy efficiency of 20% with respect to 1990. In 2012 the share of energy produced from RESs reached 14.3 % and increased further to 15.0 % in 2013 [1, 2]. Among RESs, biomasses are particularly appealing for their ease of storage, flexibility and low price as they can be considered as a waste whose disposal may even entail not negligible costs. The different types of biomass can be classified as: waste (Municipal Waste (MW), Sewage Sludge (SS), manure); processing residues (timber residues, black liquor, bagasse, rice husk, food processing waste); locally collected

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1 feedstocks (agricultural residues, forestry residues, energy crops); internationally traded feedstock  
2 (roundwood, wood chips, biomass pellets, biomethane) [3].  
3

4 Biomass exploitation may follow different routes for biological or thermal conversion. Thermal conversion  
5 can be obtained through pyrolysis, gasification or combustion. These three technologies mainly differ for their  
6 level of maturity.

7 Pyrolysis is thermal conversion of biomass in absolutely oxygen-free conditions to produce a liquid fuel  
8 called bio-oil. The major concern about pyrolysis is the bio-oil quality, which is corrosive and it needs to be  
9 refined in order to be supplied to power engines. For the same reason, bio-oil storage and transportation is  
10 problematic. The maturity of the technology does not make it appropriate for low cost diffused use.

11 Biomass gasification is a thermo-chemical conversion in a low oxygen environment, producing syngas, a  
12 mixture mainly made of carbon monoxide ( $CO$ ), hydrogen ( $H_2$ ), methane ( $CH_4$ ) and other hydrocarbons.  
13 These substances are flammable and combustible. As a result, syngas can be fed to gas engines or turbines,  
14 after being cleaned of possible contaminant [4]. Effective syngas cleaning reflects in clean engine operation.  
15 Biomass contaminants and heavy hydrocarbons can be, in principle, preventively removed before the actual  
16 combustion process, as they are collected as tar or char. While tar removal is to be optimized, char is instead  
17 a marketable product, as an additive for cement factories or as a soil amendment. Inert material becomes ash.  
18 Ash can be used in cement kilns but also by exploiting more innovative utilisation concepts like the  
19 manufacture of lightweight wall board and bricks with special properties. The presence of fine particles in  
20 the syngas is generally eliminated through cyclones or water or oil scrubbers.

21 Operating conditions of gasification significantly affect the amount of produced gas, tar and char, so that  
22 selecting the optimal gasifier and its control strategy is fundamental to achieve efficient and clean energy  
23 production.  
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25 Combustion uses the biomass as a fuel in high volumes of air to produce heat in the products of combustion  
26 as a mixture of carbon dioxide ( $CO_2$ ), water vapour ( $H_2O$ ) and nitrogen oxides ( $NO_x$ ). None of these  
27 substances can be characterized as combustible, thus a steam cycle turbine or an Organic Rankine Cycle  
28 (ORC) is needed to convert the heat into work. By-products of combustion are mainly compounded of  
29 nitrogen oxides, particulate matter and dioxins/furnas, whose regulation needs sophisticated actions to be  
30 carried out both within the combustion chamber and on the exhausts line (primary and secondary measures  
31 for pollutants reduction). These actions are critically affected by trade-offs between formed pollutants, that  
32 hardly make possible a simultaneous control of residence time, temperature and local air-to-fuel ratio. The  
33 only factor definitely favouring combustion with respect to gasification is technology maturity and cost-  
34 effectiveness.  
35

36 The present work is focused on gasification, an old solution with a proven track record (especially for  
37 processing coal), that has grown in popularity over the last years for being environmentally friendly and  
38 energy-efficient. The mathematical modelling of the underlying thermo-chemical phenomena is taken under  
39 consideration, as a valuable tool to be used either in their phase of new reactors design or for the choice of  
40 the optimal control strategy.  
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42 The operation of biomass gasifiers depends on a number of complex chemical reactions, including fast  
43 pyrolysis, partial oxidation of pyrolysis products, gasification of the resulting char, conversion of tar and  
44 lower hydrocarbons and water-gas shift. Mathematical models can clarify the influence on the producer-gas  
45 composition and calorific value of the main parameters, such as biomass moisture content or the air-to-fuel  
46 ratio. A general summary of the various numerical approaches developed up to present is firstly presented, to  
47 later focus attention on thermo-chemical equilibrium models. Although their accuracy is limited, these  
48 models are particularly useful for preliminary comparisons and for studying the influence of the most  
49 important variables, with the advantage of being independent on the specific gasifier design.

50 The paper is organised as follows. The gasification process is described in section 2 to reach a  
51 schematization of the main sub-processes and to highlight their concurring effects. The most diffused  
52 technologies are reviewed with emphasis on their possible coupling with thermal engines for power  
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generation applications or combined heat and power (CHP). Section 3 is devoted to review the most important equations used in order to develop the stoichiometric numerical model. In section 4, is shown the criteria used by authors in order to compare the numerical results with experimental values. In section 5 are shown a review of works found in the literature related to models based on the stoichiometric method, and in section 6, are presented the conclusions.

## 2. The gasification process

Gasification is the result of the partial oxidation of a solid fuel due to a gasifying agent, usually air, oxygen or steam. Partial oxidation provides heat for drying, devolatilization and reduction reactions. Table I reports the reactions to be considered during gasification.

TABLE I

In principle, gasification may be used to process any solid material of not negligible carbon content. When particles of raw material are introduced into a gasifier, they start being heated and release their moisture content (reaction  $R_M$  of Table I) to then undergo devolatilization (reaction  $R_I$ ). After devolatilization three macro-products are present: gas, tar and char. The devolatilization gas is usually composed of carbon monoxide, carbon dioxide, hydrogen, methane, water vapour and light hydrocarbons. The term tar refers to a broad range of organic compounds that are in the form of vapour at the gasification temperature (more than 400°C) but liquid at room temperature. Char is the solid residue. As oxygen encounters combustible volatiles and char, both homogeneous and heterogeneous oxidation reactions take place. Volatiles and tar combustion produces carbon dioxide and water through reactions  $R_7$ ,  $R_{10}$ ,  $R_{12}$ ,  $R_{13}$  of Table I. Char undergoes oxidation through the heterogeneous reaction  $R_2$ . This generates both  $CO$  and  $CO_2$ , whose mutual proportion is a function of temperature, oxygen availability and ash content. The combustion reactions provide heat for drying and devolatilization of the solid material and for the other reactions involved in the process. In the gaseous phase tar and  $CH_4$  are subjected to steam reforming ( $R_8$  and  $R_{11}$ ), generating  $CO$  and hydrogen. Tar can also decompose at high temperature due to thermal cracking ( $R_9$ ), so to generate lighter gases as  $CO$ ,  $CO_2$ ,  $H_2$  and  $CH_4$ . In addition, the water gas-shift reaction ( $R_6$ ) affects the concentration of  $CO$ , water, carbon dioxide and hydrogen. Char can be converted into a gas at high temperature (more than 600 °C) to  $CO$ , hydrogen and  $CH_4$  due to heterogeneous reactions with carbon dioxide ( $R_3$ ), steam ( $R_4$ ) and hydrogen ( $R_5$ ).

The most important gasification reactions to model the process are  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_{11}$ . The solution of any chemical problem requires considered reactions being independent. The concept of independence of reactions states that if for any group of reactions one of them could be written as a combination of at least two of the others, then this group is not independent and the model contains recurrent information. For example, the *Boudouard reaction*  $R_3$  and the *water/gas heterogeneous reaction*  $R_4$  can be combined to give the *water/gas shift reaction*  $R_6$  (by subtracting  $R_3$  from  $R_4$ ). This means that  $R_3$ ,  $R_4$  and  $R_6$ , are not independent. Using this concept, any combination of two of these five gasification reactions can be used to model the case where there is no presence of unconverted carbon in the products. If unconverted carbon is present in the products, three reactions are needed to complete the equilibrium model, hence there are ten possible combinations. A mathematical criterion is presented in [5] to determine the independent reactions between these ten. As already mentioned, combinations of Eqs.  $R_3$ ,  $R_4$  and  $R_6$  and Eqs.  $R_4$ ,  $R_5$  and  $R_{11}$  are dependent. The aforementioned results may appear obvious, but it is important to note that there is not a definitive reason to choose one of the eight remaining combinations with respect to another, but the validation of the model results with experimental data.

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## 2.1 Gasification technologies

The design of gasification reactors has been a subject of research for more than a century and resulted, with the result of a variety of configurations on both the small and large scales [6]. These can be classified in several ways [7], as shown in the graphs presented Fig. 1:

### FIGURE 1

Classification of gasification reactors may be based on:

- *Gasification Agent*: air-blown gasifiers, oxygen gasifiers and steam gasifiers;
- *Heat Source*: auto-thermal or direct gasifiers (heat is provided by partial combustion of biomass) and allothermal or indirect gasifiers (heat is supplied by an external source via a heat exchanger or an indirect process).
- *Gasifier Pressure*: atmospheric or pressurised.
- *Reactor Design*:
  - Fixed-bed** (updraft, downdraft, cross-draft): In the updraft gasifier the gasifying agent enters from the bottom and moves towards the top while the biomass is loaded from the top and moves downward. A grate is present at the bottom of the gasifier where biomass is ignited, thus generating increase of temperature in this zone (oxidation one). The hot gas with its low oxygen content moves upward transporting heat to the other zones of the gasifier; consequently, as the biomass enters from top, it experiences drying, devolatilization and gasification, and oxidation. The syngas temperature at the outlet is low and the tar content high, since the gas does not experience high temperature reactions where tar can be converted through  $R_8$  and  $R_9$ .

### FIGURE 2

Downdraft gasifiers can be categorized as open and close top design. The open top design (or stratified) configuration, shown in Fig.2 (1), has an open top with forced air moving downwards by suction to prevent hot spot formations. The homogeneous airflow reduces possible inefficiencies in the thermo-chemical process, as well as the formation of preferential channels or bridges. The stratified downdraft gasifier demonstrates high flexibility and appreciable efficiency in processing solid materials of poly-dispersed nature, as rice husk of small particle size and low density. Two different designs characterise the closed top gasifiers, one resembling conventional downdraft with a straight cylindrical reactor, shown in Fig. 2 (2), one with a throat in the reactor core, as in Fig. 2 (3), called Imbert gasifier [4]. The main differences between these gasifiers is that in (1) and (2) configurations the diameter is constant through the gasifier, while in (3) a throated combustion zone is present due to the different diameters of the pyrolysis and gasification zones.

The most documented configuration is that of throated gasifiers, where air enters through several radial nozzles in a zone exhibiting a restricted cross section, placed in the middle of the gasifier. The biomass is ignited in the restricted area (oxidation zone), when it is heated up and drying and devolatilization take place. After the oxidation zone, both the gas and the biomass move downwards and, due to the lack of oxygen, high temperature gasification reactions ( $R_3$ ,  $R_4$ ,  $R_5$ ) occur; this zone is often called reduction zone [4]. The tar content in this gasifier is low, due to tar cracking ( $R_9$ ) in the throat. A disadvantage of this technology is the high gas temperature at outlet, and the possible presence of alkaline vapour and particulate matter.

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1 A further reduction of tar concentration in the producer gas can be achieved in downdraft gasifiers  
2 with a double stage air supply, as shown in Fig. 2 (4). The first air supply stage is located near the  
3 top of the reactor where the feedstock is partially oxidized and thermal energy is generated. This is  
4 needed for the drying and pyrolysis phases occurring above the combustion zone. The second air  
5 supply stage is placed in the middle of the reactor, in the oxidation zone where tar decomposes into  
6 lighter compounds.

7 In crossdraft gasifiers, air enters at high velocity through a water-cooled nozzle mounted on one side  
8 of the firebox that induces substantial circulation across the bed of solid material and char. The gas  
9 is produced in the horizontal direction in front of the nozzle and passes through a vertical grate into  
10 the hot gas port on the opposite side. This produces a high temperature in a small volume, with the  
11 production of a low tar gas. However, cross draft gasifiers are not commonly used.  
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15 **Fluidised-bed** (bubbling (BFB), circulating (CFB) and twin-bed): In fluidised bed gasifiers fuel  
16 particles of specified size and mixed with another solid are suspended due to the gas flowing from  
17 the bottom of the gasifier [8]. The two most common configurations are bubbling fluidised bed and  
18 circulating fluidised bed. Heat can be provided directly, with air or oxygen injection in the bed, or  
19 indirectly by means of an internal heat exchanger, or with the fluidisation medium acting as a heat  
20 carrier between two reactors. These gasifiers are adequate for stationary processes, therefore are  
21 usually suitable for medium to large scale installations. They usually produce a gas with high  
22 particulate content; therefore a cyclone is usually a part of the installation. The gas temperature at  
23 the outlet is relatively high (800-900°C), containing alkaline vapours. These gasifiers are meant to  
24 produce more tar than downdraft gasifiers but less than updraft gasifiers. Two phases can be  
25 recognized in a bubbling bed gasifier: a dense phase (with a high solid content), located at the  
26 bottom of the reactor, and a diluted phase. In the lower zone gas bubbles formation and implosion  
27 generate high turbulence, thus favouring mixing of the solid components; the higher zone is much  
28 more likely to be represented as a plug flow reactor. In circulating beds, the gas velocity is high  
29 enough to transport all solids, thus achieving higher degree of mixing, turbulence and heat transfer  
30 [4]. Twin-bed gasification uses two fluidised-bed reactors. The biomass enters the first reactor,  
31 where it is gasified with steam, and the remaining char is transported to the second reactor, where it  
32 is oxidized with air to produce heat. The heat is transported to the gasification reactor by the bed  
33 material, normally sand. The flue gas and the producer gas have two separate exits.  
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41 **Entrained-flow**: In entrained-flow gasifiers, fine particles and oxidant (air or oxygen) and/or steam  
42 are fed co-currently [9]. This results in the oxidant and steam surrounding or entraining the solid  
43 particles as they flow through the gasifier in a dense cloud. Entrained-flow gasifiers operate at high  
44 temperature and pressure, and are characterised by an extremely turbulent flow which causes rapid  
45 feedstock conversion and allows high throughput. The gasification reactions occur at a very high  
46 rate (typical residence time is of the order of a few seconds), with high carbon conversion  
47 efficiencies (98-99.5%). Tar, oil, phenols, and other liquids produced from devolatilization are  
48 decomposed into hydrogen ( $H_2$ ),  $CO$  and small amounts of light hydrocarbons. Given the high  
49 operating temperatures, gasifiers of this type melt ash into vitreous inert slag. The fine fuel  
50 feedstock can be delivered in either a dry or slurry form. The former uses a lock hopper system,  
51 while the latter relies on the use of high-pressure slurry pumps. The slurry feed is a simpler  
52 operation, but it introduces water into the reactor which requires heat to evaporate. The result of this  
53 additional water supply is a syngas with a higher  $H_2$  to  $CO$  ratio, but with lower gasifier thermal  
54 efficiency. The feeding system needs to be properly designed along with the other process  
55 parameters. The high temperatures tend to shorten the life of the system components, including the  
56 vessel refractory.  
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Information regarding gasifier manufacturers in Europe, the United States and Canada is given in refs. [10, 11]. Over the total, 75% are fixed-bed downdraft, 20% are fluidised-bed systems, 2.5% are updraft, and 2.5% are of various other designs.

### 2.1.1 Performance Indicators

Biomass gasifiers must convert a solid material with an organic content into a gaseous fuel which is suitable of being used for various purposes. Consequently, the efficiency of a gasifier can be defined as its ability to convert the solid material and its energy content into a gas.

Different indicators can be used to evaluate the conversion rate of a biomass gasifier. The *specific gas production* is the rate between the syngas flow-rate (in Nm<sup>3</sup>/h) and the biomass fed to the gasifier (in kg/h):

$$PS = \frac{Q_{syngas}}{M_{biomass}} \left( \frac{Nm^3}{kg} \right). \quad (1)$$

This parameter can be defined in several ways, depending on the gas (wet gas or dry gas) and biomass (wet, dry or daf (dry ash free)) properties.

The *carbon conversion efficiency* is the rate between the carbon leaving the gasifier in the syngas (as CO, CO<sub>2</sub>, etc.) and the carbon entering the system:

$$CCE = \frac{Q_{syngas} \sum_{j=1}^n x_{j,c}}{M_{biomass} \gamma_c}. \quad (2)$$

The energy content of the syngas is usually expressed with its lower heating value (*LHV*) as the heat (in MJ) generated from the combustion of one Nm<sup>3</sup> of syngas. Taking into account the specific gas production and the energy content of the biomass, it is possible to define the *cold gas efficiency* as the ratio between the chemical energy leaving the system associated with the cold and tar-free syngas and the chemical energy entering the system associated with the biomass:

$$CGE = \frac{Q_{syngas} LHV_{syngas}}{M_{biomass} LHV_{biomass}}. \quad (3)$$

*LHV<sub>syngas</sub>* and *LHV<sub>biomass</sub>* are the lower heating values of the syngas and the biomass respectively. Obviously, the higher the *CGE* the more efficient is the gasifier.

Other important performance indicators are those expressing the contaminants content in the syngas. The main contaminants are:

- gases such as H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub>, HCl and other chlorinated compounds;
- tar;
- heavy metals (Hg, Cd, etc.);
- alkali
- particulate matter.

Table II reports a comparison of the literature values of the listed performance indicators for different gasifiers. Fixed bed gasifiers are likely to achieve higher conversion values than fluidised beds. This can be related to the higher biomass residence time. *CGE* and *LHV<sub>syngas</sub>* cannot be related to the gasifier design. Fixed bed gasifiers produce a syngas with lower particulate content than fluid bed gasifiers, due to lower gas velocity and drag. As mentioned, downdraft gasifiers are likely to generate the lowest tar content, while updraft gasifiers the highest.

TABLE II



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## 2.2 Operating conditions

Operating conditions of a gasifier strongly affect composition and quality of the produced syngas [21]. In the following, each effect of the main operating parameters is briefly discussed.

### Gasifying agent

The gasifying agent influences the syngas composition and heating value. Tables III and IV report an indicative variation of the syngas composition as a the gasifying agent is varied, for different gasifiers.

TABLE III

TABLE IV

Air gasification is the simple and most economic technology, suitable for small scale applications. It generates a syngas with a low  $LHV_{syngas}$  due to the high nitrogen content. Oxygen gasification increases the  $LHV$ , due to the nitrogen removal and it is an option for producing high carbon sequestration and storage. Obviously, the use of oxygen dramatically increases the plant operating costs and complexity, due to the necessity of an air separation unit and of the storage and distribution systems. Steam gasification produces an high quality syngas (high hydrogen content and high  $LHV$ ), but needs heat, therefore it is usually performed with steam/oxygen mixtures. The use of oxygen is gaining attention over the small scale with low enrichment level, to increase the gasifier flexibility for processing various kinds of biomasses.

### Equivalence ratio

The Equivalence Ratio (ER) is the main operating parameter affecting biomass gasification. This index represents (in the case of air gasification) the ratio between the masses of air and biomass (daf) under the actual operating conditions to the same ratio under stoichiometric conditions [27]. When  $ER$  is equal to zero, there is no oxidant in the system, while  $ER$  equal to one represents stoichiometric combustion. When  $ER$  is larger than one, combustion in fuel lean conditions occurs. Finally, when  $ER$  is less than one, fuel rich combustion takes place. Gasification can be considered in some sense as a fuel rich combustion: typical  $ER$  values range between 0.2 and 0.4. The equivalence ratio strongly affects the gasification process; it determines the temperature of the system, the oxygen availability, the syngas yield, hence the gas composition and heating value, as well as the tar content. The higher the  $ER$ , the higher the  $PS$  and the lower the  $LHV$  of the producer gas. This is due to the higher oxidation rate of the fuel, which leads to higher conversion into gas, higher carbon dioxide concentration and lower hydrocarbon contents, thus reducing the  $LHV_{syngas}$ . As a consequence, there is a trade-off between  $PS$  and  $LHV$ , and it is necessary to identify the optimal  $ER$  for each gasification system. With a lower  $ER$  value, char is not fully converted into volatiles and tar production is higher. For this reason, updraft gasifiers, which typically operate with  $ER$  lower than 0.25, present higher tar content. With  $ER$  above 0.25, some product gases are also burnt, with a consequent increase of temperature. In the case of gasification with air, the yield of tar in the producer gas decreases when  $ER$  increases [8].

### Temperature

Temperature has a deep impact on devolatilization [28, 29]; it modifies the macro-products (char, tar, gas) distribution as well as the gaseous species distribution. In addition, temperature also affects the equilibrium reactions involved in a gasification system. Various authors [19, 25] report an increase in syngas production and the reduction of tar content for increasing temperatures. It is worth noting that temperature could be an operating parameter only at laboratory scale, but in actual systems it cannot be controlled *a priori* and is a function of the equivalence ratio, gas and solid flow-rates and thermal dispersions.

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### ***Moisture content***

The biomass moisture content (which can be up to 70% in the natural state) strongly affects conversion of biomass into energy.

**TABLE V**

High moisture levels make combustion of biomass difficult to be self-sustained and decrease the heating value of the syngas. Consequently, the energetic efficiency of the process is reduced. In addition, the high moisture content lowers the oxidation temperature leading to an incomplete cracking of the hydrocarbons formed during pyrolysis. Among fixed beds, downdraft gasifiers are more sensitive to moisture than updraft gasifiers. The tolerable biomass moisture limits are 15% and 55%, respectively. Typical producer-gas composition for downdraft gasifiers processing low- to medium-moisture-content solid materials are presented in Table V.

### ***Superficial velocity***

The superficial velocity (SV) is defined as the ratio of syngas production rate at normal conditions and the narrowest cross sectional area of the gasifier. SV is linked to the syngas energy content, the fuel consumption rate, the char and tar production rates [30]. Low values of SV result in a relatively slow pyrolysis process, with high yields of char and significant quantities of unburned tars. On the contrary, high values of SV cause a very fast pyrolysis process, formation of a reduced amount of char and high temperature gases in the flaming zone. However, such high SV values significantly decrease the syngas residence time in the gasifier and result in lower efficiencies in the tar cracking process.

### ***Particle size***

Solid particles to be gasified must be of adequate size in order to sustain a certain consumption rate, as well as to maintain an acceptable pressure drop inside the reactor without the formation of preferential channels (bridging).

The most widely used parameter to describe the shape of a particle is sphericity, which is given by the ratio of the surface area of a sphere (with the same volume as the given particle) to the particle surface area. The particle sphericity affects the heat transfer between the solid and gaseous phases. Some recommendations are found in the literature about this aspect. As an example, the maximum particle size to be used in the Imbert downdraft gasifier is equal to one-eighth of the reactor throat diameter [31].

Regarding the effects of variation of particle diameter on the temperature and composition of the produced gas, particles with smaller diameters are heated more quickly and react before those having a larger diameter. If the phenomenon occurs more rapidly, the peak temperature reached is lower. The syngas composition does not vary appreciably with the particle size, as the greater effect is related to the composition of the biomass that obviously does not vary with size.

## **3. Models for biomass gasification**

Mathematical modelling may be undertaken with different aims: from preliminary design of an industrial process to the complex simulation of a specific unit [32]. Simulation of gasification provides a better comprehension of the physical and chemical mechanisms underlying the gasification process and assists in the design of new systems or in the development of proper control strategies of existing units, for optimizing the syngas quality.

Models help in identifying the sensitivity of the gasifier performance to variation of different operating or design parameters [33]. Models can be helpful for design, prediction of operational behavior, prediction of

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emissions during normal conditions, start-up, shut-down, change of fuel, change of load and to reduce problems related to char and tar formation. A considerable amount of work has been done in developing gasifier simulation models. These may be classified as belonging to the following groups [34]:

- Thermodynamic equilibrium models;
- Kinetic models;
- Phenomenological models ;
- Artificial Neural Network (ANN) models.

Thermodynamic equilibrium models predict the maximum achievable yield of products from a reacting system. If reactants stay in contact for an infinite time, they will reach equilibrium. The yield and composition of products under this condition are given by the equilibrium assumption between species, which concerns the reactions alone without considering the geometry of the gasifier.

In the practice, only a finite time is available for the reactant to react in the gasifier, which implies that equilibrium models may only give an ideal yield.

Kinetic models study how reactions progress in the reactor, giving the products composition at different positions along the gasifier, by taking into account the geometry and its fluid dynamics. Phenomenological models solve the set of equations of balance of mass, momentum, energy and species over a discrete region of the gasifier and give as results the distribution of temperature, concentration, and other parameters along the reactor. If the geometry and its fluid dynamics is well known, these models, that substantially consist in a Computational Fluid Dynamics (CFD) approach to a reacting multi-phase flow, provide a very accurate prediction of temperature and gas yield in the whole reactor.

Neural network analysis is a relatively new simulation tool for modelling gasifiers. It works somewhat like an experienced operator who uses his years of experience to predict how the gasifier will behave under a certain condition. This method requires little prior knowledge about the process, but a consistent amount of experimental data to train the network and assure reliability of results.

Mathematical models such as thermodynamic equilibrium and kinetics, in order to decrease the computation time, two routes for stoichiometric coefficient, can be assumed: if  $\phi = 0$ ,  $R_2$  gives  $CO$  as product, instead if  $\phi = 1$ ,  $R_2$  gives  $CO_2$  as product.

As already mentioned, in this work emphasis is on thermodynamic equilibrium models (stoichiometric method). As later highlighted, although this last may seem too restrictive under some circumstances, equilibrium models are useful to predict the maximum yield attainable by a reagent system, since they reproduce an ideal gasification performance. Due to their simplicity and the reduced computational time, these models are suitable of being employed in a first stage of analysis or within optimization procedures, where the influence of several parameters must be investigated or a choice of the optimal biomass to be treated for a certain scope is to be made.

### 3.1 Thermo-chemical Equilibrium Models

Thermo-Chemical Equilibrium (TCE) calculations are independent of the gasifier design and can be used to analyse the influence of the solid material composition or of the process parameters. Although chemical or thermodynamic equilibrium may not be reached within the gasifier, this kind of models provides designers with a reasonable prediction of the maximum achievable yield of a desired product. However, TCE models cannot predict the influence of fluid dynamic or geometric parameters, like fluidizing velocity, or design variables, like gasifier height. Chemical equilibrium may be determined by:

- *Equilibrium constant (stoichiometric method)*
- *Minimization of the Gibbs free energy (non-stoichiometric method)*

Stoichiometric models are based on the evaluation of the *equilibrium constants* of an independent set of reactions which can be associated with the Gibbs free energy. Examples of models based on this approach

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are shown later on within this work. The non-stoichiometric equilibrium modelling approach, often referred to as “*Gibbs free energy minimization approach*”, is developed on the direct minimization of the Gibbs free energy of reaction. This method is common among many researchers [35-42] and is claimed to be applicable for complex reaction pathways, avoiding the need to identify the independent set of reactions. The solutions to the resulting equilibrium model equations can be obtained by using different algorithms. However, irrespective of the differences in the two approaches, both produce similar results [43]. Generally, equilibrium models are relatively easier to implement and have faster convergence [44].

### 3.1.1 Features of Stoichiometric Equilibrium Models

As already mentioned, four zones can be distinguished in downdraft gasifiers as presented Fig. 3: drying zone when moisture is removed, pyrolysis zone of biomass into oil, char, and volatiles, oxidation zone of the volatile products of pyrolysis, and gasification zone of char (assumed as unconverted carbon) from pyrolysis. Main species resulting from thermo-chemical conversion are carbon monoxide ( $CO$ ), hydrogen ( $H_2$ ), methane ( $CH_4$ ), carbon dioxide ( $CO_2$ ), water vapor ( $H_2O$ ), nitrogen ( $N_2$ ) and tars, while unconverted carbon ( $C$ ) and ashes can be found in the residues.

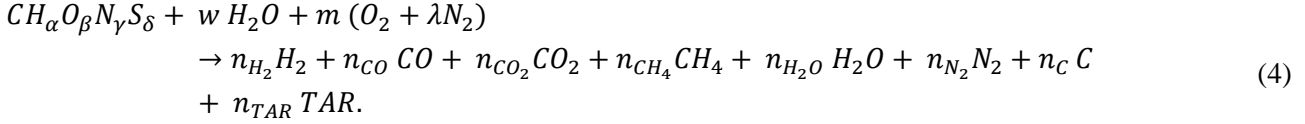
### FIGURE 3

The main thermo-chemical equilibrium models available in the literature take into account the following simplifying assumptions:

1. Infinite residence time, so that reactions have large amount of time to take place;
2. No information about reaction pathways and formation of intermediates in pyrolysis zone;
3. Perfect mixing with uniform temperature and pressure are assumed;
4. No oxygen in the produced gas;
5. Nitrogen is considered as inert;
6. Steady state is assumed;
7. Potential and kinetic energies are neglected;
8. Only major species compose the gas leaving the gasifier, namely  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $H_2O$  and  $N_2$ ;
9. Oxidant agent (air) is sufficient to convert all carbon in producer gas;
10. Tar is modeled in the gaseous state;
11. Contribution of ash to the energy balance equation is neglected;
12. Ideal gas behaviour of the gas phase;
13. The gasifier operates isothermally and at atmospheric pressure.
14. The heat losses to the environment are neglected, namely the gasifier is considered adiabatic.

The previous considerations are adopted by some authors in their respective models [32, 34], [39], [45-49].

In the overall gasification reaction in the presence of air, some models as [32], [45-47] consider as products  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $H_2O$  and  $N_2$ , instead models as [34] and [49] consider also the tar:



The feedstock material, in fact, can be represented by an equivalent molecule comprising carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S). Ash content can be considered as an equivalent quantity of SiO<sub>2</sub> and generally, as reported in the simplifying assumptions, the contribution of ash in the energy equation is neglected. Since it is inert its amount is not reported in eq. (4).

The dry biomass fuel can be expressed by a generalized unified molecular formula, where the number of atoms of hydrogen  $\alpha$ , oxygen  $\beta$ , nitrogen  $\gamma$  and sulfur  $\delta$  based on a single atom of carbon are calculate as [49]:

$$\alpha = \frac{y_H M_C}{y_C M_H} = \beta = \frac{y_O M_C}{y_C M_O} \quad \gamma = \frac{y_N M_C}{y_C M_N} \quad \delta = \frac{y_S M_C}{y_C M_S} \tag{5}$$

In this equations,  $M_C$ ,  $M_H$ ,  $M_O$ ,  $M_N$  and  $M_S$  are the molecular weights of carbon, hydrogen, oxygen, nitrogen sulfur respectively and  $y_C$ ,  $y_H$ ,  $y_O$ ,  $y_N$  and  $y_S$  are the mass fractions on *daf* basis of those elements obtained from the ultimate analysis.

To determine the eight unknowns, namely the number of mole of  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $H_2O$ ,  $C$ ,  $TAR$  and gasification temperature, atomic balance of carbon, hydrogen, oxygen, and nitrogen are written:

#### Balance of C

$$n_{CH_4} + n_{CO} + n_{CO_2} + d n_{TAR} + n_C - 1 = 0. \tag{6}$$

#### Balance of H

$$4 n_{CH_4} + 2 n_{H_2} + 2 n_{H_2O} + f n_{TAR} - \alpha - 2 w = 0. \tag{7}$$

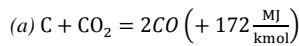
#### Balance of O

$$n_{H_2O} + n_{CO} + 2 n_{CO_2} + z n_{TAR} - w - 2 m - \beta = 0. \tag{8}$$

In the work [34], tar is considered as C<sub>6</sub>H<sub>6</sub> where  $d = 6$ ,  $f = 6$  and  $z = 0$ , instead in [49], tar is considered as CH<sub>1.003</sub>O<sub>0.33</sub>, where  $d = 1$ ,  $f = 1.003$  and  $z = 0.33$ . Tar formation can be assumed as a function of the gasification temperature [34] or also as an input parameter within the model [49].

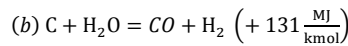
Three further equations are derived by imposing the equilibrium of the following reactions that can be chosen in accordance to the criteria previously described. For example, [32], [45] and [49] use the reactions 9 (c) and (d), [46] uses the reactions 9 (b), (d) and (e), instead [34] uses the reactions 9 (a), (c) and (d):

#### Boudouard reaction



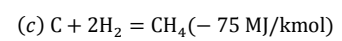
$$K_{R3} = \exp \left[ -\frac{\overline{\Delta G_T^0}}{RT} \right] = \frac{(n_{CO})^2}{n_{CO_2}} \left( \frac{P}{n_{tot} P_0} \right)$$

#### Water - gas heterogeneous reaction



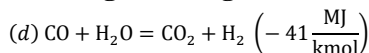
$$K_{R4} = \exp \left[ -\frac{\overline{\Delta G_T^0}}{RT} \right] = \frac{n_{CO} n_{H_2}}{n_{H_2O}} \left( \frac{P}{n_{tot} P_0} \right)$$

#### Methane formation reaction

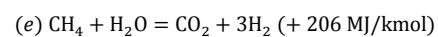


$$K_{R5} = \exp \left[ -\frac{\overline{\Delta G_T^0}}{RT} \right] = \frac{n_{CH_4}}{(n_{H_2})^2} \left( \frac{P}{n_{tot} P_0} \right)^{-1}$$

#### Water - gas homogeneous reaction



#### Methane reforming reaction



$$K_{R6} = \exp \left[ -\frac{\overline{\Delta G_T^0}}{RT} \right] = \frac{n_{CO_2} n_{H_2}}{n_{CO} n_{H_2O}} \quad K_{R11} = \exp \left[ -\frac{\overline{\Delta G_T^0}}{RT} \right] = \frac{n_{CO} (n_{H_2})^3}{n_{CH_4} n_{H_2O}} \left( \frac{P}{n_{tot} P_0} \right)^2. \quad (9)$$

Only one of these five equations does not consider the operating pressure effects, thus any combination of two or three of them allows one study to pressure effects on the gasification process.

As previously reported in eq. (9), for the computation of the equilibrium constants, the expression is a function of the temperature can be obtained by applying the thermodynamic relation starting from a temperature dependent polynomial for the specific heat at constant pressure [45-49]:

$$\ln K = -\frac{\overline{\Delta G_T^0}}{RT}, \quad (10)$$

where  $R = 8.314 \text{ kJ}/(\text{kmol K})$  is the universal gas constant,  $\overline{\Delta G_T^0}$  is the standard Gibbs function:

$$\overline{\Delta G_T^0} = \sum_{i,j} \nu_{i,j} \Delta \bar{g}_{f,T,i,j}^0. \quad (11)$$

where  $\nu_{i,j}$  are the stoichiometric coefficients of the  $i$  reactants and  $j$  products species relative to the  $\Psi = R_3, R_4, R_5, R_6, R_{11}$  reactions, and  $\Delta \bar{g}_{f,T,i,j}^0$  is the standard Gibbs function of formation at given temperature  $T$  of the  $i$  reactants and  $j$  products species relative to the  $\Psi$  reactions, which can be expressed by the empirical equation below:

$$\Delta \bar{g}_{f,T,i,j}^0 = \bar{h}_{f,i,j}^0 - a T \ln(T) - b T^2 - \left(\frac{c}{2}\right) T^3 - \left(\frac{d}{3}\right) T^4 + \left(\frac{e}{2T}\right) + f + g T. \quad (12)$$

Where  $\bar{h}_{f,i,j}^0$  is the enthalpy of formation of the  $i$  reactants and  $j$  products species relative to the  $\Psi$  reactions. The values of coefficients  $a - g$  in (12) and the enthalpy of formation of the gases are presented in Table VI [50].

TABLE VI

The thermodynamic data can be taken from the National Institute of Standards and Technology (NIST)-Joint Army-Navy-Air Force (JANAF) Thermochemical Tables, generally known as NIST-JANAF Thermochemical Tables [51].

Another group of authors [37, 39, 52, 53] uses the definition of the Gibbs free energy, as the combination of the state variables enthalpy and entropy:

$$\overline{\Delta G_T^0} = \sum_i \nu_{i,j} g_{i,j}^*. \quad (13)$$

where  $g_{i,j}^*$  is the molar specific Gibbs function of the  $i$  reactants and  $j$  products species relative to the  $\Psi$  reactions at the references state of 0.1 MPa, and at the gasification temperature  $T$ . This quantity can be expressed as:

$$g_{i,j}^* = (g_f^0)_{i,j} + (h_T - h_{T0})_{i,j} - T (s_T)_{i,j} + T_0, \quad (14)$$

where  $(g_f^0)_{i,j}$  is the molar specific Gibbs function of formation at the standard reference state ( $P_0 = 0.1 \text{ MPa}, T_0 = 25 \text{ }^\circ\text{C}$ ) of the  $i$  reactants and  $j$  products species relative to the  $\Psi$  reactions. The term  $(s_T)_{i,j}$  is the molar specific entropy of the  $i$  reactants and  $j$  products species relative to the  $\Psi$  reaction at the gasification pressure and temperature of the ideal gases:

$$(s_T)_{i,j} = (s_{T_0}^0)_{i,j} + \int_{T_0}^T C_{p,i,j} \left( \frac{dT}{T} \right) - R \ln \left( \frac{P_{i,j}}{P_0} \right). \quad (15)$$

$(s_{T_0}^0)_{i,j}$  is the molar specific entropy at the standard reference state for the  $i$  reactants and  $j$  products.

### TABLE VII

For these species, the molar specific Gibbs function of formation at the standard reference state and the molar specific absolute entropies at the standard reference state are shown in Table VII [54].

As solid carbon is an incompressible substance, the molar specific entropy in kJ/kmol K is calculated as:

$$(s_T)_C = (s_{T_0}^0)_C + \int_{T_0}^T C_c \left( \frac{dT}{T} \right), \quad (16)$$

where the specific heat capacity of solid carbon in kJ/kmolK is defined by the polynomial equation taken from ref. [55]:

$$C_c = 17.166 + 4.271 \frac{T}{1000} - \frac{8.79 \cdot 10^5}{T^2}. \quad (17)$$

The quantity  $C_{p,i,j}$  in (15) is the specific heat capacity at constant pressure of the  $i$  reactants and  $j$  products species relative to the  $\Psi$  reactions. For ideal gases used in these models, the specific heat capacities at constant pressure are calculated by third-order polynomial equations.

$$C_{p,i,j} = a' + b' T + c' T^2 + d' T^3. \quad (18)$$

The terms  $a'$ ,  $b'$ ,  $c'$ , and  $d'$  are the specific gas species coefficients, which are shown in Table VIII [56].

### TABLE VIII

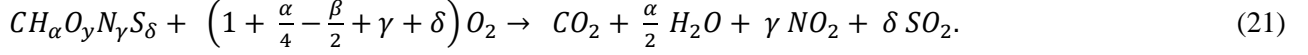
The last equation necessary for calculating the gasification temperature is the energy balance. Considering the simplifying assumptions of an adiabatic process without external work, and negligible variations of potential and kinetic energies, the following equation is obtained:

$$\sum_{i=\text{reactants}} n_i \bar{h}_{f,i}^o = \sum_{j=\text{products}} n_j (\bar{h}_{f,j}^o + \Delta h_T). \quad (19)$$

Regarding the terms present in the energy balance:  $n_i$  is the number of moles of reactants in the overall gasification reaction in the presence of air;  $\bar{h}_{f,i}^o$  is the enthalpy of formation of reactants;  $n_j$  is the number of moles of product species;  $\bar{h}_{f,j}^o$  is the enthalpy of formation of product species; and  $\Delta h_T = (h_T - h_{T_0})_j$  is the sensible enthalpy defined as:

$$\Delta h_T = (h_T - h_{T0})_j = \int_{T_0}^T C_{pj} dT. \quad (20)$$

Ref. [5] suggests a relation for finding the enthalpy of formation of biomass in reactant that is dependent upon the products under complete combustion:



$$\bar{h}_{f,biomass}^0 = LHV_{biomass} + (\bar{h}_f^0)_{CO_2} + \frac{\alpha}{2} (\bar{h}_f^0)_{H_2O} + \gamma (\bar{h}_f^0)_{NO_2} + \delta (\bar{h}_f^0)_{SO_2}. \quad (22)$$

In absence of experimental data, the lower heating value  $LHV_{biomass}$  in MJ/kg for biomass investigated can be derived using the higher heating value formula  $HHV_{biomass}$  presented in ref. [57]:

$$HHV_{biomass} = 0.3491 y_C + 1.1783 y_H + 0.1005 y_S - 0.1034 y_O - 0.0151 y_N. \quad (23)$$

$$LHV_{biomass} = HHV_{biomass} - L_{v,H_2O} \left(\frac{9y_H}{100}\right). \quad (24)$$

where  $L_{v,H_2O} = 2.256 \text{ MJ/kg}$  is the enthalpy of vaporization of water at  $P_{sat} = 0.1 \text{ MPa}$  and  $T_{sat} = 100 \text{ }^\circ\text{C}$ . The lower heating value of syngas can be calculated by multiplying the volume fraction  $x_j$  of the products of the gasification reaction for the corresponding lower heating value  $LHV_j$ .

$$LHV_{syngas} = x_{CH_4} LHV_{CH_4} + x_{CO} LHV_{CO} + x_{H_2} LHV_{H_2}. \quad (25)$$

Where [8]:

$$LHV_{CH_4} = 35.88 \left[\frac{\text{MJ}}{\text{Nm}^3}\right], LHV_{CO} = 12.63 \left[\frac{\text{MJ}}{\text{Nm}^3}\right] \text{ and } LHV_{H_2} = 10.78 \left[\frac{\text{MJ}}{\text{Nm}^3}\right].$$

The non-linear system of equations (6 - 9) and (19) with the previously cited consideration about tar and reactions that can be chosen, can be solved with the Newton - Raphson method.

Due to the simplifying assumptions, equilibrium models yield great disagreements under some circumstances. Typically, at relatively low gasification temperatures,  $H_2$  and  $CO$  yields are overestimated and  $CO_2$ ,  $CH_4$ , tars and char are underestimated [58]. The structure of the model allows modifications for more accurate modelling of gasifiers, to gain better agreement with experimental data. An approach introduced by Gumz [59] consists in using multiplication factors for the equilibrium constants [32], [34], [47] and [49]. Another thermodynamically more consistent way to adjust the equilibrium equations is to correct the equilibrium temperature by introducing artificial temperature differences. For this reason, several authors have modified and corrected the equilibrium model or used a Quasi-Equilibrium Temperature (QET) approach [38].

### 3.1.2 Equivalence ratio

Considering  $CH_\alpha O_\beta N_\gamma S_\delta$  as a model for the composition of the biomass, the ratio between the actual oxygen molar quantity  $m$  and the stoichiometric oxygen molar quantity, so called equivalence ratio, and it can be computed as follows [53]:

$$ER = \frac{m}{\left(1 + \frac{\alpha}{4} - \frac{\beta}{2} + \gamma + \delta\right)}. \quad (26)$$



The stoichiometric air-to-fuel ratio can be determined by the following expression:

$$AC_{stq} = \frac{M_{O_2} + \lambda M_{N_2}}{100} \left( \frac{y_C}{M_C} + \frac{y_H}{2M_H} + \frac{y_S}{M_S} - \frac{y_O}{M_{O_2}} \right). \quad (27)$$

Where the percentages from the ultimate analysis, in dry ash-free basis, are used [60].

### 3.1.3 Exergy analysis

Exergy analysis is an effective method of using the second law of thermodynamics, beside the conservation of both mass and energy, for design and analysis of biomass conversion by gasification. The exergetic efficiency is defined as the ratio between useful exergy outputs from the gasifier to the necessary exergy input to the gasifier. In real processes, exergy is not conserved because of irreversibility. Generally, exergy efficiency or second law efficiency is defined as:

$$\eta_{ex} = \frac{Ex_{prod}}{Ex_{biomass} + Ex_{medium}}. \quad (28)$$

where  $Ex_{prod}$  and  $Ex_{biomass}$  are exergies of producer gas and biomass, respectively, while  $Ex_{medium}$  is the exergy of the gasifying medium.

From the thermodynamics point of view, the gasification process must satisfy both first and second laws of thermodynamics. The second law of thermodynamics leads to the following equation:

$$\sum_{i=reactants} Ex - \sum_{j=products} Ex = I_{rr}. \quad (29)$$

where  $I_{rr}$  is irreversibility and represents the internal exergy lost as the loss of quality of material and energy due to dissipation. It is calculated in terms of the generated entropy during the gasification process as a result of flow of substances, heat and mass transfer and chemical reactions. It is given by the following equation:

$$I_{rr} = T_0 S_{gen}. \quad (30)$$

The exergy can be divided into two major components shown below:

$$Ex = Ex_{ch} + Ex_{ph}. \quad (31)$$

where  $Ex_{ch}$  and  $Ex_{ph}$  are chemical exergy and physical exergy, respectively. The dead state used in the following calculation is defined at  $P_0 = 101325$  Pa and  $T_0 = 298$  K.

The chemical exergy of ideal mixture gas, in kJ/kmol, can be calculated as:

$$Ex_{chj} = \sum_j x_j \bar{e}_{chj} + R T_0. \quad (32)$$

where  $x_j$  is mole fraction of the  $j$  component in the overall reaction of gasification and  $\bar{e}_{chj}$  is the standard chemical exergy of the  $j$  component expressed in kJ/kmol as presented in Table IX [61].

TABLE IX

The physical exergy of each gas species can be calculated as:

$$Ex_{phj} = (h_T - h_{T0})_j - T_0 (s_T - s_{T0})_j. \quad (33)$$

where  $h_T$  and  $s_T$  are enthalpy and entropy of the  $j$  component at any pressure ( $P$ ), temperature ( $T$ ) and  $h_{T0}$  and  $s_{T0}$  are enthalpy and entropy at  $P_0, T_0$  in the overall reaction of gasification, as previously defined in eqs. (15) and (20).

The exergy of the biomass can be calculated by using the method presented in ref. [62] as follows:

$$Ex_{biomass} = \zeta LHV_{biomass}. \quad (34)$$

where the coefficient  $\zeta$  is the ratio of the chemical exergy and the lower heating value of the biomass and is given in terms of hydrogen–carbon ratio,  $\alpha$ , and oxygen–carbon ratio,  $\beta$ , (computed by eq. (5)), according to the following equation [63]:

$$\zeta = 1.0438 + 0.0158 \alpha + 0.0813 \beta \quad \text{for } \beta \leq 0.5. \quad (35)$$

$$\zeta = \frac{1.0414 + 0.0177 \alpha - 0.3328 \beta \{1 + 0.0537 \alpha\}}{1 - 0.4021 \beta} \quad \text{for } 0.5 < \beta \leq 2. \quad (36)$$

Feedstock can be classified depending on atomic H/C ratio and atomic O/C ratio (i.e.  $\alpha$  and  $\beta$ ), as indicated in the Van Krevelen's diagram. As shown in Fig. 4, the Van Krevelen's diagram characterizes different type of feedstocks according to their respective  $\alpha$  and  $\beta$  ratio. The highest  $\alpha$  and  $\beta$  ratio represent biomasses, while the lowest  $\alpha$  and  $\beta$  ratios represent anthracite. In between are coal, lignite and peat. The lower heating values  $LHV_{biomass}$  and the ratios of chemical exergies to lower heating values  $\zeta$ , can be expressed as a function of the fuel composition. The effect of the  $\alpha$  ratio on these parameters is much smaller than that of the  $\beta$  ratio. Fuels with high  $\beta$  ratio have a smaller heating value than those with lower  $\beta$  ratio. However, the factor  $\zeta$  increases with increasing  $\beta$ , which indicates that by decomposing a fuel with high  $\beta$  ratio, physical exergy increases and relatively more work may be delivered from the obtained product.

FIGURE 4

#### 4. Development of models based on stoichiometric method

The most relevant stoichiometric equilibrium models are described in this section following a chronological order. Each model is discussed by giving a rough view of the approach followed and the main results obtained within parametric analyses aimed at evaluating the effects of equivalence ratio, initial moisture content of the biomass and gasification pressure on syngas composition and calorific value, and the gasification temperature and efficiency.

Validation of models has been based on various experimental works: downdraft gasifiers have been build and tested by several researchers, as stratified gasifiers [31, 44, 64-67], Imbert gasifiers [64, 66, 68-70], double stage air supply gasifiers [71-75], gasifiers with an internal separate combustion chamber [76], and catalytic steam gasifiers [77], among others.

**Chern's model (1991)** [78] is applied to downdraft gasification of wood in order to compute syngas composition in terms of  $N_2$ ,  $H_2$ ,  $CO$ ,  $CH_4$ ,  $H_2O$  and  $CO_2$  (that is a *reference composition* also used by all other researchers in their models), temperature and char yield at the exit of the gasifier, for a specified set of heat loss and input conditions. The reactions used in this model are  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and

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$CO_2 + CH_4 \rightarrow 2H_2 + 2CO$  (this last is obtained by combining  $R_3$ ,  $R_4$  and  $R_{11}$ ). The model is validated with experimental data obtained from the gasification of wood in a commercial-scale downdraft gasifier.

**Zainal's model (1997)** [45] is used in application of different raw materials as wood, paddy husk, paper, municipal waste [79]. Reactions  $R_5$  and  $R_6$  are used. Unknowns of the problem are the species in the producer gas and the oxygen content. Subsequently, the amount of oxygen is indeed computed by defining it in terms of some components in the producer gas. Consequently, the gasification temperature is fixed. The most important results are: content of  $H_2$  in the producer gas increases almost linearly with the increase the moisture content for all the considered materials;  $CO$  content in the producer gas decreases almost linearly with increase in moisture, while  $CH_4$  increases linearly, although its percentage is small (of the order of 1%); the calorific value of the producer gas decreases with the increase in moisture content and reduces as the gasification temperature increases in the analysed range of temperature (750-900°C). The model is validated with experimental results of ref. [80].

**Schuster's model (2000)** [81] simulates operation of a decentralized combined heat and power station based on a dual fluidised-bed steam gasifier. The reactions used in this model are  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_{11}$ . The main results when temperature increases, are:  $CH_4$  decreases and above 800 °C no  $CH_4$  is produced;  $CO_2$  and  $H_2$  decrease, while  $CO$  and  $H_2O$  increase; the heating value of the wet produced gas is nearly constant, while for the dry product it slowly increases. Regarding the product gas composition,  $LHV$  and  $CGE$  as a functions of the moisture content, it is shown that  $H_2$ ,  $H_2O$  and  $CO_2$  increase, instead  $CO$ ,  $CH_4$ ,  $LHV$  and  $CGE$  decrease.  $CGE$  goes down due to the low heating value and because biomass moisture has to evaporate in the gasifier resulting in a higher energy demand, so that more gas is recirculated into the combustion zone. The model is validated with experimental data of refs. [18] and [26].

**Mountouris's work (2003)** [46] focuses on the thermodynamic analysis of plasma gasification technology, which includes prediction of the produced gas composition and energy and exergy calculations. The model takes into account reactions  $R_4$ ,  $R_6$  and  $R_{11}$  and the approach used is similar to [45]. The gas composition as a function of the oxygen amount shows that an increase of the air flow rate is disadvantageous in all the cases because  $H_2$  and  $CO$  decrease and  $CO_2$ ,  $N_2$  and  $H_2O$  increase. Regarding the temperature effect over 800 °C, it is shown that an increase of gasification temperature leads to:  $CO$  and  $H_2O$  concentrations increase;  $H_2$  and  $CO_2$  concentrations decrease; instead  $N_2$  concentration remains approximately constant. The results are compared with refs. [37] and [45].

**Prins's model (2007)** [63] is used to describe gasification of fuels with varying composition of organic matter and to give hints about the composition to be preferred to achieve an high quality syngas. In order to describe the behaviour of fluidised bed gasifiers more accurately, the quasi-equilibrium temperature approach [59] is followed with reactions  $R_3$ ,  $R_4$  and  $R_5$ . At quasi-equilibrium conditions, less  $CO$  is present in the gas, and more  $CH_4$ ,  $H_2O$  and  $CO_2$  with respect to equilibrium conditions.  $CH_4$  formed in gasifiers, also by thermal cracking of tar, reforms too slowly, hence its concentration is higher than at equilibrium conditions. The concentrations of  $H_2O$  and  $CO_2$  are higher due to the kinetic limitations of char reforming. Exergy losses in wood gasification ( $\beta$  ratio around 0.6) are larger than those obtained for coal ( $\beta$  ratio around 0.2); at a gasification temperature of 927 °C, a fuel with  $\beta$  ratio below 0.4 is recommended, which corresponds to a lower heating value above 23 MJ/kg; for gasification at 1227 °C, a fuel with  $\beta$  ratio below 0.3 and lower heating value above 26 MJ/kg must be preferred. The equilibrium model is validated with experimental results of ref. [29].

**Sharma's model (2008)** [82] proposes a full equilibrium model of global reduction reactions for a downdraft biomass gasifier. The model takes into account reactions  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$  and  $R_{11}$ . The calorific value of the gas shows improvement with the increase in moisture content from 0% to 10%, with a maximum value

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of 4738 kJ/m<sup>3</sup> at 10% moisture, thereafter, it starts decreasing with further increase in moisture content. *CGE* also shows similar trends. However, it must be noted that *CGE* shows a peak near 20% in moisture content when all char gets consumed. The percentages of *CO* and *H<sub>2</sub>* are shown to decrease as the pressure increases, while *CH<sub>4</sub>*, *CO<sub>2</sub>*, *N<sub>2</sub>* and unconverted char increase with increasing pressure. The calorific value of the gas decreases as pressure increases, since the percentages of hydrogen and *CO* decrease significantly. The unconverted char decreases with the increase of equivalence ratio. Increasing the moisture content, the calorific value of the gas improves at lower equivalence ratios, while at higher equivalence ratios it decreases slightly. A peak in the gasification efficiency can be observed to shift toward lower equivalence ratios with the increase of the moisture content in the feedstock. Equilibrium model results are compared with the experimental data of refs. [83], [84] and data predicted by the kinetic model by [85].

**Jarungthammachote's model (2007)** [32] uses equilibrium constant for predicting the composition of the producer gas in a downdraft waste gasifier developed. With respect to the Zainal's model [45], where oxygen is not an unknown, in this model the reaction temperature is calculated if the amount of oxygen is known, and vice versa. As cited by [86], in order to obtain better agreement with experimental data, the Gumz's approach [59] is used. Coefficients equal to 11.28 and 0.91 are used to multiply the equilibrium constant of the *CH<sub>4</sub>* reaction and water-gas shift reaction respectively. After modifying the model, the amount of *H<sub>2</sub>* significantly reduces with respect to the predicted value obtained from the unmodified model. The amount of *CH<sub>4</sub>* dramatically increases and is found closer to the experimental values. For some cases, *CO* remains constant, while for other cases it slightly increases with respect to the unmodified model. Regarding the effect of the moisture content on the composition of the producer gas, similar results to ref. [81] are obtained. The modified model is validated with data reported by several researchers [37, 45, 64].

**Huang (2009)** [87] develops two models to simulate a downdraft gasifier based on the three equilibrium reactions *R<sub>4</sub>*, *R<sub>6</sub>* and *R<sub>11</sub>*. The first model does not include the simulation of the char, while the second considers also char. The equilibrium constant for *R<sub>4</sub>*, *R<sub>6</sub>* and *R<sub>11</sub>* are determined by *lnK* correlations under the given gasification temperature *T* and pressure. Then the number of moles of *H<sub>2</sub>*, *CO*, *CH<sub>4</sub>*, *CO<sub>2</sub>*, *H<sub>2</sub>O* and *H<sub>2</sub>S* is obtained by solving the nonlinear equation for the elemental balance of *C*, *H* and *O* and the equilibrium constant, under the given amount of air. As in [32], the partial equilibrium is considered: through a coefficient  $\beta_1$  that multiplies the equilibrium constant associated with reaction *R<sub>11</sub>*, and  $\beta_2$  associated to *R<sub>6</sub>*. For the first model, the modifications resulting from  $\beta_1$  improve the predictive capability, whereas the modification by  $\beta_1$  and  $\beta_2$  leads to poorer predictive capability. The results of the second model considering char, are far from the experimental data, and specifically, the simulation value of *CO* is much higher than in experimental data, while the value of *CO<sub>2</sub>* is much lower.

**Karamarkovic's model (2009)** [52], enables the determination of the Carbon Boundary Point (*CBP*) and the analysis of gasification below and above this point. Gasification implies adding sufficient oxygen until all carbon is converted into gaseous phase. This is covered by the first part of the model that can function independently of the second part of the model, is used to determine the equilibrium composition below and at the *CBP* (heterogeneous equilibrium). Further addition of oxygen above the *CBP* leads to the decrease of the heating value and the increase of the sensible heat of the product gas, until complete combustion takes place. This homogeneous equilibrium is covered by the second dependent part of the model. The unknowns in the first part of the model are: the required amount of gasifying agent; the temperature, amount and composition of the product gas. The gasifying agent, gasification pressure, and heat exchanged with the environment are common parameters for both parts of the model, which means that they are constant during simulations. The amount of unconverted solid carbon is a parameter defined only for the first part of the model. When gasification occurs at the *CBP*, the amount of unconverted solid carbon equals zero. The first part of the model calculates the heterogeneous thermodynamic equilibrium of the product gas, and a given amount of unconverted carbon. The obtained gas composition is then used in the second part of the model to

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calculate the homogeneous equilibrium at a given gasification temperature. In order to obtain a better agreement with the experimental data [59], reactions  $R_6$  and  $R_{11}$  are multiplied by 0.63 and 420, respectively. The increase of moisture in the biomass and pressure produces results similar to those of refs. [81] and [82] respectively. The efficiencies based on the chemical energy and exergy, and on the total (chemical and physical) exergy decrease with the increase of temperature above the value at *CBP*, and with the increase of moisture content in the biomass. The influence of biomass drying on the exergy efficiency is also shown. The model is validated on the basis of experimental data [64].

In **Abuadala's** work (2009) [88], hydrogen production from steam gasification is analysed through a parametric study. The assumption made by [89] to treat un-reacted char is applied (un-reacted char is equal to the 5% of the biomass carbon content) and tar formation is modelled as benzene [90] through the empirical relation proposed by [91]. Instead the energy lost to the environment  $Q_{lostwa}$  (that in ref. [5] is assumed as equal to about 1-2% of the thermal power input of the biomass), is calculated a function of the overall heat transfer coefficient between the external gasifier wall and the environment. The overall heat transfer coefficient is estimated through the empirical correlation of ref. [92]. The performed parametric study simulates steam gasification in two ways: first by varying the amount of biomass in the gasifier at fixed amount of steam and gasifier temperature, then by varying the gasifier operating temperature and keeping constant the amount of biomass and steam. When the biomass quantity increases (at constant steam quantity and gasifier temperature),  $H_2$  decreases,  $CO$  increases while  $CH_4$  exhibits a low variation.  $CO_2$  concentration decreases over the same biomass range and behaves oppositely with respect to  $CO$ . Tar yield, being a function of the gasifier temperature remains constant at the specific temperature. Char concentration being proportional to the initial biomass carbon content increases with the increase of the biomass quantity. Increasing the amount of supplied steam (constant fuel quantity and gasifier temperature), hydrogen in the product gases increases,  $CO$  decreases and  $CO_2$  increases. As the gasifier operating temperature increases in the range of 727-1227 °C (constant fuel quantity and steam quantity),  $H_2$  and  $CO_2$  decrease, while  $CO$  increases. The model is validated on the basis of different experimental data, e.g. refs. [26].

**Roesch's** model (2011) [93] is developed to predict the composition and heating value of the producer gas obtained from a commercial small scale downdraft gasifier. Eight biomasses are analyzed. The pelletized feedstock chosen for this wide availability and low cost are: alfalfa, algae, field grass, hemp, miscanthus, peanut shells, pine, and municipal solid waste (paper and plastic). The estimated gas composition for each feedstock is computed by using the equilibrium model averaged over a range of temperatures measured in the reaction zone of the gasifier and the Zainal's approach [45]. The model is validated with experimental data available from the literature as [31, 64, 94, 95].

**Vaezi's** model (2011) [47] is developed to predict the performance of a downdraft heavy fuel oil gasifier. The model is similar to those of refs. [32] and [45]. As the equivalence ratio is increased, results similar to ref. [81] are obtained. The oxygen enrichment is varied from 21% to 100%. It is shown that gasification with air produces a syngas with low hydrogen content (less than 20% in volume). As the amount of oxygen is increased, the  $H_2$  and  $CO$  in the syngas also increase: for an oxygen enrichment of 100%, the content of  $H_2$  content in the syngas increases to the value of 42.5%. The increase of  $LHV$  is due to the increase in the amount of  $CO$  and  $H_2$ . The calorific value varies from 6 MJ/m<sup>3</sup> obtained, for 21% of oxygen, to 12.5 MJ/m<sup>3</sup> gasification with pure oxygen, and the gasification temperature changes from 1027 °C to 1862 °C. As the oxygen enrichment increases from 21% to 30%, the  $CGE$  increases as much as 1.3%. Further increase of the oxygen enrichment, however, has no significant effect on the  $CGE$ . The  $CCE$  decreases when increasing the oxygen enrichment. The effect of pressure variation on the composition of syngas is also investigated (pressure ranges from atmospheric pressure to 80 atm). Similar results with respect to ref. [82] are obtained. The model is validated on the basis of the experimental data of ref. [96].

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1 In **Puig-Arnavat's model (2012)** [97], in order to increase the accuracy of the results, some modifications  
2 with respect to pure thermodynamic equilibrium model are introduced: 1) adding a pyrolysis step that uses  
3 semi-empirical correlations to predict the formation of gas, char, and volatiles; 2) considering heat losses in  
4 the pyrolysis and gasification steps (these heat losses are estimated as a percentage of biomass energy input);  
5 3) considering tar and char leaving the gasifier as a percentage of tar and char produced in the pyrolysis step;  
6 4) considering particles leaving the gasifier and set by the user as  $\text{mg/Nm}^3$  in the producer gas; 5) setting the  
7 amount of  $\text{CH}_4$  produced. The model is developed on the basis of refs. [32] and [45]. The effect of the ER on  
8 temperature and composition of the producer gas is similar to refs. [46, 47] and [82]. The effect of oxygen  
9 enrichment on producer gas composition,  $LHV$  and gasification temperature is similar to that determined in  
10 ref. [47]. The model is validated on the basis of experimental data of ref. [64].  
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15 **Balu's work (2012)** [98] discusses how the  $C$ ,  $H$ ,  $O$  content variations in the feedstock affect the thermal  
16 profiles in the different zones of the gasifier, and their impact on the final syngas composition by using a  
17 thermodynamic equilibrium model. Four different feedstock such as pine wood, horse manure, red oak, and  
18 cardboard are evaluated. In this case, an approach similar to the one proposed by [32] is used, with the  
19 difference in the calculation of the equilibrium constants for  $R_6$  and  $R_{11}$ , and enthalpy in the energy balance  
20 where the fitted values given in NIST Chemistry are used. The code is validated on the basis of the results  
21 from models by other authors [37, 45, 46].  
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25 **Azzone's model (2012)** [53] studies the feasibility of gasification of crop residues currently popular in Italy,  
26 as corn stalks, sunflower stalks and rapeseed straw. The gasifier is considered as a black box able to predict  
27 the syngas chemical composition, while pressure and temperature are given quantities. In order to consider  
28 that not all the carbon participates in the equilibrium reactions,  $\kappa$  factor is introduced to represent the carbon  
29 fraction that takes part in the equilibrium reactions, while the remaining carbon by-passes the reaction zone  
30 (char is mainly made up of carbon). The molar quantity of carbon that by-passes the chemical equilibrium is  
31 equal to  $(1 - \kappa) = (1 - \mu)$ , where the parameter  $\mu$  is a function of the ER. The reactions used are similar to  
32 those of ref. [32] and [46]. By increasing the process temperature at environment pressure, the syngas  
33 composition presents the same results of ref. [81], but a lower heating value decreases instead of increasing  
34 as in ref. [81]. The effect of the biomass humidity and oxidant agent produce results that are similar to the  
35 models of refs. [32], [46], [49], [58], [81, 82]. The syngas composition changes as a function of the process  
36 pressure for a temperature of 1050 K and similar results are obtained with respect to refs. [47] and [82],  
37 except for  $\text{N}_2$  that decreases and  $LHV$  that increases.  $CGE$  decreases as the process pressure increases. The  
38 model is validated on the basis of experimental data deduced from [48] and [99].  
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45 In **Syed's model (2012)** [100], four kinds of feedstock such as RTC coal, pine needles, ply-wood and lignite  
46 are processed. The mass balance of carbon, hydrogen and oxygen and the equilibrium constants for  $R_3$ ,  $R_5$   
47 and  $R_6$  are used in order to compute the number of mole of the syngas reference composition and the solid  
48 un-burnt carbon (char). The energy equation is used to calculate the gasification temperature. Solid un-  
49 converted carbon is incorporated in the product species and is accounted for in the mass balance of carbon.  
50 The results obtained are similar to those refs. [47] and [97] for the gasification temperature as a function of  
51 the air supply for all the investigated biomasses.  
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55 **Barman's model (2012)** [49] for fixed bed downdraft biomass gasifiers considers tar as one of the  
56 gasification products. A representative tar composition is used as an input parameter to the model. In  
57 particular, ref. [101] classifies the as gravimetric tar and GC-detectable tar. According to the results, the  
58 maximum tar yield is 4.5% (mass percentage). This model takes into account the same value of the tar yield  
59 and considers the corresponding mole value  $n_{tar}$  as an input parameter for the gasification model. The  
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representative formula of tar from ref. [102] equal to  $CH_{1.003}O_{0.33}$  is taken. Reactions  $R_5$ ,  $R_6$  and  $R_{11}$  are considered and in particular the equilibrium constants of the water gas homogeneous reaction and the  $CH_4$  reforming reaction are determined by the expressions shown below:

$$K_{R6} = e^{\left(\frac{4276}{T} - 3.961\right)}; \quad K_{R11} = 1.198 \cdot 10^{13} \cdot e^{-\frac{26830}{T}}. \quad (37)$$

In order to increase the accuracy of the model, an approach similar to the ref. [32] is followed. The equilibrium constant for the  $CH_4$  reaction is multiplied by a constant, which is initially taken equal to one and then gradually increased by an increment of 0.5. The performance analysis of the gasifier is shown with variation of gas composition with the air-to-fuel ratio, variation of gross calorific value with air-to-fuel ratio, and variation of gas production with mole of moisture per mole of biomass. Similar results with respect to refs. [46, 47], [81], and [97] are obtained. A comparative study is performed with various experimental results obtained from the literature [66, 103-105].

**Pandey's model (2013)** [106] has several analogies with ref. [45]. A parametric analysis for Eucalyptus wood is made that leads to result similar to those of refs. [32], [45, 46], [49], [81, 82]. The reaction temperature for self sustaining gasification is 800 °C. With the increase of the moisture content, the equivalence ratio necessary to maintain a temperature 800 °C increases.

**Simone's model (2013)** [107] uses a new simplified approach for a pilot scale downdraft gasifier operated with different feedstock (biomass pellets and vine prunings) where two empirical parameters are used, called by-pass and permeability index. The approach shows that, biomass is completely dried and devolatilized into char, tar, water and permanent gases in the upper section of the gasifier and the lower section of the downdraft gasifier is schematized with two parallel reactors. These are a mixed reactor representing the ideal behavior of the gasifier (where the devolatilization products in the mixed reactor are burned with air in the oxidation zone) and a by pass section accounting for the fraction of devolatilization products which by-passes the oxidation and reduction zone. The by-pass index is defined as the fraction of devolatilization products entering the by-pass section. The parallel reactor is a completely stirred tank reactor where tar cracking and reforming reactions occur. In the work, the reduction zone temperature is plotted against the by-pass index for different values of the permeability index. It can be seen that the average temperature of the reduction zone increases with increasing the permeability index, due to the higher equivalence ratio attained. The effect of the by-pass index is not as linear. When the by-pass index is set to zero the gasifier is represented as an ideal equilibrium reactor. It can also be seen that, the effect of the permeability index on the composition becomes less important, as at this point the final syngas composition is mostly independent of this parameter. The tar content in the syngas plotted against the by-pass index for different permeability indexes is shown: increasing the by-pass index, the tar content increases dramatically. The model is validated on the basis of the experimental tests on biomass pellets and vine prunings made in their gasifier.

In **Mendiburu's work (2014)** [60], four models are developed and tested, called  $M_1$ ,  $M_2$ ,  $M_3$  and  $M_4$ , where particular feedstock (blend of hardwood chips and glycerol at 80% and 20% respectively) are used. Model  $M_1$  is an unmodified equilibrium model that uses the equilibrium equations of the methane formation and water-gas homogeneous reactions presented in Table X. Model  $M_2$  implements a modification of the equilibrium constant used in model  $M_1$ , by multiplying these the variables  $\sigma$  and  $\tau$  respectively presented in Table X. Model  $M_3$  implements correlations for  $CO/CO_2$  and  $CO/H_2$  presented in Table X. Model  $M_4$  implements a modification of the equilibrium constant for the water-gas homogeneous reaction and the methane reforming reaction by substitution of their respective equilibrium constants with the relationships presented in Table X, derived from ref. [49].

TABLE X

The preferred criterion in order to quantify the amount by which numerical results differ from experimental values is the evaluation of the root mean square error [108]:

$$RMS_{error} = \sqrt{\frac{\sum_{j=1}^N (Experiment_j - Model_j)^2}{N}} \quad (38)$$

where  $Experiment_j$  is the value from the experimental results,  $Model_j$  is the predicted value from the model, and  $N$  is the number of data. On the basis of the  $RMS_{error}$ , it is concluded that model  $M_2$  is the best among the four. The effects on gasification of input parameters such as equivalence ratio, moisture content and oxygen percentage in the gasification agent are found similar to the previously cited models of refs. [32], [45 - 47] and [81, 82]. The four models are validated with experimental data presented in the literature [37, 45, 64, 67, 68] and compared with previously published models [32, 37, 46, 49, 80, 81].

In Costa's (2015) [34], novel model is developed for coupling a thermo-chemical equilibrium model, that considers tar and char formation, with an optimization software based on genetic algorithm, in order to calculate the optimal correction factors able to minimize the error between computed and experimentally measured yields and temperatures. The approach is repeated to simulate the thermal treatment of different biomasses with increasing carbon content, such as straw, rubber wood, treated wood and sawdust. Similar considerations proposed by [88] and [100] for tar and char respectively are made. The model is validated with experimental data presented in ref. [64] for biomass rubber wood.

## 6. Conclusions

Technology for thermo-chemical conversion of biomasses is one of the key elements to make the vision of an energy system without fossil fuels a reality in the near future. In this context, gasification technology fits perfectly into the energy conversion mix of the future, especially when it involves biomass resources being residuals of human activities such as for industrial wood or food processing and forest management devoted to wild fire prevention and brushwood removal that can give new job opportunities and occasions to make not economically disadvantageous the maintenance of the territory could derive from the possibility to valorise locally available resources. Since depopulation of rural and mountain areas is a problem of sustainable models of social development at European level, biomass exploitation may become an important flywheel in terms of economic, social and environmental impact. For this reasons, market on mCHP for decentralised power supply in rural areas or mountain zones is increased and research on biomass gasification technologies is becoming important areas that needs more attention.

In order to study complex processes like gasification, without having relying on experimental methods, which are time consuming and expensive, modelling and simulation studies can be particularly helpful.

Many modelling studies focus on the thermo-chemical equilibrium hypothesis because of its simplicity. However, equilibrium modelling provides the maximum yield achievable under equilibrium conditions, which is not the real condition of a gasifier operation. Hence, the results produced are less reliable and should be better focused on more accurate modelling techniques like kinetic modelling.

The present work is a review of the most important models in the scientific literature applying the so-called stoichiometric method. The authors' aim is to discuss dedicated analyses regarding the effect of biomass moisture content, gasification equivalence ratio, pressure variations and oxygen enrichment on the quality of the produced syngas in particular in terms of lower heating value and cold gas efficiency. Essentially, almost all presented models show that: an increase of moisture content produces a decrease of lower heating value,



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1 due to a reduction of the  $CO$  yield that has a greater weight with respect to the increase of  $H_2$ ; an increase of  
2 equivalence ratio and pressure variations produce a decrease of lower heating value, due to the simultaneous  
3 decrease of  $CO$  and  $H_2$ ; an increase of oxygen enrichment produces an increase of lower heating value, due  
4 to the simultaneous increase of  $CO$  and  $H_2$ . Analogous considerations are applicable the cold gas efficiency  
5 of the gasification process.  
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## Nomenclature

<i>Latin symbol</i>	<i>Quantity</i>	<i>SI Unit</i>
$AC_{stq}$	Stoichiometric air-to-fuel ratio	-
$C$	Char as unconverted carbon	-
$C_c$	Specific heat capacity of solid carbon	kJ/kmol K
$CCE$	Carbon conversion efficiency	-
$Cd$	Heavy metal cadmium	-
$CGE$	Cold gas efficiency	-
$C_{p,i,j}$	Specific heat capacity at constant pressure of the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	kJ/kmol K
$CH_4$	Methane	-
$C_2H_4$	Ethylene	-
$C_6H_6$	Benzene	-
$CO$	Carbon monoxide	-
$CO_2$	Carbon dioxide	-
$D$	Atom of carbon in the molecule of tar	-
$Ex_{biomass}$	Biomass exergy	kJ/kmol
$Ex_{ch}$	Chemical exergy	kJ/kmol
$Ex_{medium}$	Gasifying medium exergy	kJ/kmol
$Ex_{ph}$	Physical exergy	kJ/kmol
$Ex_{prod}$	Producer gas exergy	kJ/kmol
$ER$	Equivalence ratio	-
$f$	Atom of hydrogen in the molecule of tar	-
$g_{i,j}^*$	Molar specific Gibbs function of the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	kJ/kmol
$(g_f^0)_{i,j}$	Molar specific Gibbs function of formation at the standard reference state of the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	J/kmol K
$H_2O$	Water	-
$H_2S$	Hydrogen sulfide	-
$HCl$	Hydrochloric acid	-



1	$Hg$	Heavy metal mercury	-
2	$HHV_{biomass}$	Higher heating value biomass	MJ/kg
3			
4	$\bar{h}_{f,biomass}^0$	Enthalpy of formation of biomass	J/mol
5			
6	$\bar{h}_{f,i}^0$	Enthalpy of formation of reactants	J/mol
7			
8	$\bar{h}_{f,j}^0$	Enthalpy of formation of product species	J/mol
9			
10	$I_{rr}$	Internal exergy lost	kJ/kmol
11			
12	$L_{v,H_2O}$	Enthalpy of vaporization of water	MJ/kg
13			
14	$K_{\Psi}$	Equilibrium constant for $\Psi = R_3, R_4, R_5, R_6, R_{11}$	-
15			
16	$LHV_{biomass}$	Lower heating value of biomass	MJ/kg
17			
18	$LHV_j$	Lower heating value of products in the overall gasification reaction	MJ/Nm <sup>3</sup>
19			
20	$LHV_{syngas}$	Lower heating values of the syngas	MJ/Nm <sup>3</sup>
21			
22	$m$	Number mole of oxygen per mole of biomass	mol
23			
24	$M_{biomass}$	Biomass fed to the gasifier in wet, dry or daf basis	kg/h
25			
26	$n_i$	Mole of $i$ th component of reactants species for $i = CH_{\alpha}O_{\beta}N_{\gamma}S_{\delta}, H_2O, (O_2+\lambda N_2)$	mol
27			
28	$n_j$	Mole of $j$ th component of product species for $j = N_2, H_2, H_2O, CO, CO_2, CH_4, C, TAR$	mol
29			
30	$NO_2$	Nitrogen dioxide	-
31			
32	$NO_x$	Nitrogen oxides and their mixtures	-
33			
34	$O_2$	Oxygen (diatomic)	-
35			
36	$P$	Pressure	Pa
37			
38	$P_0$	Standard reference state pressure and dead state pressure	Pa
39			
40	$PS$	Specific gas production	m <sup>3</sup> /kg
41			
42	$Q_{syngas}$	Syngas flow-rate	Nm <sup>3</sup> /h
43			
44	$Q_{lostwa}$	Heat transferred to ambient	kJ
45			
46	$R$	Universal constant of ideal gases	J/mol K
47			
48	$S_{gen}$	Generated entropy during the gasification process	kJ/kmol K
49			
50	$SO_2$	Sulfur dioxide	-
51			
52	$(s_{T0}^0)_{i,j}$	Molar specific absolute entropy at the standard reference state for the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	J/kmol K
53			
54			
55			
56			
57			
58			
59			
60			
61			
62			
63			
64			
65			

1	$(s_T)_{i,j}$	Molar specific absolute entropy for the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	J/kmol K
2			
3	$T_0$	Standard reference state temperature and dead state temperature	K
4			
5	$T$	Temperature	K
6			
7	$w$	Number mole of moisture per mole of biomass	mol
8			
9	$x_j$	Mole fraction of products	-
10			
11	$y_C$	Carbon mass fraction from ultimate analysis	-
12			
13	$y_H$	Hydrogen (monoatomic) mass fraction on <i>daf basis</i> from ultimate analysis	-
14			
15	$y_N$	Nitrogen (monoatomic) mass fraction on <i>daf basis</i> from ultimate analysis	-
16			
17	$y_O$	Oxygen (monoatomic) mass fraction on <i>daf basis</i> from ultimate analysis	-
18			
19	$y_S$	Sulfur mass fraction on <i>daf basis</i> from ultimate analysis	-
20			
21	$z$	Atom of oxygen in the molecule of tar	-
22			
23			
24			
25			
26			
27	<b><i>Greek</i></b>		
28	<b><i>symbol</i></b>	<b><i>Quantity</i></b>	<b><i>SI Unit</i></b>
29			
30	$\alpha$	Mass fraction hydrogen based on a single atom of carbon	-
31			
32	$\beta$	Mass fraction oxygen based on a single atom of carbon	-
33			
34	$\beta_1$	Coefficient used for equilibrium constant associated to $R_{11}$	-
35			
36	$\beta_2$	Coefficient used for equilibrium constant associated to $R_6$	-
37			
38	$\gamma$	Mass fraction nitrogen based on a single atom of carbon	-
39			
40	$\delta$	Mass fraction sulfur based on a single atom of carbon	-
41			
42	$\bar{\epsilon}_{ch j}$	Standard chemical exergy for $j$ components in overall reaction of gasification	kJ/kmol
43			
44	$\zeta$	Ratio of chemical exergy and lower heating value of biomass	-
45			
46	$\eta_{ex}$	Exergetic efficiency	-
47			
48	$\eta_{th}$	Thermal efficiency	-
49			
50	$\eta_{tot}$	Total efficiency	-
51			
52	$\kappa$	Carbon fraction that takes part in the equilibrium reactions	-
53			
54	$\Lambda$	Nitrogen to oxygen mole ratio in the gasification agent	-
55			
56	$M$	Parameter as function of equivalence ratio	-
57			
58			
59			
60			
61			
62			
63			
64			
65			

1	$v_i$	Stoichiometric number of the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	-
2			
3	$\sigma$	Multiplicative factor used for $K_{R5}$	-
4			
5	$T$	Multiplicative factor used for $K_{R6}$	-
6			
7	$\Delta\bar{g}_{f,T,i,j}^0$	Standard Gibbs function of formation at given temperature $T$ of the $i$ reactants and $j$ products species relative to the $\Psi$ reactions	-
8			
9			
10	$\overline{\Delta G_T^0}$	Gibbs free energy of formation variation for a certain reaction	J/mol
11			
12	$\Delta h_T$	Sensible enthalpy of overall products gasification reaction in the presence of air	J/mol
13			
14	$\Phi$	Stoichiometric coefficient of the oxidation reaction	-
15			
16	$\psi$	Referred to reactions $R_3, R_4, R_5, R_6, R_{11}$	-
17			
18			
19			
20			
21	<b>Subscript</b>	<b>Quantity</b>	<b>SI Unit</b>
22			
23	$0$	Referred to standard reference state and dead state	-
24			
25	<i>Biomass</i>	Referred to biomass exergy	-
26			
27	$C$	Referred to solid carbon	-
28			
29	$Ch$	Referred to chemical exergy	-
30			
31	<i>Lostwa</i>	Referred to lost from receiver wall	-
32			
33	$Ph$	Referred to physical exergy	-
34			
35	<i>Prod</i>	Referred to producer gas exergy	-
36			
37	$R_3$	Referred to Boudouard reaction	-
38			
39	$R_4$	Referred to the Water - gas heterogeneous reaction	-
40			
41	$R_5$	Referred to the Methane formation reaction	-
42			
43	$R_6$	Referred to the water-gas shift homogeneous reaction	-
44			
45	$R_{11}$	Referred to the Methane reforming reaction	-
46			
47	$F$	Referred to the enthalpy of formation	-
48			
49	$G$	Referred to the water in gaseous phase	-
50			
51	$I$	Referred to reactants species	-
52			
53	$l$	Referred to the water in liquid phase	-
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55	$j$	Referred to product species	-
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*sat*

Referred to saturation

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*T*

Referred to temperature

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