Review

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*Review*

# Modelling of Biomass Gasification: From Thermodynamic to Process Simulations

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**Abstract:** Biomass gasification acquired great interest over the past decades as an effective and trustable technology to produce energy and fuels with net-zero carbon emissions. Moreover, using biomass waste as feedstock enables to recycle organic wastes and to fit the circular economy goals thus reducing the environmental impacts of waste management. Even if many studies have been already carried on, this kind of process must still be investigated and optimized with the final aim to develop industrial plants for different applications, from the hydrogen production to net-negative emission strategies. Modeling and developing of process simulations became an important tool to investigate the chemical and physical behavior of the plant, allowing to make a first raw optimization of the process and to define heat and material balances of the plant as well as to define optimal geometrical parameters with cost and time effective approaches. The present review paper focuses on the main literature models developed until now to describe biomass gasification process, and in particular on kinetic models, thermodynamic models, and computational fluid dynamic models. The aim of this study is to point out the strengths and the weakness of those models, comparing them and indicating in which situation is better to use an approach instead of another. Moreover, theoretical shortcut models and software simulations, not explicitly addressed by prior reviews, are taken into account. For researchers and designers this review provides a detailed methodology characterization as a guide to develop innovative study or project.

**Keywords:** biomass gasification; process simulation; thermodynamic equilibrium; kinetic model; ANN; multivariate data analysis

## 1. Introduction

During the Anthropocene, the pressure on environment is increasing exponentially along with global warming. On the other hand, the need for each country to be energy-independent and to find low-price solution for energy production, represent an actual challenge.

In order to deal with those problems, many researchers pointed out that it is possible to make an energetic transition from fossil fuels to renewable energy sources. Among the most investigated renewable energy sources, biomass is confirmed as the most favourable one, since it is the widest source of energy after coal, oil, and natural gas [1–4]. Using biomass as feedstock for energy production allows to achieve both green energy production and national energy security goal. Moreover, using biomass waste instead of energetic culture accomplish the request for circular economy to reuse those organic wastes that otherwise would be dispose polluting soil and air and also avoiding the fuel vs. food issue [5–7].

During the last years, many processes for biomass conversion into energy were investigated, and gasification was highlighted as one of the most efficacious [8–10]. Gasification is a thermo-chemical technology to convert biomass into a combustible gas mixture by the partial oxidation of the biomass at high temperature (750-950 °C) in presence of a gasifying agent [11–14]. Fluidized bed reactor was confirmed as the most suitable as gasifier reactor due to the excellent thermal and mixing properties that ensure high heat transfer rates, high efficiency, low combustion temperature and low pollutant emissions [15,16]. The gas mixture produced by gasification process is called syngas and it is mainly made of $H_2$, CO, $CO_2$, $CH_4$, $H_2O$, along with organic and inorganic contaminants [17]; the quantity of each produced component depends on feedstock characteristics, gasifying agent, operative conditions of the process, reactor design, etc. [18,19].

To investigate biomass waste gasification process, modelling approaches and simulation software provide useful tools to investigate different operative conditions, to make a first raw optimization of the process obtaining the most suitable syngas for the desired uses and to scale-up lab-scale and pilot apparatus. Results coming from simulative models must be the base for the realization of pilot plant, allowing to reduce cost, avoiding risk for human health as well as to interpret the experimental data and build the foundations of knowledge necessary for the realization of a project [20]. Both mathematical and numerical simulative models are suitable for those purposes since they both are able to predict the performance of the process and to give a good representation of the chemical and physical phenomena occurring, in order to optimize the process with swift time and minimal cost [21]. Then, it is also possible to choose to simulate the process in steady state condition (time independent) or in dynamic condition (time dependent), according to what is the focus of the investigation. Kinetic, thermodynamic, Computational Fluid Dynamic (CFD), and Artificial Neural Network (ANN) models have been adapted and implemented for the study of syngas production from a wide variety of feedstocks [22–25].

Kinetic models take into account the kinetic of the gasification reactions given the reactor properties (residence time, operative temperature, and pressure). They predict the syngas yield, the produced syngas composition after a finite time, or in a finite volume in a flowing medium. These models, after a proper validation, allow to predict the process performances for a specific operating conditions and reactor design [26,27].

Since kinetic models depend on the specific fluid-dynamics and geometry of the case study, their applicability is restricted to specific reactor configurations. Complex configuration of the reactors enhances the complexity of the describing model.

Thermodynamic models predict the syngas composition based on the assumption that the reactants react in a fully mixed condition for an infinite time, so to reach the thermodynamic equilibrium [28]. The main advantage of those models is the independency from the gasifier design [29], that means thermodynamic models can be used to describe a wide range of plants, without any particular restrictions, despite kinetic models.

CFD models describe the gasification process based on the conservation of mass, momentum, species, and energy into a certain portion [28,30]. Those models are able to predict a very accurate syngas composition when coupled with a well-known fluid-dynamic of the gasifier and are especially suitable for fluidized bed reactors, in which they provide important information about temperature profiles and species concentration.

Black-box approaches, including algorithms of Artificial Intelligence as ANN, are considered a relatively new approach for modelling biomass gasification process. They have the great merit to not require the formulation of a complex mathematical equations and also to be able to understand and identify non-linear relations [31]. Therefore, ANN modelling is acquiring great interest when the aim of the study is to investigate biomass gasification process there complex non-linearities occur in the dataset [32].

The aim of the present paper is to investigate the most recent simulative models and results from scientific literature, in order to provide a critic review that is able to indicate which is the best approach, among kinetic, thermodynamic, CFD, Multivariate Data Analysis (MVDA) and ANN to describe a biomass gasification process according to the specifications and the desired goal.

## 2. Biomass gasification principle and technology

Gasification is a partial thermal oxidation, occurring at high temperature (in the range 750-900 °C) in presence of a gasifying agent (steam, air, oxygen, or a mixture of them) that reacts with biomass producing a gaseous product mainly composed of $H_2$, CO, $CH_4$, $CO_2$ along with small quantities of solid product (char), inorganic contaminants (mainly $H_2S$ and HCl), and organic contaminants (tar). The amount of final inorganic compounds depends on biomass inlet properties, for instance, it is recommended to take as low as possible the inlet concentrations of S and Cl. The gasifying agent influences the final gas composition (see Table 1), steam provides the highest $H_2$ content and the highest Low Heating Value (LHV), while air provides a lower quality syngas due to the bigger amount of inlet $N_2$.

**Table 1.** Effect of gasifying agents on the composition of gas products [25].

| Gasifying agent | $H_2$ (%mol) | $CO_2$ (%mol) | CO (%mol) | $CH_4$ (%mol) | $N_2$ (%mol) | LHV (MJ/kg) |
|---|---|---|---|---|---|---|
| Air | 3-13 | 10-18 | 5-28 | 0-7 | 40-50 | 4-6 |
| Oxygen | 20-30 | 25-40 | 20-30 | 5-10 | 0-1 | 7-8 |
| Steam | 30-50 | 8-25 | 20-40 | 6-15 | 0-1 | 9-11 |

The chemistry of biomass gasification is quite complex. The reactions involved in the process are listed in Table 2, while the gasification stages can be summarized as follow [8,33]:

- *Drying*. Occurring at 100-200 °C, drying stage reduces the moisture content of biomass below 5%.
- *Devolatilization (pyrolysis)*. In this step, the thermal decomposition of biomass occurs, in absence of oxygen or air. The volatile matter is decreased, releasing hydrocarbon gases from biomass, which is then reduced to solid charcoal.
- *Oxidation.* In this stage, $CO_2$ is produced from the reaction of solid carbonized biomass and oxygen in the air. $H_2$ present in the biomass is oxidized to produce water. Then, if oxygen is present in sub-stoichiometric quantities, partial oxidation of carbon may happen, producing CO.
- *Reduction.* At high temperature (800-950 °C) several reduction reactions occur in the absence (or sub-stoichiometric presence) of oxygen. Those reactions are water-gas reaction, Boudouard reaction, water-gas shift reaction and methane reaction.

**Table 2.** – Chemical reactions of gasification process [8,34,35].

**Oxidation reaction**

**Volatiles**

$$CO + \frac{1}{2}\,O_2 \leftrightarrow CO_2 \qquad (1)$$
ΔH= - 283 kJ/mol

$$H_2 + \frac{1}{2}\,O_2 \leftrightarrow HO_2 \qquad (2)$$
ΔH= - 242 kJ/mol

**Char**

$$C + \frac{1}{2}\,O_2 \leftrightarrow CO \qquad (3)$$
ΔH= - 111 kJ/mol

$$C + O_2 \leftrightarrow CO_2 \;.. \qquad (4)$$
ΔH= - 394 kJ/mol

**Boudouard reaction**

$$C + CO_2 \leftrightarrow 2CO \quad (5) \qquad \Delta H = -172 \text{ kJ/mol}$$

**Water-Gas reaction**

Primary

$$C + H_2O \leftrightarrow CO + H_2 \qquad (6)$$
ΔH= - 131 kJ/mol

Secondary

$$C + 2H_2O \leftrightarrow CO_2 + 2H_2 \quad (7)$$
ΔH= - 90 kJ/mol

**Methanation reaction**

$$C + 2H_2 \leftrightarrow CH_4 \quad (8) \qquad \Delta H = -75 \text{ kJ/mol}$$

**Water-Gas shift reaction**

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (9) \qquad \Delta H = -41 \text{ kJ/mol}$$

**Steam Reforming reaction**

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (10)$$
ΔH= 206 kJ/mol

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$$C_nH + nH_2O \leftrightarrow nCO + \frac{n+m}{2}H_2 \qquad (11)$$

**Dry Reforming reaction**

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad (12)$$

$\Delta H$= 247 kJ/mol

$$C_nH_m + nCO_2 \leftrightarrow 2nCO + \frac{m}{2}H_2 \qquad (13)$$

## 2. Thermodynamic models

Thermodynamic models describe the thermodynamic equilibrium (temperature, pressure, and composition), achieved by perfect mixing and infinite reaction time. The system is time-invariant and not depending on kinetic factors such as the design of reactor and fluid dynamics [29]. This property makes the models at thermodynamic equilibrium very flexible to use and suitable for a wide variety of process without any specific constraints. Indeed, they provide information about limit gas yield, gas composition, and even if they apply under many rescripted assumptions, still they provide insights about unit operation, process optimization, energy recovery and also life-cycle assessment and techno-economic analysis [2,36–38]. Equilibrium models have a wide range of applicability since usually gasification process is driven close to equilibrium [29]. Thermodynamic equilibrium models can be classified into [39–41]:

- Stoichiometric models, which are based on equilibrium constants: the specific chemical reactions of the process must be declared;
- Non-stoichiometric models, which are based on minimisation of the Gibbs free energy, neglecting the chemical reactions involved. Only the definition of a set of chemical compounds that are expected at equilibrium is needed.

Stoichiometric models and non-stoichiometric models, even if built with a completely different mathematical implementation, were demonstrated to reach close results if some conditions are satisfied [42]. Even if stoichiometric models are based on simple mathematical formulation, they have not been widely utilized in literature, while non-stoichiometric models are used in approximately 73% of equilibrium simulations in literature, while 27% of literature relies on stoichiometric ones [39].

Stoichiometric models include mass balances and the calculation of equilibrium constants at a given temperature. The mathematical model combines the conservation laws of atomic species with those of thermodynamic equilibrium by referring to the global gasification reaction starting from reactants and inert compounds in the feed. The result is a tool to predict the composition of the produced gas, once the characteristics of the feed to be gasified are known (proximate and ultimate analysis), such as the operating conditions in terms of pressure, temperature, and steam/feed ratio. Mass and energy balances result into a system of non-linear algebraic equations for each reaction, whose unknown variables are the extent of each reaction; the solution is found applying the classic methods to evaluate the roots of non-linear algebraic equations, such as the Newton-Rapson one. Once computed the extents of all reactions at equilibrium, it is possible to compute the equilibrium composition of the products at a given temperature. If the temperature is unknown, it is necessary to couple an energy balance taking into account the enthalpies of the reactants and products, thus increasing the complexity of the system. These models are commonly based on the following assumptions [43]:

a) all the reactions considered are at thermodynamic equilibrium equivalent to an infinite residence time;
b) all the carbon is gasified and is not present among the reaction products;
c) the products leaving the gasifier, except for the ashes in the solid phase, are in the gaseous phase and consist of CO, $CO_2$, $H_2O$, $H_2$, $CH_4$, $N_2$;
d) among the reaction products there is no tar.

The mass balances in presence of the equilibrium reaction require the molar concentrations and the molar ratios of components in the feedstock. Since the solid feedstock (solid biomass) is often a complex mixture, it is described by a brute formula derived from the ultimate analysis of dry and ash-free biomass samples. Thus, the feedstock is represented as a single component $CH_mO_pN_q$ reacting as:

$$CH_mO_pN_q + wH_2O \rightarrow aCO + bCO_2 + cH_2 + d\,CH_4 + eH_2O + fN_2 \tag{14}$$

$$K_{eq} = e^{\frac{-\Delta G_T^0}{RT}} \tag{15}$$

$$\frac{\Delta G_T^0}{RT} = \frac{\Delta G_{298}^0}{R \cdot 298.15} - \int_{298.15}^{T} \frac{\Delta H_T^0}{RT^2}\,dT \tag{16}$$

$$\Delta H_T^0 = \Delta H_{298.15}^0 + \sum \int_{298.15}^{T_2} v_i C_{p,i}(T)dT \tag{17}$$

$$\Delta H_{298.15}^0 = \sum v_i\, H_{298.15\,products}^0 - \sum v_i\, H_{298.15\,reactants}^0 \tag{18}$$

$$\Delta G_{298.15}^0 = \sum v_i\, G_{298.15\,products}^0 - \sum v_i\, G_{298.15\,reactants}^0 \tag{19}$$

$$C_{p,i}(T) = a + bT + cT^2 + dT^3 + \frac{e}{T^2} + \frac{f}{T^{0.5}} \tag{20}$$

$\Delta G^0$ and $\Delta H^0$ are the variation of standard Gibbs free energy and enthalpy formation, respectively.

Assuming to know the composition of the biomass and the characterization of the reactants, including the biomass moisture and the gasifying agent (steam), it is possible to develop the model taking into account two chemical reactions: water-gas shift (9) and steam reforming (10). The solving system is represented by the four mass balance equations and the two chemical equilibrium equations (21)-(26).

$$1 = a + b + c \tag{21}$$

$$m + 2w = 2c + 4d + 2e \tag{22}$$

$$q = 2f \tag{23}$$

$$p + w = a + 2b + e \tag{24}$$

$$K_1 = \frac{\left(\frac{P_{CO_2}}{P_0}\right) \cdot \left(\frac{P_{H_2}}{P_0}\right)}{\left(\frac{P_{CO}}{P_0}\right) \cdot \left(\frac{P_{H_2O}}{P_0}\right)} = \frac{b \cdot c}{a \cdot e} \tag{25}$$

$$K_2 = \frac{\left(\frac{P_{CO}}{P_0}\right) \cdot \left(\frac{P_{H_2}}{P_0}\right)^3}{\left(\frac{P_{H_2O}}{P_0}\right) \cdot \left(\frac{P_{CH_4}}{P_0}\right)} = \frac{a \cdot c^3}{d \cdot e \cdot n_T^2} \tag{26}$$

$P_0$ represents the system operative pressure, while $P_{CH4}$, $P_{H2}$, $P_{H2O}$, and $P_{CO2}$ are the partial pressures of $CH_4$, $H_2$, $H_2O$, and $CO_2$, respectively. $n_T$ are the total moles of produced gas.

In Table 3 are listed the values of coefficient a, b, c ,d, e, and f, following the Hougen-Watson approach [44]. In Table 4 are listed the values of standard Gibbs free energy and enthalpy formation.

**Table 3.** – Coefficients for the computation of the specific heat at constant pressure [44].

| Compound | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| $CH_4$ | 4.75 | 1.200E-02 | 3.030E-06 | -2.63E-09 | 0 | 0 |
| $H_2O_{(gas)}$ | 6.97 | 3.464E-03 | -4.833E-07 | 0 | 0 | 0 |
| CO | 6.48 | 1.566E-03 | -2.387E-07 | 0 | 0 | 0 |
| $CO_2$ | 18.036 | -4.474E-05 | 0 | 0 | 0 | -158.08 |
| $H_2$ | 6.424 | 1.039E-03 | -7.804E-08 | 0 | 0 | 0 |
| $N_2$ | 6.50 | 1.00E-03 | 0 | 0 | 0 | 0 |
| $H_2O_{(liquid)}$ | 18 | 0 | 0 | 0 | 0 | 0 |

**Table 4.** - Standard Gibbs free energy and molar enthalpy formation [43].

| **Compound** | $H^0$ **(kcal/mol)** | $G^0$ **(kcal/mol)** |
|---|---|---|
| $CH_4$ | -17.810 | -12.057 |
| $H_2O_{(gas)}$ | -57.7979 | -54.6351 |
| CO | -26.416 | -32.808 |
| $CO_2$ | -94.052 | -94.26 |
| $H_2$ | 0 | 0 |
| $C_{(solid)}$ | 0 | 0 |

These models are of rapid use and are based on solid theoretical foundations widely developed in chemical engineering and reactor engineering textbooks. On the other hand, they often generate a non-negligible error due to the following reasons: the reactions really occurring are only partially known, they describe only the gaseous phase, at a given fixed temperature where all reactions are in equilibrium.

Non-stoichiometric models demonstrated their reliability over the years since were successfully used in modelling the gasification process, especially in fluidised-bed gasifiers [40,45,46], allowing to evaluate the effect of temperature, equivalence ratio, steam to biomass ratio, moisture content of feedstock on the gasification process.

Non-stoichiometric equilibrium models may be upgraded into the so called quasi-equilibrium approach, that is a compromise between equilibrium thermodynamic models and experimental data in reaction conditions close to the equilibrium [9,29], providing more accurate results about syngas composition.

The non-stoichiometric equilibrium modelling approach is founded on the direct minimization of the Gibbs free energy of reaction species. This methodology can be used to find equilibrium compositions "virtually" including unknown reaction paths. On the other hand, the minimization of the Gibbs free energy can be stopped in non-equilibrium conditions as explained in our previous works [43,47] and in some cases referred to as quasi-equilibrium temperature (QET) approach. This latter is actually considered the most effective way to model the gasification process [48] and have also been adopted by commercial process simulators as mentioned in the next chapters. The final composition is derived by setting a QET for each reaction that occurs into the gasifier. In this way each reaction occurs at its equilibrium temperature instead of the gasification temperature set for the gasifier block [49]. On the other hand, the minimization can be stopped by introducing other criteria. For instance, in our previous work [47] we defined an algorithm based on the minimization of the error model predictions and experimental data. In this way it is possible to train a quasi-equilibrium model and then use it as a scaling-up tool. We report below the formulation of a non-stoichiometric model based on the minimization of Gibbs free energy (G) for the previously selected set of reactions: steam reforming and water gas shift. It must be premised that this type of modelling starts following a first devolatilization defining the composition of the gaseous state that participates in the reaction. This preliminary phase is often trained on experimental data to get a more realistic description of the formation of ash, char, and tar. In fixed temperature and pressure conditions, the function G depends only on the extent of the reactions $\alpha$ and $\beta$, expressed as an extensive variable as follows:

$$G(\alpha,\beta)|_{T,P} = \sum_i n_i(\alpha,\beta) \cdot \mu_i(\alpha,\beta,T) \tag{27}$$

$$\mu_i = \mu_i^0(T) + RT\ \ln P_i \tag{28}$$

$$P_i = \frac{n_i(\alpha,\beta)}{n_{TOT}(\alpha,\beta)}\ P \tag{29}$$

$$\mu_i = \mu_i^0(T_0)\frac{T}{T_0} - T\int_{T_0}^{T}\frac{H_i(T)}{T^2}\,dT + RT\ \ln P_i \tag{30}$$

where i = CO, $CO_2$, $H_2O$, $H_2$, $CH_4$, $N_2$, $H_2S$. The partial pressure Pi is written by assuming an ideal mixture of gases. $n_i$ is the number of moles of the i-component; $\mu_i$ is the chemical potential; $H_i$ is the standard molar enthalpy of the component i in the gaseous phase, calculated at the temperature T of the system. $\mu_i^0(T)$ is the standard chemical potential of the i-component at temperature T. R is the universal constant of gas and $P_i$ is the partial pressure of i-component.

Once the chemical potentials of the components present in the system have been defined, at a given temperature, it is possible to evaluate the total free energy of the system at fixed $G(\alpha,\beta)|_{T,P}$ in equation (27) as function of two independent variables $\alpha,\beta$. In other words, the free energy $G(\alpha,\beta)|_{T,P}$ is as a surface in the space $(\alpha,\beta,G)$ and is characterized by the presence of a minimum which corresponds exactly to the equilibrium conditions of the system. The Gibbs Free Energy Gradient Method Model (GMM) exploits the thermodynamic principle stating that a system always reaches the equilibrium conditions starting from initial conditions by minimizing the energy value. The minimum energy value corresponds to the condition of all reactions being at the equilibrium simultaneously. From a theoretical point of view, the equilibrium condition is reached after an infinite time.

In practice, real systems can reach, even in very low time, conditions so close to the equilibrium that the difference lies within the error threshold of the current measurement methods, entering a kind of "grey zone", not observable.

In an industrial equipment, the system will reach this "grey zone" if the residence time is large enough, according to the reactor geometry and operating conditions. Among the infinite routes between the initial point ($\alpha = \beta = 0$) and the equilibrium point, the system chooses the path that offers the maximum gradient $\nabla G(\alpha, \beta)$ [43,47].Through a purposed set of experiments, it is possible to train the model by comparing the simulated with the experimental states. Figure 1 reports a comparison of trajectories following the $\nabla G(\alpha, \beta)$ between the GMM method and the final equilibrium state in a given experiment [43,46].

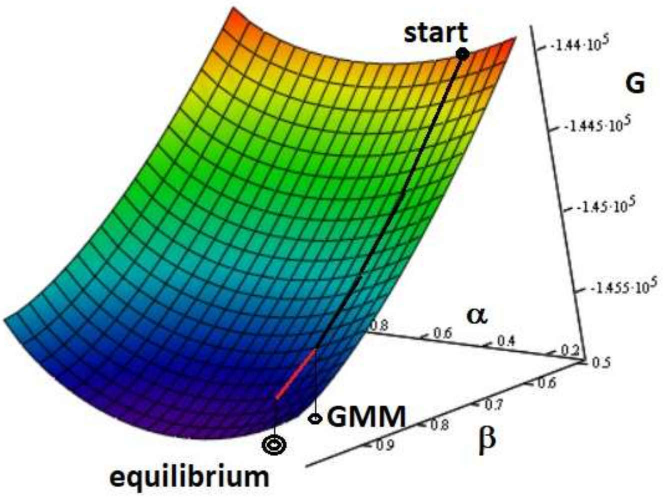


**Figure 1.** - GMM training pathway: 2-D representation in the α, β plan and highlights on the equilibrium and non-equilibrium coordinates [46].

Even if some studies over the past decades focused on the improvement of the evaluation of the QET by means of a data-fit made by experimental data [50–52], there is still a lack of comprehensive studies applied to fluidised-bed gasifier taking into account the use of different gasifying agents and also the undesired by-products (organic and inorganic compounds). Marcantonio et. al [29] proposed a process simulation study that tried to overcome this issue by developing a quasi-equilibrium model that includes air/steam/oxygen biomass-gasification in presence of organic and inorganic by-products. The results were in good agreement with experiments, and it was also possible to make an optimization of the process investigating the effect of gasification temperature and S/B ratio on the gas composition for different gasifying agents.

The most common properties whose experimental observation mostly deviates from ideal equilibrium prediction are the concentration of methane and the amount of unreacted char. The under or over prediction of methane is an ordinary issue in equilibrium models [53]. Indeed, in real case the conversion of methane is kinetically limited, so the final methane concentration is controlled by non-equilibrium factors and it is not possible to obtain a good prediction by means of equilibrium model [54]. The unreacted char issue is best dealt with and avoided by only computing the equilibrium of the volatile gas-phase components rather than the complete heterogeneous equilibrium or otherwise setting as input the specific amount of unreacted char from experimental results. Loha et al. [55,56] compared an equilibrium model of steam gasification in a fluidized-bed reactor with the correspondent experimental data. They showed that the actual deviation of methane increases at higher temperature, against the “general rule” stating that at higher temperatures reduce the gap between equilibrium model and experimental case. Applying a QET approach to simulate the syngas concentration at 750 °C Loha et al. found that the experimental molar dry concentration of methane was 4.2% against the simulated 2%. Many other studies in literature confirmed this trend of methane to be even twice in experimental case compared with equilibrium simulation [57]. As for the other main syngas components (hydrogen, carbon monoxide, carbon dioxide, steam) there is a good agreement between the simulations in QET conditions and corresponding experimental data, whit poor deviations (within 5% molar fraction) [58]. More in general, however, thermodynamic equilibrium model poorly applies to specific gasifier conformations and under some operating conditions, in particular for reactors operating at low temperatures [8,59,60].

## 2. Kinetic models

Kinetic models are commonly used in chemical reactor engineering to predict non-equilibrium product distributions, evolution of the system over time as a function of temperature and residence time. For their nature, they should be also accompanied by thermal energy and momentum balance. In order to obtain the information listed above, the kinetic equations must be very accurate, that means the reaction mechanism and the kinetic constant of the process must be validated on a wide range of experimental conditions. For these reasons, the kinetic model developed is strictly dependent on the geometry of the reactor and on the characteristic of the specific process and, if used to simulate other processes with different specifications, it can result an unpredictable error. The majority of kinetic models in literature is built to calculate the kinetic parameters to predict biomass feedstock conversion, syngas yield and composition.

Castello and Fiori [61] proposed a simplified model for hydrothermal gasification of methanol, they adapted the kinetic model according to elementary equations of combustion. They pointed out the relevance of two reactions among others: water-gas shift and CO methanation, which mostly influence the process. Another way to simplify the kinetic modelling of gasification process is through the lumped method, considering a pseudo-mono-component for the intermediate products and assuming that the syngas is produced from the decomposition of this single component [62]. Resende and Savage [63] developed a lumped first-order kinetic model to describe the gasification of cellulose and lignin fitting the experimental results in order to adjust the output. The model was able predict gas yield and syngas composition for different feeds. The results from this kinetic model were compared with those from a thermodynamic equilibrium model, adopting Gibbs free energy minimization method, found a good agreement. Guan et al. [64] studied hydrothermal gasification of algae by means of a lumped first-order kinetic model, which was able to give the precise gas yield and also the effect of water density and biomass inlet on the final gas composition. Jin et al. [65] investigated the gasification of lignite by means of lumped method; they were able to predict the gas yield in good agreement with experimental data obtained by means of a micro quartz tube reactor.

Even if the lumped first-order method seems promising in estimating gas yield and gas composition, it is not flexible for all processes. For instance, it is not suitable to predict the syngas composition in supercritical water gasification, whose reaction conditions strongly depend on structures and distributions of pores in the feedstock material, which vary their structure along with the gasification process in turn affecting the reaction rate [66,67]. For this reason, some authors proposed a kinetic alternative model based on random pore size distribution. Vostrikov et al. [68] proposed a kinetic model based on random pore size distribution for the investigation of supercritical water gasification of coal. The study confirmed that the model is suitable for describing the rate of coal conversion dependent upon the coal conversion degree. Moreover, it was highlighted that random pore size distribution model is not trustable when catalytic effects occurred in non-uniform way.

Di Carlo et al. [69] developed a semi-empirical kinetic model for steam gasification via fluidized-bed gasifier. The reactor was a cylinder, and the model was based on a mono-dimensional modelling of the mass and energy balance in order to calculate the syngas composition along the axis of the cylinder. The corresponding algorithm flowchart implemented by the authors is shown in Figure 2. Kunii and Levenspiel [70] developed a hydrodynamic model in order to describe the multiphase (bubble and emulsion) nature of reacting mixture phases and their interaction.

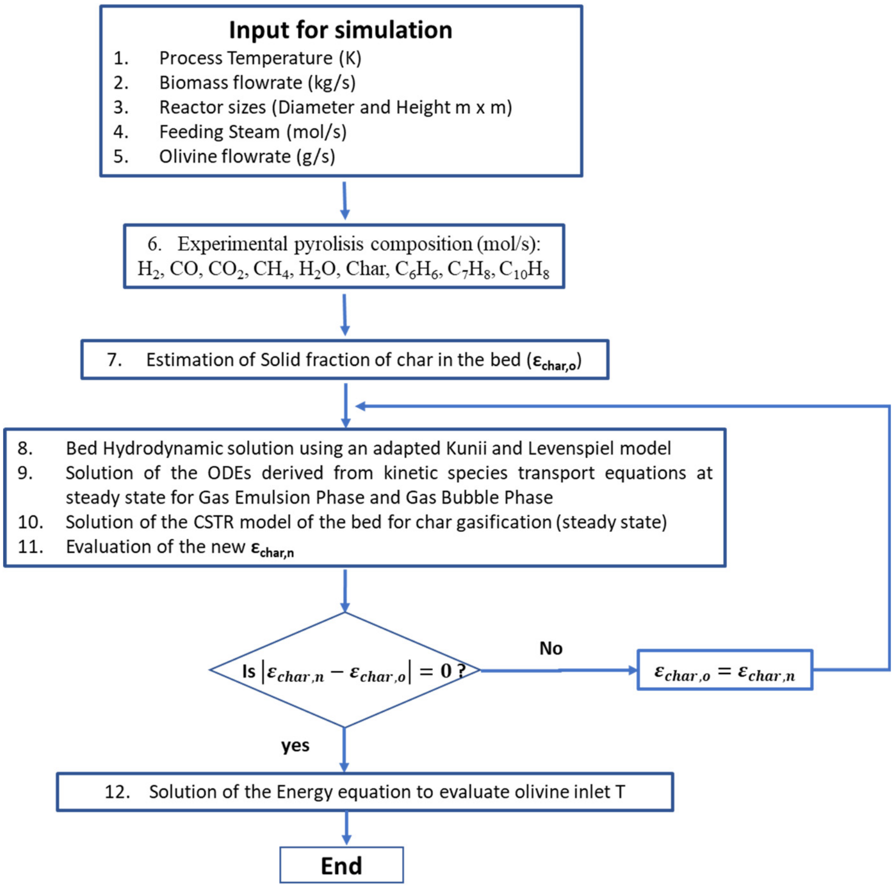


**Figure 2.** – Model algorithm flowchart developed by [69]**.**

The kin-semi approach helps simplifying the complexity of kinetic models by assuming local equilibrium for specific reactions and/or gasifier zones, while concentrations and temperatures of the other reactions and/or zones are kinetically controlled [71–73]. The most common choice for the kin-semi model is to consider homogenous gas-phase equilibrium of reacting components from the step of pyrolysis; the equilibrium compositions is computed through three equilibrium constants or by minimizing Gibbs free energy.

Then, the produced gas mixture is mixed with the gasifying agent and char and became the inlet of a kinetic module were the final gas composition is computed using kinetic models [74,75]. Kin-semi approach are easier to use compared with kin-total one, indeed it need less kinetic information and parameters, while kin-total model describes with kinetic reaction rates both the volatile and char gasification reactions. For this reason, kin-semi model provides more precises output results when the gas phase is near to the chemical equilibrium.

To come to the point, kinetic models have the potential to indicate which reaction route or pathway is responsible for the production of a particular gaseous product and are also able to give precise output results only if the reaction rates, kinetic constant and gasifier geometry are well-known. However, this means that these models are not flexible to use, since it must be developed precisely on a specific process with given conditions, and moreover it is also though to develop since the required input information is not easy to reach and scientific literature is still struggled to obtain them. On the other, it is possible to use simplified kinetic models providing quite accurate results for gas yield and gas composition. However, the simplified models are not able to identify which reaction route or pathway is responsible for the production of a particular gaseous product, so when such information is needed it is possible to overcome the limitation of the simplified models coupling them with a CFD model.

## 4. CFD models

CFD modeling is based on fluid mechanics principles and the use of numerical methods to solve the Navier-Stokes equations [76,77]. It is a powerful tool to simulate the interaction among fluids that have surfaces inside specific boundary conditions. In literature, there are several examples of CFD models to simulate biomass conversion processes such as thermochemical gasification [23,78,79] and pyrolysis [80,81]. CFD models are widely used to optimize the design of fluidized-bed reactor since they are able to predict inert material concentration of in-bed gasifier, emissions, operational parameters, fuel mixing efficiency, temperature profiles, heat flux, etc. [82,83].

It is possible to classify the CFD numerical approaches into three classes:

- Eulerian-Lagrangian Discrete Particle Model (DPM), which considers gas as continuous and particle as discrete phase. It is used where there are diluted particle conditions, such as freeboard of reactor. CFD DPM models consider particles trajectory in a continuous phase of fluid and take into account the interaction between particles by means of the heat and mass transfer as the governing phenomena [84,85]. The main advantage is the simple accounting of the particle size, allowing to track the changes in physic-chemical characteristics of the biomass particles during conversion along their path through the reactor.
- Eulerian-Eulerian Two Fluid Models (TFM), which is used to investigate both the gaseous and solid (particle) phase. Interaction of granular and continuous phase is considered via momentum transfer contribution based on drag models [86]. The CFD TFM approach has the disadvantages of high computational demand when a wide range of particle sizes have to be investigated because each size fraction of the distribution is accounted as a separated phase. Moreover, another drawback of these models is they are poor in recognizing the discrete character of the particle phase, so they are consequently poor in modeling flows of particles with a wide size and in tracking movement and conversion of single particles.
- Eulerian-Eulerian Discrete Element Model (DEM) within Eulerian-Lagrangian framework, which uses Eulerian method for gas phase and discrete element method for particle phase, tracking individually each particle and associating it with multiple physical (size, density, composition, and temperature) and thermo-chemical (reactive or inert) properties [87,88]. The main disadvantages of this method is the extremely small required time-steps, making this approach highly computationally demanding thus practically avoiding for design and optimization of industrial scale facilities [89].

In literature many studies [90–94] investigated coal gasification in fluidized-bed by means of CDF TFM approach. Those studies showed great potential in modelling gasification process, but at the same time the still need to be improved in describing chemical reactions, especially pyrolysis step.

Adnan et al. [95] made a comparison between CDF TFM and CFD DPM model, showing similar results for the fluid dynamics of a fluidized-bed gasifier. More in general, DPM models are more suitable for large-scale applications, where there is more independency from grids.

Ramos et al. [30] investigated results from a CFD TFM and CFD DEM model, concluding that the latter gives a more accurate prediction. However, when the prediction is given for a local discrete temperature value, TFM models were demonstrated to be more accurate compared with DEM model. Moreover, DEM approach requires about twice the time needed to execute TFM model.

## 5. Process modelling

Process modelling is a sequential approach in which each process is divided into unit operation and a series of equations are solved by means of kinetic or thermodynamic models. The most used software in this field is Aspen Plus [1,21,96]. Developed by Massachusetts Institute of Technology (MIT), Aspen Plus is a chemical engineering process optimization software that utilizes unit operation blocks, such as reactors, pumps, columns, heat exchangers, etc. Unit blocks are connected to each other through mass and energy streams, and this is represented in terms of a flowchart of the whole process. The software is based on a sub-sequential modular approach and the simulation calculations use the in-built physical properties database [48]. The main advantage of Aspen Plus is that each unit can be analyzed independently and the properties of the outlet stream of each unit depends only on its inlet stream properties. In order to evaluate all physical properties of conventional components in the gaseous phase of the gasification process, the most suitable description is provided by the Peng-Robinson equation of state, with the Boston-Mathias (PR-MB) modification [29], present in the default simulation setting of the Aspen Plus software. The evaluation of the enthalpy and density of the non-conventional components (biomass and ash), is obtained choosing the modules HCOALGEN and DCOALGEN, for enthalpy and density, respectively [29]; those settings are meant for the general coal model, but they are now used for other non-conventional feedstock too, despite the reported deviations in the estimated heating value of biomass [97].

The main merits of process modelling are [12,27,39]:

- the whole process is taken into account (e.g., separators, mixers, heat exchangers, pumps, etc.) and not only the reaction unit.
- overall energy duty of the process is estimated.
- optimization to improve CAPEX and OPEX are allowed.

The main assumptions for process modelling in Aspen Plus are:

- process is steady-state and isothermal [98];
- volatile products are H2, CO, CO2, CH4 and H2O [99];
- char is 100% carbon [100];
- all gas mixtures are supposed to behave as perfect gases;
- pressure drops and heat losses are neglected.

When process modelling is based on thermodynamic modelling, it is possible to obtain a QET approach also in process models, with the same benefits listed in paragraph 2. *Thermodynamic models.*

Several authors investigated biomass gasification process by means of Aspen Plus, demonstrating that it is a powerful tool to describe biomass gasification [12,101–104]. However, in literature there is a lack of scientific articles that point out the basic understanding of each model type and its applicability for designing a common biomass gasification process. In order to fill that gap, in Table 5 are shown the basic unit that make up the gasification model, considering both the thermodynamic equilibrium and the kinetic approach.

**Table 5.** – Basic blocks for gasification process in Aspen Plus.

| Aspen Plus Block Name | Description |
|---|---|
| | *Thermodynamic equilibrium approach* [53,104] |
| RYield<br><br> | Usually called DECOMP block (DECOMP stays for *decomposition*), it is a yield reactor which converts the non-conventional inlet stream of biomass into its conventional components (carbon, hydrogen, oxygen, sulphur, nitrogen, and ash) by specifying the yield distribution according to the biomass ultimate analysis. |

| | |
|---|---|
| RStoic<br>RStoic | Stoichiometric reactor, used to simulate the production of inorganic compounds. Indeed, DECOMP block creates N, Cl and S as elemental components that are known to produce mainly HCl, $NH_3$ and $H_2S$, and the results of the real fractional conversion model are closer to the experimental data than that of the chemical equilibrium. This is the reason why a stoichiometric reactor is needed to simulate the production of $H_2S$, $NH_3$ and HCl specifying the proper reactions and the fractional conversion for S, Cl2 and N. |
| RGibbs<br>RGibbs | Gibbs free energy reactor, which simulates drying, pyrolysis, partial oxidation, and gasification. It is possible to let the software individuate all the possible products without specifying any reactions or products by means of the option "*Calculate phase equilibrium and chemical equilibrium*". Otherwise, it is also possible using the QET approach of the specified reactions to set the syngas composition by specifying a temperature approach for individual reactions by means of the option "*Restrict chemical equilibrium – specify temperature approach or reaction extents*". |
| *Total kinetic approach* [105,106] | |
| RYield<br>RYield | Yield reactor represents the virtual reaction step that decomposes the biomass into its three principal biochemical building blocks: cellulose, hemicellulose, and lignin. This reaction step does not represent any part of the actual pyrolysis reaction mechanism but is necessary for the following interlinked reaction model. The yields are calculated iteratively by an embedded Excel worksheet which determines the cellulose, hemicellulose, and lignin composition of the biomass according to its elemental composition. |
| RCSTR or RBatch<br>RCSTR RBatch | In the second phase, a kinetic reaction model is implemented for the primary pyrolysis reactions. It is an interlinked model of individual decomposition reactions of cellulose, hemicellulose and lignin, according to [62,107]. The reactor type can be chosen according to the pyrolysis reactor that wants to be modelled. For fast pyrolysis, the RCStir reactor is used, while the RBatch-type reactor is more suitable for slow pyrolysis modelling. |
| RYield<br>RYield | The secondary vapor reactions at longer residence times are implemented in Aspen Plus as an embedded Excel sheet which determines the yields of the RYield type secondary reactions reactor. The complete methodology and the corresponding equations |

The units listed in Table 5 are the strictly required three units needed to develop a thermodynamic or kinetic process model by means of Aspen Plus software. Beyond the kinetic approach reported in Table 3, the semi-kinetic method using a DECOMP block (yield reactor) provide a simpler approach to convert the non-conventional inlet stream of biomass into its conventional components (carbon, hydrogen, oxygen, sulphur, nitrogen, and ash). The biomass ultimate analysis provides information to specify the yield distribution, the char gasification is performed in a CSTR introducing the reaction kinetics written through an external FORTRAN module [71] (see Figure 3). The separation column separates the volatile matter and solid matter, followed by a RGibbs reactor where the volatile combustion occurs, according to the hypothesis that reactions in gaseous phase occurs at Gibbs equilibrium. Moreover, the authors implemented hydrodynamic parameters to divide the gasifier in two parts: bed and freeboard, both modelled as CSTR reactors. Using FORTRAN code, each RCSTR is divided into a series of CSTR reactors with equal volume. The number of the elemental reactors depends on residence time, reactor dimensions, and operational conditions. Char gasification was performed in the RCSTR by means of kinetic reactions introduced through an external Fortran module. The model is used to predict the results of lab-scale gasification of pine with air and steam and gave results in good agreement with experimental data.

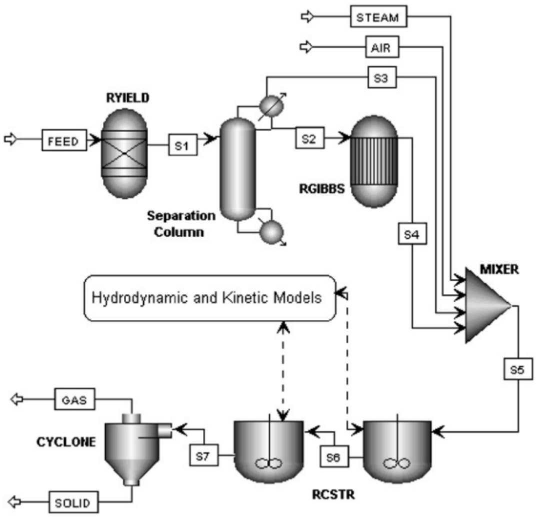


**Figure 3.** – A basic kinetic model for biomass gasification [71].

An example of basic equilibrium process model, developed by Marcantonio et al. [53] by means of Aspen Plus software, is shown in Figure 4. The modelling was done using the main units reported in Table 5 and adding a mixer to mix the biomass volatile stream with gasifying agent stream (oxygen, steam, air, or a mix of them). Moreover, the total amount of char was splitted according to literature experimental data and only 89% went to the gasifier while 11% was unreacted [104]. The simulative process was validated against experimental data showing good correlation between simulations and experiments. The maximum error for the concentration of hydrogen, the main product of the gasification process, was 16.3%.

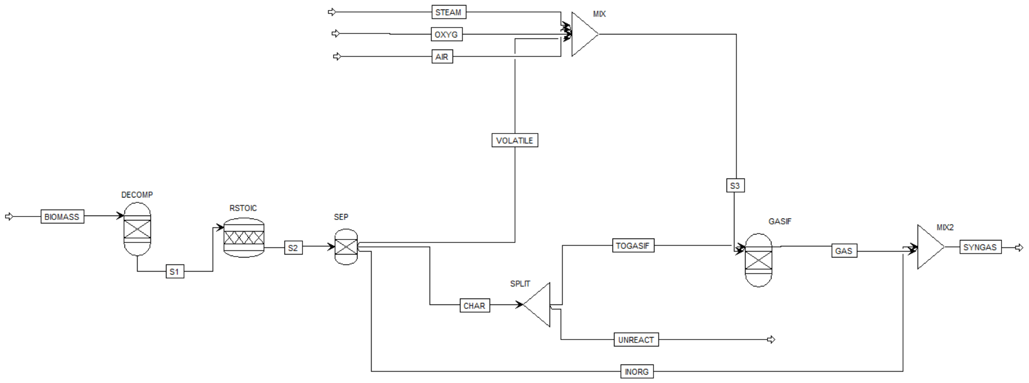


**Figure 4.** - A basic thermodynamic equilibrium model for biomass gasification [53].

Process models, as thermodynamic models, are not accurate at low temperature or at large scale. To overcome such limitations, some authors suggested to improve the equilibrium model with adjustable parameters and semi-empirical correlations [47].

## 6. Multivariate Data Analysis (MVDA) and Model Validation

In the ever-evolving fields of process and chemical engineering, managing and interpreting vast amounts of data is critical for optimizing processes, ensuring product quality, and making informed decisions [108,109]. In the area of biomass valorization and biorefinery processes, the process control is particularly challenging due to the high variability of biomass (feed) properties [110,111]. For instance, Williams et al. [110] reviewed the effect of biomass properties variability in different processes of energy conversion - fermentation, hydrothermal liquefaction, pyrolysis, and direct combustion - with a special focus on ligno-cellulosic feedstock. They underlined the relevance of some parameters, such as biomass moisture, in all process stages and on its performance, even hindering the large-scale use of biomass as carbon-neutral source for energy production.

Statistical methods can be used to manage the biomass variability [112]. Multivariate Data Analysis (MVDA) is a classical tool to extract meaningful insights from complex datasets, providing engineers with a deeper understanding of their systems and enabling them to enhance efficiency, reduce costs, and improve overall performance [109,113]. Multivariate Data Analysis (MVDA) focuses on uncovering the connections among variables by leveraging correlation patterns. In broader terms, MVDA enables the following [114]:

- Reducing the number of variables while maintaining the system's descriptive capacity.
- Grouping variables into categories.
- Utilizing correlations between variables to characterize system behavior.

The simplest MVDA tool relies on the Pearson correlation coefficient, which establishes direct correlations between pairs of variables. However, in complex systems, this approach may not yield a definitive response, as a high correlation coefficient (close to unity in absolute value) does not always indicate a genuine causal relationship between the two variables. For instance, such a correlation might be the result of a third variable's influence, which is independently highly correlated with both. Therefore, additional methods are necessary to elucidate the true interdependencies between variables.

Principal Component Analysis (PCA) [115] offers a solution by transforming the original variables dataset into a new set of orthogonal variables known as Principal Components (PC). Principal Components (PCs) are linear combinations of the initial dataset. Let X = { 〖x〗 _1 , 〖x〗 _2 ,..., 〖x〗 _m } represent the original dataset with m variables (LCA outputs), recorded on n samples (statistical units). PCA transforms X into a new set of variables, PC = {P 〖C〗 _1 ,P 〖C〗 _2 ,...,P 〖C〗 _k }, where $k \leq m$. PCs are mutually orthogonal and ordered based on the descending values of explained variance. Given the PC set, the loadings matrix L = { 〖λ〗 _((i,j)) } reports the correlation coefficient between the i-th original variable, 〖x〗 _(i ), and the j-th principal component P 〖C〗 _j, where each 〖λ〗 _((i,j)) represents a generic element in the matrix. Another tool of MVDA is the Canonical Correlation Analysis (CCA) [116]. CCA relies on initially dividing the entire dataset into two or more categories. Variables within each category are then combined linearly to generate k variables, known as Canonical Variables (CVs). The value of k corresponds to the minimum rank (number of variables) among all categories. The scores obtained through linear combinations aim to maximize the Pearson correlation coefficient between variables. As a result, CCA calculates the correlations between different classes (categories) of variables, effectively describing the system's behavior. Consequently, a high correlation coefficient between the first canonical variables of two categories indicates a strong interdependency between the variables in those respective categories. Similarly, in the loading's matrix L={ 〖λ〗 _((i,j)) }, the generic element 〖λ〗 _((i,j)) denotes the correlation between the i-th canonical variable of a given category and the j-th variable from the original dataset. The complexity of the gasification reactions produces a large number of variables required to describe the kinetic and thermodynamic properties of the reacting phases. MVDA is an elective tool for the analysis of the resulting data set; several works deal with the MVDA application to gasifiers, providing unique information for their optimization [105,117–124].

Gil et al. [125] adopted a multifaceted Multivariate Analysis of the data of gasification of ten different biomasses (almond shells, chestnut sawdust, torrefied chestnut sawdust, cocoa shells, grape pomace, olive stones, pine leaves, pine sawdust, torrefied pine sawdust and pine kernel shells). The experimental data were collected in a bubbling fluidized-bed gasifier under an air-steam atmosphere. The analysis was carried out on the variables of the gasification outlet streams and biomass properties. The analysis included different MVDA methods, including PCA: the ten different biomasses were classified into two groups according to their gasification products. The findings revealed that gasification of pine kernel shells, pine leaves, torrefied pine sawdust, olive stones, and pine sawdust resulted in substantial quantities of combustible gaseous products, including CO and CH. Additionally, their gasification exhibited high conversion rates and cold gas efficiency. Thus, it was inferred that C and H contents and the HHV of the biomass are the most important biomass properties for promoting the gas production, calorific value of the product gas, gasification conversion and energy efficiency. On the other hand, gasification of cocoa shells and grape pomace produced high $H_2$ concentration and $H_2$/CO molar ratio in the gas product, mainly due to the higher H/O ratio and $K_2O$ ash content of the biomass. Through a simple correlation analysis, the $H_2$ concentration in the product gas were found negatively correlated to the O and volatile matter contents of the biomass.

All in all, this study demonstrated the potentiality of the MVDA in analyzing the gasification data, so as to reach valuable insight about the influence of the biomass properties on the gasification results.

Similarly, Dellavedova et al. [121] analyzed biomass characterization, gasification process conditions and obtained syngas properties from literature data by means of Principal Component Analysis, showing again biomass can be characterized and classified on the basis of its properties; this study showed that the most important variables for this model are the equivalence ratio (ER, i.e. the actual air fuel ratio divided by the stoichiometric air fuel ratio), the steam to biomass ratio (SB, i.e. the weight ratio between the amount of vapor used in the process and the biomass treated), the high heating value HHV, the carbon content and temperature.

It was observed a strong direct correlation between SB and the syngas characteristics. On the other hand, a negative correlation was found between syngas features and ER.

These two models show the potentiality of the MVDA in providing a data-driven description of gasification processes and, more in general, of complex reacting systems where the detailed description of all reactions and the characterization of the reactants can be very challenging.

### *6.1. Black-box approaches*

Artificial Neural Networks models are inspired by natural neurons: they are composed of a wide number of strictly interconnected processing elements, called neurons or nodes, working all together at the same time to solve a given problem [126,127]. The nodes are organized in separated layers and interconnected with a given architecture. Each layer has a weight matrix, a bias vector, and an output vector [128].

This kind of model does not require physical description of the phenomena and is able to approximate arbitrary non-linear functions, that is why it was found a suitable approach to simulate and up-scale complex biomass gasification process [32].

Puig-Arnavat et al. [32] proposed a model to predict gas composition and gas yield from biomass gasification in a fluidized-bed gasifier. The model structure developed by the authors is shown in Figure 5.

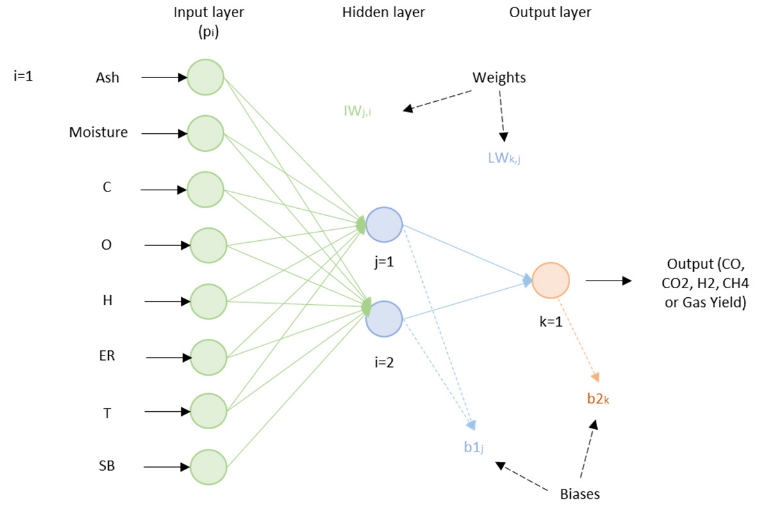


**Figure 5.** - ANN model structure to predict producer gas composition and gas yield from biomass gasification in a fluidized-bed gasifier [32].

Input and output variables used by Puig-Arnavat el al. [32] in their developed model are shown in Table 6.

**Table 6.** - Input and output variables in the ANN model of [32].

| | Range |
|---|---|
| *Input variables* | |
| Ash content of dry biomass (g/kg) | 5.5-11.0 |
| Moisture content of wet biomass (g/kg) | 62.8-25.0 |
| Carbon content of dry biomass (g/kg) | 458.9-505.4 |
| Oxygen content of dry biomass (g/kg) | 411.1-471.8 |
| Hydrogen content of dry biomass (g/kg) | 56.4-70.8 |
| Equivalence ratio (ER) | 0.19-0.47 |
| Gasification temperature (T) (°C) | 700-900 |
| Steam to dry biomass ratio (SB) (kg/kg) | 0-0.04 |
| *Output variables* | |
| Gas yield ($m^3$/kg) | 1.17-3.42 |
| $H_2$ volume fraction, dry basis (%) | 4.97-26.17 |
| CO volume fraction, dry basis (%) | 10-29.47 |
| $CO_2$ volume fraction, dry basis (%) | 9.82-18.60 |
| $CH_4$ volume fraction, dry basis (%) | 2.40-6.07 |

Results from the computational implementation of the ANN model were demonstrated to be in a good agreement with experiments.

Brown et al. [129] integrated an ANN approach with an equilibrium model for biomass gasification in a fluidized-bed. The authors performed a non-linear regression with ANN to compute temperature changes, fuel composition and operational variables. They demonstrated that the application of the ANN model improved the accuracy of the equilibrium model and, consequently, the quantity of required input data decreased.

Sreejith et al. [130] developed an ANN model to predict the output gas composition, the heat content, and the temperature profile in a fluidized-bed gasifier. Results obtained from the model were in good agreement with experimental data: at steam to biomass of 2.5 the simulative results of $H_2$ concentration was found to be 28.2 %, while the experimental result was 29.1 %.

Although the application of ANN method has yielded positive results in biomass gasification, it remains a scarcity of studies on the subject in the current literature. It is important to emphasize that ANN models are limited to the range of operating conditions used in their previous training study. To enhance the effectiveness of ANN predictions, expanding the experimental database with a broader range of operating conditions could be highly beneficial.

## 7. Discussion

Table 7 shows features, pros, and cons of the three modelling approaches discussed in the previous paragraphs.

**Table 7.** – Description of gasification modelling approaches.

| Approach | Features | Pros | Cons |
|---|---|---|---|
| Kinetic modelling | • Finite time or volume<br>• Explicitly accounts reactions kinetic, | • Accurate and detailed results even at low temperatures | • Computationally intensive<br>• Dependent on geometric parameters, so the |

| | | | |
|---|---|---|---|
| | system hydrodynamics and particle size distribution | • Able to predict the spatial distribution of products in the reactor | applicability is limited to the specific plant the model is built for<br>• Complete reaction mechanisms are often unknown or only partially known<br>• Sensitive to gas-solid contacting process |
| Thermodynamic modelling | • Assumption: the reactants react in a fully mixed condition for an infinite period of time<br>• Zero dimensional<br>• No chemical reactions or conversion mechanisms are needed<br>• Can be improved by using the coefficients for equilibrium constants or yields distribution | • Simple and easy to develop and implement<br>• Independent of gasifier design, so the applicability is not restricted, and the model is flexible for various feedstocks and process parameters<br>• Good prediction of maximum yield | • Equilibrium condition may not be reached in real cases, especially at low temperatures<br>• Over-under estimations of the amount of produced methane and char |
| CFD modelling | • Based on mass, momentum, and heat balances in presence of gasification reactions<br>• It applies the principles of fluid dynamics, numerical methods, and different algorithms to solve Navier-Stokes equations | • It produces temperature, pressure, and velocity profile across the reactor at a steady or transient state<br>• It can predict the flow pattern of reactants through the reactor together with the heat and mass transfer<br>• Accurate prediction of syngas yield | • Special software are often used for analysis, most of which are expensive<br>• Large number of experimental data are required<br>• Huge computational power is needed |
| MVA analysis | • It applies the statistics principles to understand and | • It is able to strongly reduce the number of | • It does not add any physical interpretations of correlation |

| | | | |
|---|---|---|---|
| | exploit the correlation patterns between gasification variables | variable to be monitored<br>• It provides prediction of both dynamic behavior and equilibrium conditions<br>• It requires a light computational burden | |
| Process Simulation modelling with commercial software | • The process is represented by means of single unit operations<br>• A series of equations are solved based on kinetic or equilibrium models. | • It takes into account the global process (i.e., exchangers, pumps, reactors, etc.) and not only the reaction step<br>• It allows the estimation of the overall energy duty and economics of the system | • Based on thermodynamic or kinetic modelling, it takes all their pros and cons. So, process simulation based on kinetic model is more complex to be developed, but more accurate, while when based on thermodynamic model is easier to develop but less trustable<br>• Purposed and expensive software is required, such as Aspen Plus, Chemcad, Aspen HYSYS, etc. |
| Artificial neural network modelling | • The model is trained on syngas composition and other experimental parameters | • It is able to represent non-linearity<br>• It accurately predicts experimental data used for the training set | • Required a wide dataset of experimental data |

The choice of the model depends on the objectives and the experimental information available.

A first raw prediction of gasification process performance is well given by thermodynamic modelling, easy to implement and flexible to use thanks to the independence of geometry. However, this approach does not give a realistic representation of the process at low temperature; and, moreover, it is not able to predict gasification process far from equilibrium (controlling kinetics and fluid dynamics phenomena, such as unconverted solid carbon and the formation of gaseous hydrocarbons).

Kinetic modelling gives a more accurate description of phenomena, but it requires a complete description of the reaction mechanisms, often unknown or only poorly known.

The main limitation of both kinetic and thermodynamic modelling in the investigation of gasification process is related to the interaction between solid and gas phases reactions, highly undescribed. In order to overcome this issue, CFD modelling is used to answer about interaction between solid and gas phases reactions involving a combined solution of mass, momentum, energy balances, including turbulence regimes and multiphase hydrodynamics. In turn, the CFD computational complexity is very high, so it is reasonably used if some reliable experimental data are known and used as reference. The black box approaches do not require any preliminary understanding and description of the physical phenomena.

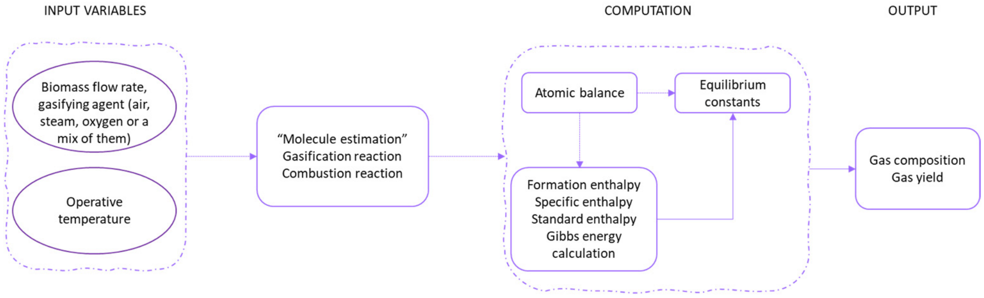
Compared with other modeling approaches, ANN copes non-linearity in a superior manner. Moreover, it does not require any mathematical or physical description of the phenomena and is able to adapt and learn, for those reasons ANN modelling makes the computational tool able to update itself. On the other hand, it works only within the specific range of operational conditions it was trained on.

Finally, MVA and more in general statistical methods provide insight about the correlation patterns of variables in gasification process: this information is particularly valuable in the case of systems controlled by a large number of variables, such as in the case of gasification. High correlation may infer a causal link between variables, worth to be explored through more detailed physical descriptions.

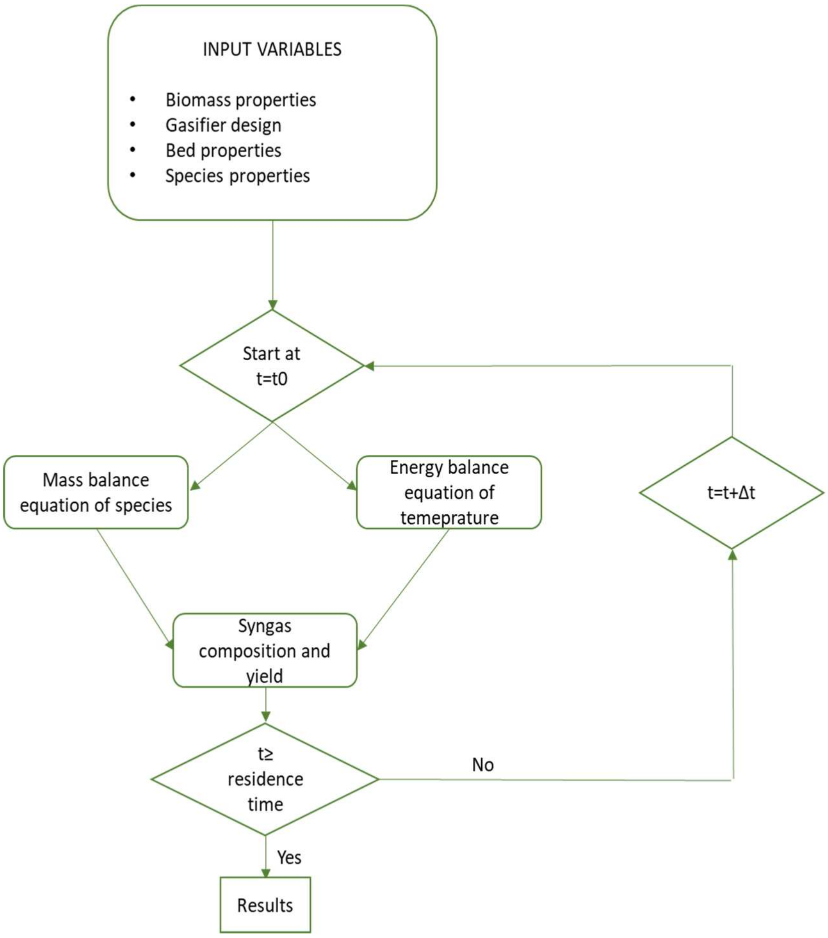
Additionally, the correlation analysis is the basis for the sensitivity analysis, which guides the optimization methods for process engineering.

In summary, it is possible to affirm that black-box models with some empirical constraints are enough for preliminary predictions (e.g., quasi-equilibrium model).

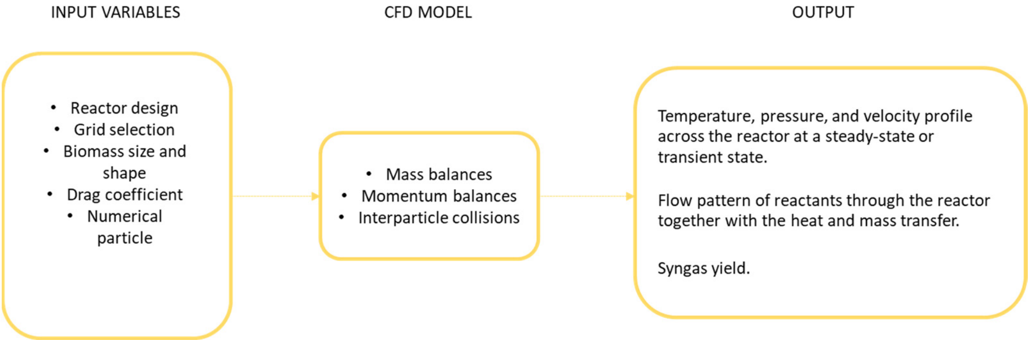
In Figure 6 (a)-(e) is briefly reported a schematic approach of each modelling.



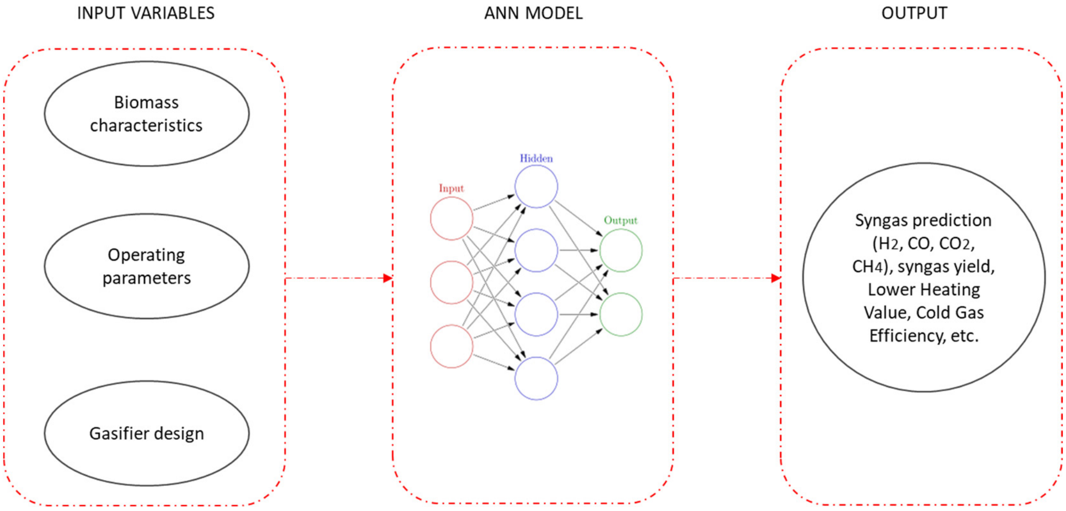
a)


INPUT VARIABLES
Biomass properties
Gasifier design
Bed properties
Species properties
Start at t=t0
Mass balance equation of species
Energy balance equation of temeprature
t=t+Δt
Syngas composition and yield
t≥ residence time
No
Yes
Results

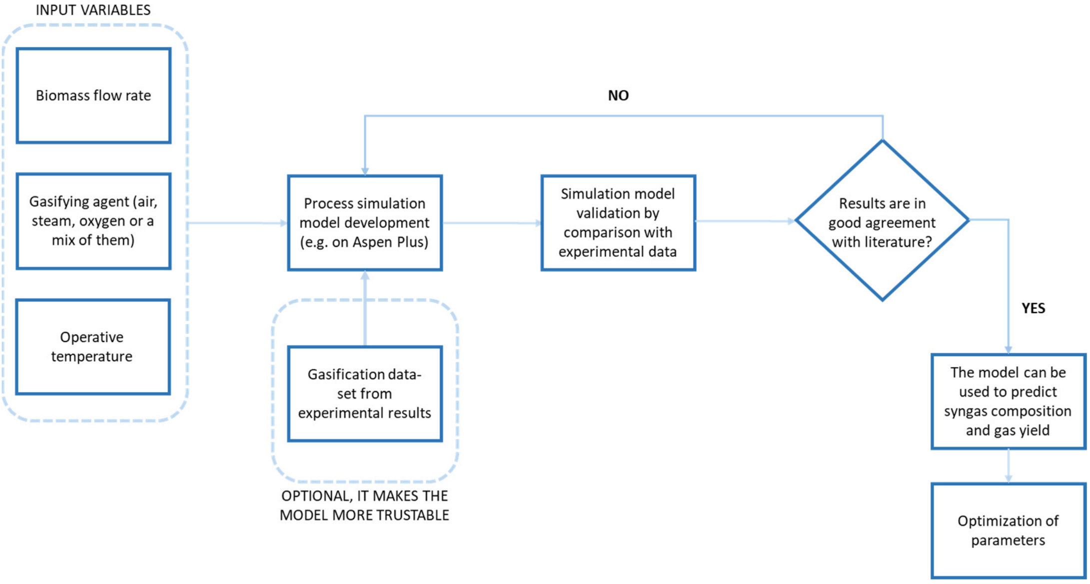
(b)


INPUT VARIABLES
CFD MODEL
OUTPUT
Reactor design
Grid selection
Biomass size and shape
Drag coefficient
Numerical particle
Mass balances
Momentum balances
Interparticle collisions
Temperature, pressure, and velocity profile across the reactor at a steady-state or transient state.
Flow pattern of reactants through the reactor together with the heat and mass transfer.
Syngas yield.

c)


INPUT VARIABLES
ANN MODEL
OUTPUT
Biomass characteristics
Operating parameters
Gasifier design
Input
Hidden
Output
Syngas prediction ($H_2$, CO, $CO_2$, $CH_4$), syngas yield, Lower Heating Value, Cold Gas Efficiency, etc.

(d)



(e)

**Figure 6.** – Basic input/output diagram of (a) thermodynamic equilibrium modelling, (b) kinetic modelling, (c) CFD modelling, (d) ANN modelling, (e) process modelling for biomass gasification process**.**

## 8. Conclusions

A review of the most important and recent gasification modelling approaches was presented. Even if the most appropriate choice of model depends on factors such as the scope of the simulation, the type of gasifier, the feedstock, and operational parameters several general observations can be made.

Equilibrium models are the simplest and easiest to develop and implement and have the advantage of being independent of gasifier design. They are able to predict the maximum achievable yield of a desired product from a reacting system and the gas composition. But they lost their accuracy at low temperature. Unlike equilibrium models, kinetic models predict the progress and product composition at different positions along a reactor, also providing a useful design aid in evaluating the possible limiting behavior of a system that is difficult or unsafe to reproduce experimentally. However, kinetic models are strictly dependent on the geometry, and they cannot be used for system different from the ones they are built for. CFD model results showed a good agreement with experimental data in many cases. However, CFD models are computationally intensive and still have many approximations as well as assumptions and there are many aspects of fluidized-bed reactor where the application of CFD modeling still needs to be explored (i.e., fuel combustion/gasification behavior during feeding, mixing of fuel in the dense bed, ash sintering, fuel characteristics, char reactivity, fragmentation of fuel in dense bed). In order to avoid complex processes and develop the simplest possible model that incorporates the principal gasification reactions and the gross physical characteristics of the reactor, process simulation models were developed, using the process simulator Aspen Plus. Process simulation models are able to give a first raw evaluation of the overall energy duty and economic of the system, bust they have all the pros and cons of the modelling they are based on (thermodynamic or kinetic modelling). ANN models offer some contribution to research in gasification process. Literature results show how the percentage composition of the main four gas species ($H_2$, CO, $CO_2$ and $CH_4$) in producer gas and producer gas yield for a fluidized-bed gasifier can be successfully predicted by applying a neural network. However, ANN models still need to be trained and improved, for this reason it is necessary to enlarge the literature database adding more experimental data. MVA analysis provides a good prediction of both dynamic behavior and equilibrium conditions, requiring a minimal computational burden, but it does not add any physical interpretation of the phenomena occurring.

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## Nomenclature

**Acronyms**

ANN Artificial Neural Network
CCA Canonical Correlation Analysis
CFD Computational Fluid Dynamics
CSTR Continuous-flow Stirred-Tank Reactor
DEM Discrete Element Method
DPM Discrete Particle Model
GMM Gibbs Free Energy Gradient Method Model
LHV Low Heating Value
MVDA Multivariate Data Analysis
QET Quasi-Equilibrium Temperature
PCA Principal Component Analysis
TFM Two Fluid Model

| Symbols | Unit | Description |
|---|---|---|
| $C_{p,i}$ | J/(mol·k) | Specific heat at constant pressure of the i-component |
| H | kJ/mol | Enthalpy |
| $\Delta H^0$ | kJ/mol | Enthalpy formation |
| G | kJ/mol | Gibbs free energy |
| $\Delta G^0$ | kJ/mol | Gibbs energy formation |
| $n_i$ | mol | Number of moles of the i-component |
| $n_T$ | mol | Total moles of produced gas |
| P | Pa | Pressure |
| $P_i$ | Pa | Partial pressure of i-component |
| $P_0$ | Pa | Operative pressure of the system |
| R | J/(mol·k) | Universal constant of gas |
| T | K | Temperature |

**Greek letters**

| | |
|---|---|
| $\alpha$ | Reaction coordinate of water gas shift reaction |
| $\beta$ | Reaction coordinate of steam reforming reaction |
| $\mu_i$ | Chemical potential |
| $\mu_i^0(T)$ | Standard chemical potential of the i-component |

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