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Modelling and analysis of an innovative CHP system based on biomass gasification, hot gas cleaning and conditioning and SOFC by means of Aspen Plus

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*I Know who I am,
and that's all that matters*

Abstract

In the last decades, global warming, climate change, national energy security and energy dependency issues have led to the need for an alternative to fossil fuels. In this delicate context, biomass gasification has been demonstrated to be a very useful technology to produce power and hydrogen. Nevertheless, in literature, there is a lack of a flexible and fast, but accurate, model of biomass gasification that can be used with all the combinations of oxidizing agents, taking into account both organic and inorganic contaminants and able to give results that are more realistic.

In order to do that, in the present thesis, a model of biomass gasification has been developed using the Chemical Engineering software Aspen Plus. The developed model is based on the Gibbs free energy minimization applying the restricted quasi-equilibrium approach via Data-Fit regression from experimental data. The simulation results obtained, considering different mixes of gasifying agents, were compared and validated against experimental data reported in literature for the most advanced fluidized bed technology. The maximum discrepancy value obtained for hydrogen, with respect to experimental data, is of 8% and all the other values reached by the developed simulations, considering both organic and inorganic compounds, are in good agreement with literature data. The gas yield reached by the developed simulation is in the range of 1.1-1.3 Nm³/kg.

An important aspect in the usage of producer gas is the removal of harmful contaminants from the raw syngas, since the contaminants present in the raw syngas can ruin the equipment of the plant by corrosion, catalyst poisoning, etc.. Thus, the second object of this study is the development of a simulation model for an innovative hot gas cleaning constituted by a combination of catalyst sorbents inside the gasification reactor, catalysts in the freeboard and subsequent sorbent reactors, which is coupled with the gasification model. The gas cleaning chain simulates the raw syngas clean-up for several organic and inorganic contaminants, i.e. toluene, benzene, naphthalene, hydrogen sulphide, hydrogen chloride and ammonia. The tar and inorganic contaminants final values achieved are under 1 g/Nm³ and 1 ppm respectively, that are the allowable level for the main applications (methanol synthesis, gas turbine, solid oxide fuel cell, etc.).

In order to trust the feasibility of the developed model, it was coupled:

- with the model of a Solid oxide fuel cells (SOFC), that have proved to be an excellent energy conversion device. The SOFC modelling was done without external subroutines, unlike most models in the literature, using only the existing ASPEN Plus blocks; making the model simpler and more reliable. The analysis indicate that there must be a trade-off between voltage, electrical efficiency and power with respect to current density and it's

preferable to stay at low steam to biomass ratio. The electrical efficiency achieved under the operating conditions is 57%, and its high value making these systems very attractive;

- with a 100 kWe micro Gas Turbine (mGT) and an Organic Rankin Cycle (ORC) unit, as the bottom cycle. The integrated system operates with higher net electric power than its nominal operation thanks to the bottom ORC unit and steam injection in the combustion chamber. However, results have shown that the overall electric efficiency is penalized slightly by adopting the wet cycle. The syngas-fuelled system, at its maximum electric power, produces the net power of 127.6 kWel with 23.6 % overall electric efficiency using 25 g/s steam injected into the combustion chamber. Moreover, results confirm the reduction of performance of the integrated system especially the overall electric efficiency when the mGT is fuelled with syngas instead of its nominal fuel, natural gas. Nevertheless, the produced thermal power in the condenser of the ORC unit is increased showing the ability of the integrated system to meet higher users' thermal demands.

Keywords: biomass gasification, quasi-equilibrium model, hot gas cleaning, SOFC, , Steam Injected micro Gas Turbine, Organic Rankine Cycle system.

List of publications (published during my PhD)

- V. Marcantonio, D. Monarca, A. Colantoni and M. Cecchini, 2019, “**Ultrasonic waves for materials evaluation in fatigue, thermal and corrosion damage: a review**”, Mech. Syst. Signal. Process., 120, pp. 32-.42, 10.1016/j.ymssp.2018.10.012;
- Villarini, M., Marcantonio, V., Colantoni, A., Bocci, E., 2019, “**Sensitivity Analysis of Different Parameters on the Performance of a CHP Internal Combustion Engine System Fed by a Biomass Waste Gasifier**”, Energies, 12(4), p. 688, <https://doi.org/10.3390/en12040688>;
- Marcantonio, V., De Falco, M., Capocelli, M., Bocci, E., Colantoni, A., and Villarini, M., 2019, “**Process Analysis of Hydrogen Production from Biomass Gasification in Fluidized Bed Reactor with Different Separation Systems,**” Int. J. Hydrogen Energy, <https://doi.org/10.1016/j.ijhydene.2019.02.121>
- Colantoni, A.; Villarini, M.; Marcantonio, V.; Gallucci, F.; Cecchini, M., 2019 **Performance Analysis of a Small-Scale ORC Trigeneration System Powered by the Combustion of Olive Pomace.** Energies 2019, 12, 2279.
- V. Marcantonio, E. Bocci, JP. Ouweltjes, L. Del Zotto, D. Monarca, 2020, “**Evaluation of sorbents for high temperature removal of tars, hydrogen sulphide, hydrogen chloride and ammonia from biomass-derived syngas by using Aspen Plus**”, International Journal of Hydrogen Energy 45 (11), 6651-6662
- R. Moradi, V. Marcantonio, L. Cioccolanti, E. Bocci, 2020, “**Integrating biomass gasification with a steam-injected micro gas turbine and an Organic Rankine Cycle unit for combined heat and power production**”, Energy Conversion and Management 205, 112464
- V. Marcantonio, E. Bocci, D. Monarca, 2020, **Development of a Chemical Quasi-Equilibrium Model of Biomass Waste Gasification in a Fluidized-Bed Reactor by**

Using Aspen Plus, Energies 13 (1), 53

- Mauro Villarini, Sara Rajabi Hamedani, Vera Marcantonio, Andrea Colantoni, Massimo Cecchini, Danilo Monarca, **Comparison of Environmental Impact of Two Different Bioelectricity Conversion Technologies by Means of LCA**, International Mid-Term Conference of the Italian Association of Agricultural Engineering 2019/9/12, 619-628
- Bocci, E.; Del Zotto, L.; Monforti Ferrario, A.; Marcantonio, V.; Di Calro, A.; Di Giuliano, A.; Savuto, E.; Barisano, D.; Mac Phail, S.; Della Pietra, M.; Pumiglia, D.; Cocchi, M.; Ouweltjes, J.P.; Wang, L.; Van Herle, J., **First results of the H2020-LC-SC3-RES-11 BLAZE project: Biomass Low cost Advanced Zero Emission small-to-medium scale integrated gasifier fuel cell combined heat and power plant**, Proceedings of EFC2019, 8th European Fuel Cell Technology & Applications Piero Lunghi Conference - EFC19, Napoli (Italy), 9-11 Dicembre 2019
- V. Marcantonio, A. Monforti Ferrario, A. Di Carlo, L. Del Zotto, D. Monarca, E. Bocci, 2020, **Biomass Steam Gasification: A Comparison of Syngas Composition between a 1-D MATLAB Kinetic Model and a 0-D Aspen Plus Quasi-Equilibrium Model**, Computation 8 (4), 86
- V. Marcantonio, D. Monarca, M. Villarini, L. Del Zotto, E. Bocci, 2020, **Biomass Steam Gasification, High-Temperature Gas Cleaning, and SOFC Model: A Parametric Analysis**, Energies 13(22), 5936
- A. Colantoni, E. Paris, L. Bianchini, V. Marcantonio, S. Ferri, M. Carnevale, A. Palma, V. Civitarese, F. Gallucci, 2021, **Spent coffee ground characterization, pelletization test and emissions assessment in the combustion process**, Scientific Reports 11 (5119)
- V. Marcantonio, E. Bocci, A. Di Carlo, D. Monarca, **Modelling of a chemical quasi-equilibrium system of fluidised-bed biomass gasifier multiphase reactor using Aspen Plus**, 11th International Symposium on Catalysis in Multiphase Reactors, AIDC 21-24 Marzo 2021

The present thesis is based on all these publications.

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1 Introduction

In the last decades, global warming, climate change, national energy security and energy dependency issues have led to the need for an alternative to fossil fuels. Every year a great amount of agro-industrial, municipal and forestry residues are treated as waste; instead, they can be recovered and used to produce thermal and electrical energy by biological or thermo-chemical conversion processes [1,2]. Biomass, the fourth largest source of energy in the world after oil, coal and natural gas, seems one of the most favorable renewable energy source to replace fossil fuels [3–5]. Biomass can be converted in various forms of energy by various processes, according to its characteristics. Biomass use is a carbon-free process since the producing CO₂ was previously captured by the plants. At present, biomass use in modern big plants (e.g., Integrated Gasification Combined Cycle, IGCC, for power or Biomass To Liquid plants) is the most cost-effective biomass use for power (efficiencies up to 45%) or biofuel (efficiency up to 80%) generation [6–11]. Analysis shows that every additional 1% in energy savings leads to a reduction of about 2.6% in gas imports [12]. The Renewable Energy Directive, 2009/28/EC, has driven a rapid deployment of renewable energy. In 2012, energy from renewable sources was estimated to have contributed 14.1% of EU final energy consumption meanwhile the EU target to 2040 is 50% of EU primary energy [13–15]. Contrary to biological methods, thermo-chemical ones are more viable allowing the treatment of a wide range of feedstock in shorter residence time [16,17]. Among thermo-chemical processes, biomass gasification is one of the most efficacious conversion technologies because of lower investment costs while maintaining the ability for high-rate fuel gas production [18,19]. This process utilizes oxidizing agents (oxygen, air, steam or a mix of them) at high temperature (in the range of 750-1000 °C) to produce a fuel gas, called syngas, mostly rich in hydrogen, carbon monoxide, carbon dioxide, methane and steam along with several unwanted by-products [16]. A good quality syngas is characterized by low level of N₂, high level of H₂, low level of contaminants and high heating values (LHV) [20,21]. Further studies have demonstrated that the fluidized-bed is a promising type of gasifier, which ensures high reaction rates and conversion efficiencies thanks to good mixing and gas-solid contact [22,23]. Process and system simulation models have obtained great interest in the prediction of performance, giving a good description of both chemical and physical phenomena occurring into the gasifier and allowing to assess the plant behavior with the purpose of optimizing the gasifier design and its operation with minimal temporal and costs [24]. Among the system simulators which can be used in simulating thermochemical plants, Aspen Plus represents one of the most powerful and versatile option[3,24,25]. 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. Each unit block is linked to another by material and energy streams to create a flow sheet for the whole process. The program is based on a sub-sequential modular approach and the simulation calculations use the in-built physical properties database [26]. Several authors investigated biomass-gasification process by using Aspen Plus. Different approaches can be used, among them kinetic and equilibrium models are the most used [25,27]. Kinetic models can be used to predict syngas yield, the products of syngas composition achieved by a gasifier after a finite time (or in a finite volume in a flowing medium), profile of temperature inside the reactor and all the gasifier performance for a stabilized operating condition and gasifier configuration [28,29]. In order to do that, kinetic models consider the kinetic of the gasification reactions and the hydrodynamics of the gasifier. Thus, these models contain parameters that can restrict their applicability to specific plants; moreover, increasing the complexity in the design of the gasifier, the complexity of the model increases since the model is based on reactor hydrodynamics. Anyway, in literature, there is a lack of a flexible and fast, but accurate, model of biomass gasification that can be used with all the combinations of oxidizing agents, taking into account both organic and inorganic contaminants and able to give results that are more realistic. So, the present thesis, want first to contribute in order to try to fill that lack.

A gasification process combined with the cogeneration of heat and power has been considered more and more important, especially as a consequence of the growing interest toward small sizes plant. Anyway, the cogeneration system has specifically requirements for contaminants level, in fact impurities contained in syngas can severally affect the equipment: tar are known for their toxic and carcinogenic properties, sulphur compounds are a well-known catalyst poison and are responsible for polluting the environment, chlorine compounds may cause corrosion of metal equipment, health problems and environmental issues, while ammonia compounds may act as a poison for catalyst and may produce NO_x [30–33]. Thus, the raw syngas has to be cleaned for contaminants before it's used in downstream applications aiming for fuel or heat and power production [34,35]. There are two main possibilities for gas cleaning [36,37]: low-temperature processes (e.g. an amine scrubber) or mid- to high-temperature cleaning processes (e.g. filter candle, sorbent reactor). Low temperature clean-up in amine scrubbers, by using chemical absorbers in the liquid state at a temperature lower than 50°C in counter-current with syngas with a temperature of 850°C (temperature of gasification), have several disadvantages: tar condensation may cause plugging and fouling of the condenser and downstream process piping, causing reduction of the efficiency of the power plant, because of inevitable consumption of water and production of a great amount of polluted water, with

subsequent cost for its purification [38,39]. In order to overcome the problems encountered in low-temperature clean-up, and since the syngas has a high temperature, it is most appropriate to carry out its cleaning also at increased temperature, in order to reach an optimum cycle efficiency and protect downstream equipment and catalysts [21,40]. So, new mid- (400-600 °C) to high-temperature (600-850 °C) syngas cleaning methods, firstly developed for fuel cell applications, offer potential economic advantages [21,36]. Treatments inside the gasifier (so-called primary methods) for tar removal have been widely studied and can be mainly divided into two applications: in-bed gasifier sorbent and catalytic filter candles. In-bed gasifier sorbents are a viable option to reduce tar compounds at the gasification temperature [41,42]; calcined dolomite is one of the best catalysts thanks to its low cost and wide availability and there are a lot of publications [43–45] that demonstrate its efficiency. Another primary method for hot gas cleaning and conditioning is represented by catalytic filter candles [46,47] that are inserted directly in the freeboard of the gasifier and have the advantage of operating at a temperature close to the gasification temperature. By means of the catalytic filter candle, tars can be converted by reforming reactions into syngas. Sorbent reactor for removing inorganic impurities can be considered the final step of the hot gas cleaning chain [48]. Several types of sorbents based on zinc, iron, copper, cerium, manganese, calcium, titanium have been developed over the last years and they are able to remove inorganic contaminants from syngas at mid- to high-temperature ranges [49–53]. The main criteria that these sorbents must satisfy are: high adsorption capacity for inorganic impurities in order to reduce both sorbent quantity and process equipment size, fast adsorption kinetics, high equilibrium constant, ability to tolerate high temperature, capacity of regeneration maintaining efficient sorption and multifunctional removal [36]. The Aspen Plus simulator has been demonstrated as a very powerful tool for chemical plant investigation. Up to now, most simulations using Aspen Plus have been focused on the gasification process with different biomass feedstocks, temperatures, oxidising agents, and steam to biomass (S/B) ratios in order to improve syngas composition and system efficiency. There are a few studies that have also considered the formation of tars and inorganic contaminants and, thus, the integration of gas cleaning steps. Detchusananard et al. [54] studied the integration and the optimization of a sorption enhanced gasification (SEG) of biomass combined with a solid oxide fuel cell (SOFC) and gas turbine for the production of power and heat from eucalyptus wood chips. For this purpose, they investigated the hot gas cleaning units, developing a CaO chemical looping that reduces the tar concentration (they have considered toluene, naphthalene, phenol and pyrene) increasing hydrogen, and introducing a ZnO sorbent reactor for the adsorption of H₂S. Puig-Gamero et al. [55] developed an Aspen Plus simulation for biomass

gasification coupled with hot gas cleaning based on dolomite to reduce tar (the only tar considered was benzene), and Cu/ZnO catalyst to remove H₂S.

So, the second aim of this thesis is to improve a reliable biomass gasification simulation, using Aspen Plus, that considers the removal of tars (toluene, naphthalene and benzene) and inorganic contaminants (H₂S, NH₃ and HCl) and to evaluate different configurations of hot gas cleaning chains for the raw syngas in order to obtain the maximum level of hydrogen, while respecting limits for contaminants after the raw syngas clean-up.

The contaminants limits were set on the SOFC applications, since the values are the same of the other most common cogeneration system: gas turbine application and methanol synthesis production.

So, the whole system made of gasification model, gas cleaning model and SOFC system was studied and an application with a gas turbine instead of a SOFC is also gave.

1.1 Aim

The aim of this study can be divided in four main points:

- 1) The first aim was to develop and to validate, against experimental data, a quasi-equilibrium model of air/steam/oxygen biomass-gasification that includes organic and inorganic products. In this way the model was able to predict syngas composition and contaminants;
- 2) The second aim was to investigate the difference in syngas composition by the comparison of the thermodynamic model developed with a kinetic one, in order to point out when it is better to use a thermodynamic model rather than a kinetic one;
- 3) The third aim was to add an innovative hot gas cleaning, constituted by a combination of catalyst sorbents inside the gasification reactor, catalysts in the freeboard and subsequent sorbent reactors, in order to reduce the level of both organic and inorganic contaminants under the limit level associated to SOFC applications (these values are the same of the other most common cogeneration system);
- 4) The fourth aim was the integration of the developed gasfier and gas cleaning model with SOFC, and then with a gas turbine and an ORC, in order to achieve higher conversion efficiencies and to reduce emissions in power systems.

The software used is the Chemical Engineering software Aspen Plus.

1.2 Outlines

The present thesis is divided as follow:

- Chapter 2 describes the biomass gasification process and how to model it, pointing out the difference between thermodynamic equilibrium model and kinetic model and between stoichiometric model and non-stoichiometric model;
- Chapter 3 briefly describes the SOFC system and how to model it coupled with a gasification system by means of Aspen Plus Software;
- Chapter 4 deeply describes the risks of contaminants in SOFC;
- Chapter 5 describes the gas cleaning technologies;
- Chapter 6 contains all the simulative test conducted;
- Chapter 7 presents the results and carries the discussion of the simulative models;
- Chapter 8 proposes another application of the developed model;
- Chapter 9 contains the conclusions.

2 Gasification process

Gasification is the transformation of solid or liquid feedstock into a gas called “syngas”. The syngas is applied as a chemical feedstock or is used directly as a fuel to produce heat, electricity, or both. The gasification process is made of the following steps: drying, pyrolysis, oxidation (combustion), reduction (char gasification), and cracking [56]. Usually, the moisture in the biomass feed is in the range 5-35%, which is lowered under 5% during drying step. In the pyrolysis stage, the biomass is heated from 200 up to 700 °C with limited oxygen or air. In this way, the volatile compounds in the biomass are vaporized, becoming syngas, that is mostly composed by hydrogen, carbon monoxide, carbon dioxide, methane, tar (heavier hydrocarbon), inorganic contaminants (mainly hydrogen sulphide, hydrogen chloride, ammonia, alkali metals, etc.) and steam [96]. Tar gases created during the pyrolysis stage undergo cracking in the gasification step, which produces a mixture of non-condensable gas, light hydrocarbons, and unconverted tar.

2.1 Gasification technologies for biomass

Gasification reactors can be categorized into two principal kind: fixed-bed gasifier and fluidized-bed gasifier.

2.1.1 Fixed-bed gasifier

Fixed-bed gasifier are reactors filled by solid fuel particles and they are divided in [57]:

- Updraft, when both the gasifying media and the gas rise;
- Downdraft when both the gasifying media and the gas descend;
- Cross-draft when both the gasifying media and the gas flow horizontally through the reactor.

The gasifying media may be air, steam, oxygen, or a mixture of them.

Fixed-bed gasifiers are characterized by two great advantages: they are cheaper than fluidized-bed reactors for small scale applications and they are able to produce a clean syngas with low dust and low tar content.

Anyway, fixed-bed gasifiers are affected by the disadvantage that they could give poorer heat transfer and temperature in homogeneity, and they do not scale up as well as fluidized-bed gasifiers.

Moreover, fixed-bed gasifiers usually need stricter feed specifications (such as a moisture content under 20% and a uniform particle size for the biomass, in order to avoid clogging and channeling)

2.1.2 Fluidized-bed gasifier

The fluidized-bed gasifier [57] is generally made by a cylindrical column which contains particles and through which fluid flows. The fluid, that could be gaseous or liquid, has a speed rate that is enough high to keep the particle in suspension inside the column. In this way, a wide surface area is providing for the fluid to make contact with, and this is the best advantage of fluidized-bed gasifier. Moreover, fluidized-bed reactors have higher heat and material transfer among gas and solid phases, are able to keep a homogeneous temperature range and are more flexible with the variations in fuel quality respect to fixed-bed.

The disadvantage of fluidized-bed gasifier is the higher production of dust and particulate in syngas, this means they need specific gas cleaning technologies downstream.

Fluidized-bed reactors are actually the most promising candidates for bio-fuel production plants.

2.2 Biomass gasification models

2.2.1 Thermodynamic equilibrium models vs kinetic models

Gasification, involving heterogeneous reactions, does not reach thermodynamic equilibrium (gasification reaction rates are not fast enough and residence times are not long enough for the equilibrium state to be reached) and so thermodynamic models with experimental corrections and kinetic models are mainly applied. Thermodynamic models, depending only on thermodynamic properties, i.e., temperature and pressure, are independent from reactor/particle typologies. On the other hand, kinetic models can be more realistic but are more complex, requiring the implementation of reaction kinetics, hydrodynamic equations.

Among the main advantageous of thermodynamic equilibrium models we can mention simple method, not required to take into account chemical reactions, flexible for various feedstock input and gasifiers, very good representation for high temperature (750-1000 °C), possibility to improve the model by means of yield distribution or equilibrium constant.

On the other hand, among the main disadvantageous of thermodynamic equilibrium models, there are: assumption that the components react in a fully mixed condition for an infinite time,

assumption that the reactor is zero dimensional, formation of tar is not considered, heat loss is not taken into account, not sully trustable for low temperature.

Among the main advantageous of kinetic models: finite time or finite volume, accurate results, good response at low temperature, consideration of both kinetic and hydrodynamic reactions inside the gasifier, useful for the evaluation of particle size impact, able to predict the product composition at different positions along a reactor.

Among the main disadvantageous of kinetic models: sensitive to the gas–solid contacting process, computationally intensive and limited applicability to various plants.

Aspen Plus and MATLAB represent two of the most used simulation tools for biomass gasification [18,56,58–60].

Aspen Plus, a chemical engineering process optimization software developed by Massachusetts Institute of Technology (MIT), uses unit operation blocks, such as reactors, columns, pumps, heat exchangers, etc. The unit blocks are connected by material and energy streams in a flow sheet workspace, utilizing sub-sequential modular approach and in-built physical property databases [26]. Although Aspen Plus presents thermodynamic (e.g., GIBBS, i.e., reactor based on the minimization of the free Gibbs energy) and kinetic (e.g., RYIELD, i.e., a simple kinetic reactor based on the reaction yield) reactors, it is typically used for thermodynamic simulation. In order to obtain results closer to experimental values also in thermodynamic equilibrium models, many authors adopt the *quasi-equilibrium approach*. This approach was introduced by Gumz [61] and it is based on the use of QET (Quasi-Equilibrium Temperature) at which the specific chemical reaction is assumed to reach equilibrium [22], instead of the actual operating temperature of the reactor. This approach does not require specific information regarding the dimensions, capacity and structure of the gasifier but only a set of experimental data. Doherty et al. [62] used the quasi-equilibrium approach based on Gibbs free energy minimization and the restricted equilibrium method to calibrate it against experimental data by the specification of a temperature approach for the gasification reactions. In this way the model was able to evaluate all the main gasification parameters (syngas composition, conversion efficiencies and heating values) and the effect of several variables (like gasification temperature and equivalence ratio (ER, defined as the ratio of the actual fuel/air ratio to the stoichiometric fuel/air ratio)) on such parameters. Arteaga-Pèrez et al. [63] implemented a quasi-equilibrium biomass gasification system and, by changing the gasifier temperature and the air factor, identified that the maximum yield of syngas is achieved at 850 °C and at air ER equal to 0.3. Mirmoshtaghi et al. [64] built a model for biomass gasification in a fluidized-bed gasifier with air oxidant with QET, predicting the volume fraction of the major components (hydrogen, carbon monoxide, carbon dioxide and methane) in product gas. The temperature range of the gasification

was set to 730–815 °C, with an ER between 0.22 and 0.53. Giuliano et al. [65] describes the biorefinery process by Aspen Plus, using corn stover as feedstock. Thus, Aspen Plus is widely applied to the biomass valorization processes but, up to now, no specific comparison has been done between the gas composition resulting from a Aspen plus thermodynamic (with experimental calibration) model and a kinetic model (normally done via MATLAB).

MATLAB is a customizable programming environment for numerical calculation and statistical analysis, created by MathWorks, which can be tailored for system analysis and simulation. Regarding biomass thermo-chemical conversion, many efforts have been made in order to obtain a modelling tool which predicts the effects of different operating conditions such as steam to biomass ratio (S/B) and reactor temperature. Inayat et al. [58] developed a simulation model in MATLAB in order to evaluate the influence of temperature and S/B ratio on biomass gasification for hydrogen production, based on kinetic models and preliminary results. Giuliano et al. [66] implemented a mathematical program consists in discrete optimization problems concerning a multiproduct lignocellulosic biorefinery using MATLAB. Hosseini et al. [67] developed a MATLAB model for air and steam biomass gasification. Lu et al. [68] also developed air-steam gasification in fluidized bed which accounts for both hydrodynamics and chemical kinetics. The customizable nature of MATLAB modelling is advantageous for simulating unconventional concepts and components, which lack of specific property libraries implemented in commercial software. In this sense, Di Carlo et al. [7] developed a 1-D semi-empirical model of a fluidized bed steam-steam/oxygen gasifier by combining governing hydrodynamic equations and kinetic reaction rates. The 1-D modelling approach allows to implement a resolution of the mass and energy balance along the axis of the reactor (considering uniform conditions in the cross section) obtaining the trend of syngas composition and characteristics along the axis of the reactor.

Thus, taking the set of values obtained at the exit section of the kinetic models as outlet composition, is possible to compare with thermodynamic.

Even though kinetic models are the only ones that can be used to design the reactor (encompassing time, dimensions, etc.), both models can be used to evaluate the steam gasification producer gas composition (i.e., gas flow and yield, gas composition, gasification efficiency, carbon and water conversion, etc.). In literature no specific comparison of the two models has been presented in order to understand the differences and so applicability of the model regarding the prediction of the steam gasification producer gas composition. Thermodynamic seems more suitable than kinetic ones due to their enhanced simplicity and generalized approach but they still can assess, also if they are improved with overall mass and energy balance of the plant and the composition of the main gases.

2.2.2 Stoichiometric vs non-stoichiometric models

As already told, the thermodynamic equilibrium model allows to predict the syngas composition based on the assumption that the reactants react in a fully mixed condition for an infinite time [69]. This model is independent of the gasifier design and so it may be more suitable for process studies on the influence of the different process parameters. Then, equilibrium models are divided into two sub-categories: stoichiometric models and non-stoichiometric ones. Stoichiometric models are based on equilibrium constants, so they need specific chemical reactions involved in the process. Non-stoichiometric models are based on minimization of the Gibbs free energy and they offer the advantage of not considering the chemical reactions. The equilibrium models have been used successfully by many researchers in modelling the gasification process in fluidized-bed gasifiers [18,19,70], allowing to evaluate the effect of temperature of reactor, equivalence ratio, steam to biomass ratio, moisture content of feedstock on the gasification process. An upgrade of the non-stoichiometric equilibrium model is the quasi-equilibrium approach, that is a compromise between equilibrium thermodynamic models and experimental ones, and does not require specific information on the dimensions, capacity and structure of the reactor. This approach gives a more accurate description of the syngas composition and is considered one of the most effective ways to simulate the performance of a gasifier [26]. In order to evaluate the QET, a Data-Fit made by experimental data can be used. Nevertheless, even if some QET models for fluidized bed gasifiers are present in literature, there is a lack of QET models that encompass air/steam/oxygen gasification and form inorganic (hydrogen sulphide, hydrogen chloride and ammonia) and organic (toluene, benzene and naphthalene) products. Arteaga-Pérez et al. [71] developed a quasi-equilibrium biomass gasification system by means of Aspen Plus. The gas composition out of the gasifier was corroborated with the experimental data in a bubble fluidized-bed pilot scale. The parameters varied during the case studies were the gasifier temperature and the air factor. It was found that the maximum yield of syngas is achieved at 850 °C and at air equivalent ratio (ER) equal to 0.3. The unique contaminant compound considered by Arteaga-Pérez et al. was naphthalene and the only oxidizing agent was air. Mirmoshtaghi et al. [64] developed a model for biomass gasification in a fluidized-bed gasifiers with QET by using Aspen Plus, predicting the content (volume fraction) of the four major components (H_2 , CO, CO_2 and CH_4) in product gas, and not considering any kind of contaminants. The oxidizing agent was only air. The temperature range of the gasification was set to 730-815 °C and the ER was between 0.22 and 0.53.

2.3 Biomass gasification coupled with other energy systems

In general, the produced syngas in the gasification process can be used in different energy systems to convert the potential chemical energy to electricity. Depending on the level of gas conditioning performed on the syngas, a viable solution is its use in external or internal combustion engines (ECEs or ICEs). In case of poor conditioning, tar and alkali compounds are expected to be present in the syngas, and consequently, externally-fired combustors are preferred. In this case, the syngas can be ignited at the same pressure of the gasifier (usually atmospheric pressure) and the fuel booster is not required. As a result, there is no necessity to cool down the syngas. Hence, the syngas can be directly injected into the combustion chamber at high temperatures resulting in a more efficient gasification process [72]. However, a high-temperature heat exchanger is required to transfer the heat from the combustion chamber to the working fluid of the power cycle [72], which represent a significant item of cost in small-scale plants.

Otherwise, if the syngas passes through adequate conditioning stages, it can be exploited directly in ICEs, or it can be injected into the combustor of the Gas Turbines (GTs). In these cases, the syngas must be pressurized to a pressure slightly higher than the pressure in the engine or in the combustion chamber, thus a fuel booster must be considered in the system.

One the most promising option is the use of SOFC technology which realizes a direct electro-chemical transformation of the syngas. Because of this direct energy conversion, SOFCs show higher electrical efficiencies compared to other conversion technologies, but the compatibility of the SOFC material with the typical contaminants of the syngas is still an issue. Biomass gasification coupled with SOFC gives an electrical efficiencies up to 60% [73]. The SOFC has become a very important energy application, due to its clean, greener and efficient operation [74,75].

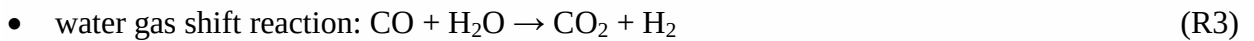
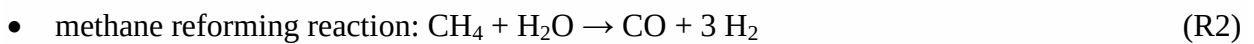
3 SOFC system

3.1 SOFC overview

A SOFC is a device that converts chemical energy contents in the fuel into electrical energy through a series of chemical and electrochemical reactions. The basic design of a SOFC consists of an anode, an oxide ion conducting electrolyte and a cathode, and in order to get a continuous reaction the electrons need to be passed through an electrical circuit. There are many different designs and configurations of SOFCs, depending on the materials used and the shape of the cell, resulting in different advantages and disadvantages for each cell. SOFC operates at high temperature between 600 and 1100 °C and, for this characteristic, can utilise a wide spectrum of fuels [76]. The oxidation energy of gaseous fuels is used by the SOFC in the anode in presence of an oxidant in the cathode, usually air, to produce electricity from hydrogen [77]. The most important advantages of the solid oxide fuel cells are: ability to consume CO as a fuel, high energy conversion efficiency thanks to the high rate of reaction kinetics, ability to incorporate bottom cycles to generate additional power from high temperature exhaust stream, no need for noble metal, ability to reform hydrocarbons, which determinates fuel flexibility. The main disadvantages include the thermal and mechanical stress of materials affected by high temperatures [78].

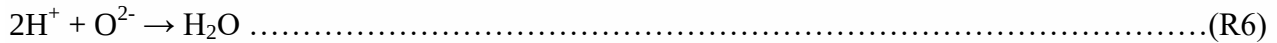
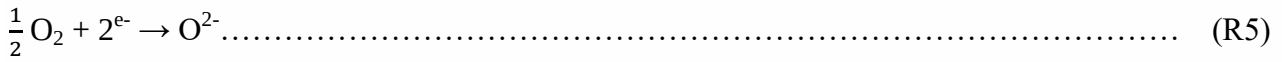
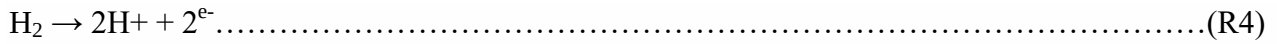
The stoichiometry of the electrochemical reaction is based on the reaction of hydrogen with oxygen, so the reaction R1 is the main reaction of the SOFC.

The reactions involved are:



So, in the methane reforming the CH_4 is converted in CO and H_2 , then in the water gas shift it is shifted in H_2 . For this reason, normally [20] the SOFC models consider only H_2 oxidation as electrochemical reaction, due to the fact that if there are CH_4 and CO as fuel these are mainly converted H_2 and CO_2 .

The fundamental reaction of the SOFC (R1) can be separated into three reactions (R4-R6):



Reaction R4 occurs mainly at the Triple Phase Boundary (TPB), where the fuel, catalyst and electrolyte meet. The fuel, in this case hydrogen, is oxidised into hydrogen ions and electrons. The electrons are then transferred through an electrical circuit to the cathode. The cathode is exposed to air containing oxygen, which is reduced by the electrons from the anode according to reaction R5. The formed oxide ions will be transported from the cathode, through the electrolyte until they reach the anode. The final reaction will occur at the anode, reaction R6, the hydrogen ions and the oxide ion is combined forming water and heat.

3.2 SOFC models coupled whit biomass gasification

In the last years many works were carried out to study the optimal operating conditions, the overall system performance, the limitations and the potentials of a variety of SOFC power plants integrated with biomass gasification systems. However, the current commercial process simulation software packages do not include built-it models for SOFC. In the literature, the most common SOFC system modelling approach is to integrate process simulators with a stack model in a programming language, such as Fortran, C++ and so on [79–81]. This way of working needs of a subroutine that has to include chemical/electrochemical reactions and heat and mass transfer, making this approach difficult to develop and use. The first one who proposed a method to avoid the creation of external subroutine to call in the process simulators was Zhang et al. [82], whom used existed ASPEN Plus unit operation blocks without linking with other software. The model proposed by Zhang has been developed based on literature descriptions of a tubular internal reforming SOFC technology from Siemens-Westinghouse, then was validated against experimental data. For the voltage calculations, Zhang used a semi-empirical correlation developed using a reference polarisation curve. The sensitivity analysis that was carried out shows that the cell net electrical efficiency reaches a maximum value of 52% when the utilization factor U_f is 85% and any increase of U_f will increase the CO_2 concentration at the anode outlet stream. Doherty et al [83], based on the previous work of Zhang et al., simulated a 100 kWe biomass power plant based on Gibbs free energy minimization and developed a SOFC model using ASPEN Plus blocks, performs heat and mass balances and considers ohmic, activation and concentration losses for the voltage calculation, estimating a net

electrical efficiency around 33%. The model proposed by Doherty et al. is capable of predicting system performance under various operating conditions and using diverse fuels. Starting from a gas composition Doherty et al. investigated the effects of varying the current density (j_{cell}), the steam to carbon ratio and the U_f on SOFC stack performance. The results indicate that there must be a compromise between voltage, efficiency and power with respect to j_{cell} and the stack should be operated at low steam to carbon ratio and high U_f . In both Zhang et al. and Doherty et al., the simulation of the SOFC on ASPEN Plus, considering a natural gas and syngas input respectively, has been modelled by the presence of an ejector, a pre-reformer besides an anode, a cathode, a burner and heaters.

4 The impact of contaminants on SOFC system

4.1 Exposure to tar

Besides particulates, tars belong to the major contaminants generated during the gasification of biomass. Their formation is connected to two distinct pathways: 1) the immediate liberation of aromatic structures in lignin devolatilization, and 2) the operation of hydrogen extraction and acetylene addition [84]. Kinoshita et al. [85], showed that tar yield and tar amount reduce with the increasing of the equivalence ratio due to the availability of oxygen to have a reaction thanks the presence of volatile compounds. Then, it was showed that tar yield is moderately affected by the residence time, instead of the tar composition, that has severely affected, in fact the quantities of the species that contain oxygen drop when the residence time increases, resulting in a decreasing yield of 1- and 2- ring compounds (excluding C_6H_6 and C_7H_8) while the amount of 3-ring and 4-ring species rise. The main species of tar that are produced during gasification process and that can stay as vaporized component in the hot syngas or as constant aerosol. Anyway, normally, they condense at lower temperatures.

Similar to lower hydrocarbons like alkanes, tars could decompose because of reforming reactions, cracking and solid carbon formation. Tar could be defined as an aggregation of hydrocarbons that could be condensed, mainly composed of aromatic compounds [86].

The definition of the European commission (DG XVII) and the US DoE specifies that tars are hydrocarbons with a molecular weight higher than benzene [87]. The typical composition of biomass tar is reported in Figure 1; it depends on several parameters like the genre of biomass feedstock, the variety of gasifier, the type of gasifying agent, and operating conditions.

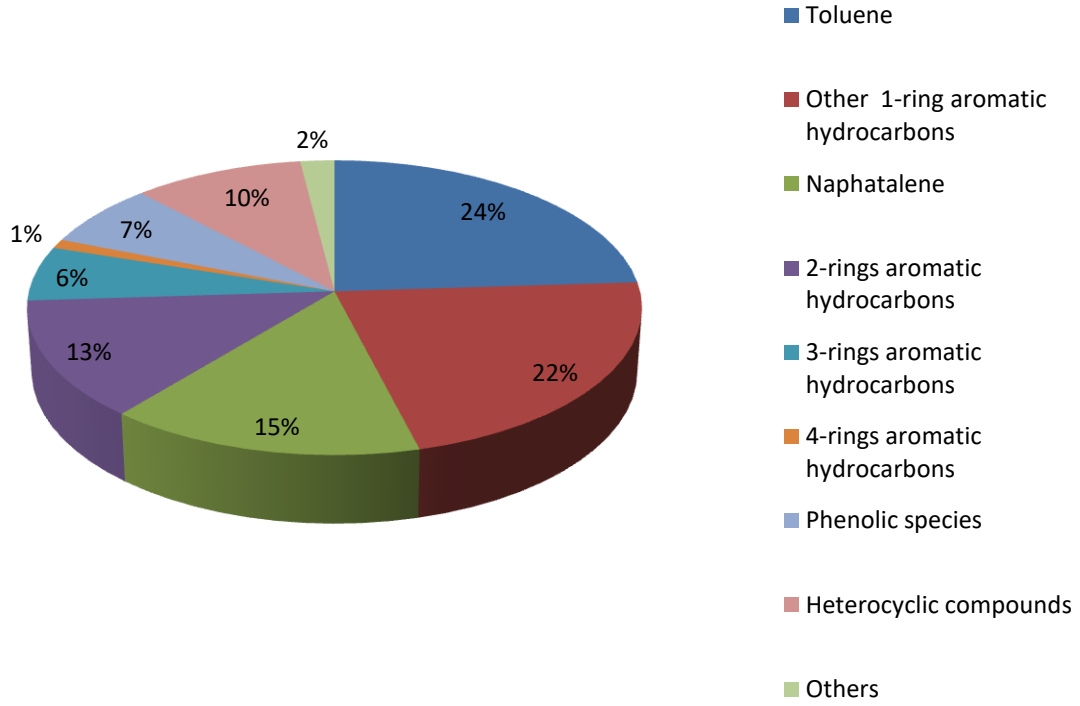
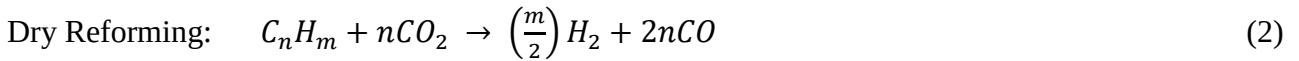
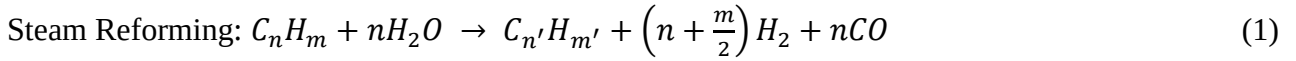


Figure 1 - Typical composition of biomass tar [88]

The successive overall reactions (1-6) are fundamental for the conversion of tar species [89–91].



Equations (1)-(6) are quite restricted by kinetics. The estimation of conversion kinetics for only one decomposition phenomenon is laborious, since the most part of the (1)-(6) happen at the same time or in consecution. So, it is usual to indicate kinetics for tar conversion by declaring an all-inclusive rate of tar departure, in which all reactions are combined [92]. Furthermore, it should be

noted that higher hydrocarbons, such as naphthalene, are higher adsorbed on the nickel catalyst than lower hydrocarbons. Hence, the reaction rate is perhaps best described as being proportional to the fraction of (the hydrocarbons that are adsorbed) the covered surface. Then, it is useful to use a kinetic approach such as the one proposed by Langmuir–Hinshelwood to describe the conversion rate of tars [93].

Regarding how SOFC operating condition can affect the rate of carbon deposition when utilising tar-laden bio-syngas, Singh et al. [94] presented an extensively thermodynamic analysis. That analysis arised from the Gibbs free energy method, which was used in a SOFC system feeding with a gas constituite by C_7H_8 , $C_{10}H_8$, $C_{16}H_{10}$ and C_6H_5OH ; moreover the equilibrium concentration of 32 different species was taken into account, including hydrogen, ammonia, carbon monoxide, carbon dioxide, methane, steam and solid carbon. They found that the stream betwee the cells keeps away from the probability of $C(s)$ production. With the increasing of steam in the fuel stream, $C(s)$ decreased until zero. The highest rate of $C(s)$ deposition is achieved at 600 °C, while it is lowest around 900 °C.

Mermelstein et al. [95] showed alike theoretical results, stating through a initial thermodynamic calculation that the reduction of carbon deposition is favourable by the current density and the S/C ratio > 1 due to the attendance of C_6H_6 in a H_2 - N_2 combination. Thermodynamic analysis reccomended that operation over 750 °C are unfavourable to carbon accumulation due to syngas having up to 15 g/Nm³ of C_6H_6 .

Catalytic studies by Coll et al. [96] show that for aromatic compounds the catalytic reactions conducing to coke production are faster than the rates of the carbon gasification and reforming reactions. The sequence of reactivity was $C_6H_6 = C_7H_8 > C_{14}H_{10} > C_{16}H_{10} = C_{10}H_8$ (see Figure 3). It was further shown that the mechanisms concerned in coke accumulation are catalytic, not pyrolytic, as the most favourable conditions were always at the lowest temperature. This indicates the high thermal stability of aromatic compounds. In Figure 3 are reported the conversions of the most common aromatic compounds at different S/C ratio against temperature.

Findings from Jess [97], who performed a catalytic study on the conversion of methane, benzene and naphthalene in H_2 - H_2O , further indicate that the conversion of C_6H_6 and CH_4 does not take place up to $C_{10}H_8$ was totally adsorbed. This is due to the high adsorbition of naphthalene on the nickel surface, reducing the conversion of the other hydrocarbons. Once naphthalene was converted, yielding CO, H_2 and benzene, the weakly adsorbing benzene and methane were converted in a non-competitive fashion.

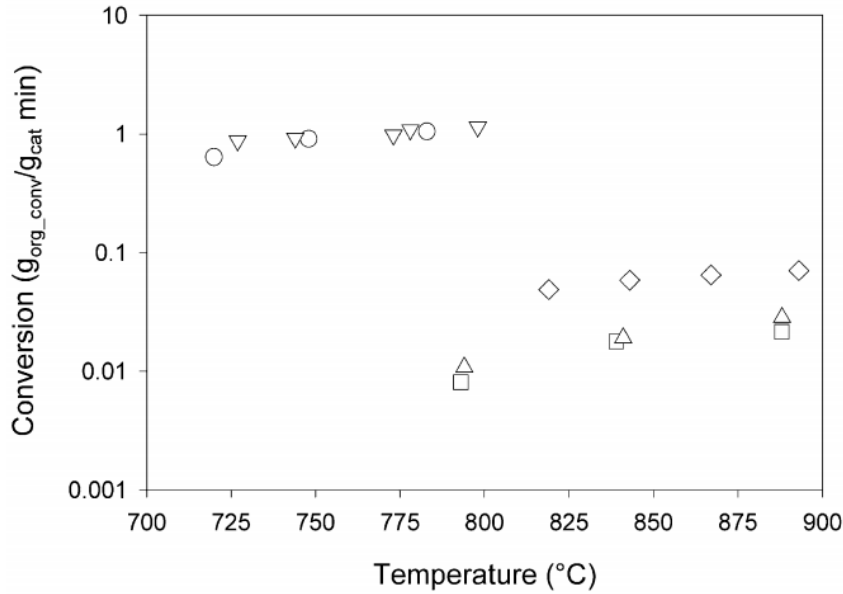


Figure 3 -. Comparison of conversion of C_7H_8 at S/C 3.8 (○), C_6H_6 at S/C 4.3 (▽), $C_{10}H_8$ at S/C 4.2 (□), $C_{14}H_{10}$ at S/C 12.2 (◇), and $C_{16}H_{10}$ at S/C 12.6 (△) vs T (°C) [96].

4.1.1 Impact of tars on Ni-Zirconia Anode

With respect to experimental results obtained on SOFCs with Ni-YSZ or Ni-ScSZ anode on tar-laden fuels, the following statements come from literature:

- Mermelstein et al. [95,98] report about the operation of Ni-YSZ at 775 °C with humidified hydrogen including 15 g/Nm³ benzene, toluene or a real tar mix. It concerned screen printed Ni-YSZ applied on a button cell.
- Hackett [99] et al. report about the operation of Ni-YSZ at 800 °C with a methane-free syngas and up to 150 ppm benzene. It concerned an anode-supported button cell.
- Lorente et al. [100,101] report about the operation of Ni-YSZ at 765 °C with humidified hydrogen including 15 g/Nm³ toluene or a real tar mix. It concerned screen printed Ni-YSZ applied on a button cell.
- Liu et al.[102] report about the operation of Ni-YSZ at 800 °C with syngas including 6.3 g/Nm³ toluene. It concerned screen printed Ni-YSZ applied on a button cell.
- Namioka et al. [103,104] reports about the operation of Ni-ScSZ at 800 °C with humidified hydrogen including toluene up to 50 g/Nm³. It concerned screen printed Ni-ScSZ applied on a button cell.
- Baldinelli et al. [105] reports about the operation of Ni-YSZ at 800 °C with syngas including 10 g/Nm³ toluene. It concerned an anode-supported button cell.

- Pumiglia et al. [106] reports about the operation of Ni-YSZ at 650 °C with syngas including up to 536 mg/Nm³ toluene. It concerned an anode-supported button cell.
- Geis et al. [107,108] and Jeong et al. [109] report about the operation of Ni-YSZ (both Ni-8SZ and Ni-3YSZ) at 700 °C with syngas including phenol up to 8 g/Nm³. In a recent publication, they also report about the operation of such cells under bio-syngas laden with a tar mix, both with and without the presence of sulphur. It concerned anode-supported cells with an active area of 81 cm².
- In a recent publication, Jeong et al. [110] also report about the operation of such cells under syngas including a tar mix, both with and without the presence of sulphur. It concerned a stack with anode-supported cells with an active area of 81 cm².
- Madi et al. [111] report about the operation of Ni-YSZ at 800 °C with humidified hydrogen or synthetic-bio-syngas including toluene up to 4350 ppm (22.8 g/Nm³). It concerned an anode-supported cell with an active area of 8 cm².
- Papurello et al. [112] reports about the operation of Ni-YSZ at 750 °C with humidified hydrogen or synthetic bio-syngas including naphthalene up to 10 ppm (52 mg/Nm³). It concerned a anode-supported button cell.

Futhermore, there is literature available on the operation of alternative SOFC anode materials, predominantly Ni-GCO, either mentioned in comparative studies or from independent investigations. From these publications it has become clear that Ni-GCO is a better option for operation under hydrocarbon fuels due to the higher opposition to carbon production. This is related to the properties of the catalyst support which, due to the improved oxygen ion mobility and electric conductivity, impedes the production of carbon accumulations in the anode microstructure. Only in cases where results obtained with Ni-GCO have led to improved understanding on the carbon deposition phenomena, which otherwise should have been kept unmentioned, they are reported below.

4.1.2 Impact of tar present in hydrogen

Mermelstein et al. [98] found from their investigations on benzene, toluene and a tar mix in dry hydrogen that toluene had the highest impact on the I-V behaviour of their SOFC with Ni-YSZ anode when the cells were operated at 765 °C, while benzene had the lowest impact. The anode exposed to 15 g/Nm³ tar mix had a performance between that of benzene and toluene. They further verified that thermal decomposition of benzene did not occur in their experimental set-up. The impedance spectra that they obtained are difficult to interpret due to large overlap in the polarization contributions and are therefore omitted here. Likely they were obtained at open circuit

conditions, where results may be very different from those obtained under load. SEM-EDX observations on the tested anodes and nickel catalyst samples exposed to the tars indicate that both pyrolytic carbon and whisker carbon had formed with both model tars and the real tar mix but there appears to be an inconsistency to which extent coking occurred. In work from a year later they showed that even when steam is added, Ni-YSZ anode is prone to carbon deposition at 765 °C upon exposure to 15 g/Nm³ benzene in H₂ up to a S/C ratio of 3 [95].

In a publication from Lorente et al [100], who followed the same experimental approach as Mermelstein, it was reported that nickel catalyst samples exposed for 30 minutes at 765 °C to 15 g/Nm³ toluene or real tar in hydrogen at a S/C ratio of 1 were both prone to carbon deposition, but toluene caused more carbon deposition than the real tar. TPO experiments revealed that the carbon resulting from real tar was more easily oxidised than carbon resulting from toluene. This seems to be in line with experiments from the same group reported a year later, where they exposed Ni-YSZ catalyst for 60 minutes at 765 °C to appr. 15 g/Nm³ tar fractions with different boiling points. It followed that carbon deposition was predominantly observed when the catalyst sample was exhibit to the lightest tar fraction, and that this carbon was also more graphitic in nature, and that these lighter tars also have a greater propensity to form larger polyaromatic species and eventually graphitic carbon on the anode material [101].

Namioka et al. have stated about the tolerance of Ni-YSZ anode at 800 °C and 0.5 A/cm² current density. Over a period of 10 h, cells were exposed to different toluene concentrations ranging from 0 to 50 g/Nm³ in hydrogen at a S/C ratio of 1. SEM-EDX observations after testing revealed no deposition of carbon until 10 g/Nm³ toluene, while carbon deposition took place at tar loads of 20 and 50 g/Nm³. In addition, it was observed that although the anode exposed to 10 g/Nm³ toluene did not reveal carbon deposits, it did show an alteration of its free surface, indicating nickel depletion due to nickel dusting [103]. In a publication from the same group one year later it followed that the problem of metal dusting was even more apparent than initially assumed. It was found that nickel dusting took place already at 3 g/Nm³ toluene at 800 °C, which hardly improved when the operating temperature reaches 900 °C. It also followed that the problem became more severe when the anode was kept at OCV while it became less apparent at increased S/C ratio, and thus that the severity of metal dusting was directly related to the amount of available steam [104].

Madi et al. [111] have reported about an anode-supported cell with Ni-YSZ anode at 750 °C and 0.25 A/cm² current density over a test period of 300 h under dry hydrogen including toluene up to a concentration of 7.3 g/Nm³. They measured an impact of toluene on the cell voltage at a concentration of 3.6 g/Nm³ and higher, with a dramatic drop in performance at the highest toluene

concentration. Post mortem analysis revealed that middle zones of the cell were harmed and that the nickel current collecting mesh had partially disintegrated, indicating metal dusting.

Papurello et al. [112] showed about the operation of an anode-supported cell with Ni-YSZ and 0.33 A/cm² current density over a test period of 7 h and measured no consequence on the cell voltage up to a naphthalene concentration of 33 ppm. Post mortem results are not available because the cell was later on operated under syngas.

4.1.3 Impact of tar present in syngas

Liu et al. [102] performed tests on an SOFC with Ni-YSZ anode at 800 °C with syngas including 2.5-10% steam and 6.3 g/Nm³ toluene. From thermodynamic calculations it followed that 2.5% steam would be sufficient to prevent carbon formation. Nevertheless the tests suffered from carbon deposits after operation for 5 h at 10% steam and 0.1 A/cm² current density. The interpretation of the impedance spectra obtained during the tests is confusing due to large overlap in the polarization contributions and is therefore omitted here.

Baldinelli et al. [105] performed tests on an anode-supported SOFC with Ni-YSZ anode at 800 °C and 0.25 A/cm² current density with syngas with up to 10 g/Nm³ toluene (total toluene exposure period 2 h). Thermodynamic calculations indicated carbon free conditions. Post mortem analysis revealed no carbon deposits, nor any other morphological changes compared with freshly reduced anode material.

In addition to their results obtained under tar laden hydrogen fuel, Madi et al. [111] disclaimed about the activity of an anode-supported cell at 750 °C and 0.25 A/cm² current density with syngas including up to 16 g/Nm³ toluene. At low toluene concentrations of 1.7 g/Nm³ and 5.6 g/Nm³, no impact on the cell voltage was observed, but degradation occurred at 13.1 and 16 g/Nm³. After the test, which altogether lasted 25 h, it was found that middle zone of the cell were harmed and that the nickel current collecting mesh had partially disintegrated, indicating metal dusting.

Papurello et al. [112] reported about the impact of toluene on the performance under syngas when using a Ni-YSZ anode-supported cell operated at 750 °C. Substantial degradation was observed at 24 ppm toluene, most clearly being reflected in the low frequency polarization contribution related to mass transport and gas diffusion, while there was hardly an effect at 4 ppm toluene.

Pumiglia et al. [106] carried out tests on an anode-supported SOFC with Ni-YSZ anode at 650 °C and 0.4 A/cm² with a methane-free bio-syngas and up to 0.53 g/Nm³ toluene over a period of 150 h. In comparison to a cell that was operated under tar-free syngas, which operated stably, the cell with the tar-laden syngas degraded substantially. Post mortem analysis indicated deposition of carbon

and, presumably as a result of pore clogging, local nickel oxidation. In addition, YSZ phase segregation and cracks were observed indication substantial mechanical stress during operation.

The impact of benzene was investigated by Hackett et al. [99]. From their tests, which were performed at 800 °C at 0.25 A/cm² current density with a methane-free syngas, it follows that benzene has no negative effect on the cell voltage up to a concentration of 150 ppm over a test period of 500 h. Post mortem analysis revealed no presence of carbon, but clear changes in the nickel microstructure which authors speculated to be related to the formation of an amorphous solution of carbon with nickel.

Geis et al. [107] performed tests on anode-supported cells with Ni-YSZ anode at 700 °C and 0.34 A/cm² with syngas and up to 1.4 g/Nm³ phenol. Total test time was 300 h. During the test, some degradation occurred but this could not unambiguously be correlated to phenol. Post mortem analysis revealed some carbon deposits between the anode-sided nickel current collecting mesh and the gold sensing wires, but no carbon was found on the anode itself. On the other hand, a spot was revealed on the anode surface where the anode microstructure had changed. Further results followed in a publication from the year 2018 by Geis et al. [108]. Here, a similar anode-supported cell was operated under comparable conditions but up to 8 g/Nm³ phenol. At 4 g/Nm³ phenol the cell started to exhibit voltage degradation, which became more aggravated when this was increased to 8 g/Nm³ phenol. It was further observed that addition of phenol to the fuel stream caused voltage increase. Increased pressure drop over the housing at higher phenol loads indicated issues with the flow, likely due to carbon build-up. In addition, the results from three tests with an anode-supported cell with Ni-3YSZ anode were tested under comparable conditions and phenol loads of 0, 1.5 and 2.0 g/Nm³, respectively. A voltage increase due to the presence of phenol was rarely observed during these tests. Voltage degradation was lower with the lower phenol load, but still higher than with clean syngas. After testing, the cells exposed to phenol indicated some carbon deposition adjacent to the anode nickel current collecting grid. In addition, substantial anode microstructural damage was observed in the fuel inlet manifold and in the fuel flow channels. Local detachment of the anode microstructure was observed, even for the lowest phenol concentration, which was speculated to be related with nickel dusting. All these degradation phenomena were not observed for the cell operated under clean syngas. Deeper microstructure analyses on these cells, in particular those that were operated with 2.0 and 8 g/Nm³ phenol, have been reported by Jeong et al. [109]. This made clear that the local detachment of the anode microstructure triggered the production of trenches in the anode support up to 150 microns deep, which appeared to be related to the local gas flow speed along the anode surface and thus the amount of tar that was in contact with the anode. In addition, a substantial increase of the substrate porosity and phase changes in the YSZ phase of the Ni-YSZ

microstructure were observed, as well as the deposition of carbon fibers in the anode microstructures, the latter being more pronounced for the cell operated with 8 g/Nm^3 phenol, and up to a distance of 100 microns from the anode surface. As even in the case of 8 g/Nm^3 the formation of carbon deposits was expected based on thermodynamic calculations, it was finally hypothesised that reforming of phenol is at least partially triggered by substantial local cooling of the involved anode particles which would lead to conditions where solid carbon is more stable. Although metal dusting did not cause substantial degradation during the test, it is considered by be detrimental during long-term operation as the phenol progressively attacks the anode microstructure. No further explanation was given on the pressure drop build-up reported by Geis et al. [108], and thus its exact cause is still an open question.

After finishing measurements under naphthalene-containing hydrogen gas, Papurello et al. investigated the impact of this tar component at $750 \text{ }^\circ\text{C}$ up to concentrations of 10 ppm in syngas. Introduction of naphthalene caused voltage loss at concentrations as low as 1 ppm but then stabilised. This behaviour was seen up to 5 ppm. Higher concentrations were observed to cause a progressive decline in cell voltage, indicating considerable voltage loss upon prolonged operation. After removing naphthalene from the gas stream, the voltage recovered partially. It was further observed that adding naphthalene induced a drop in cell temperature, which the authors assumed to be connected to inhibition of the exothermic reaction (7) but additional tests under different fuel compositions confirmed that also the methane reforming reaction was inhibited [112].

Further information about the influence of naphthalene on the operation of an anode-supported cell at $800 \text{ }^\circ\text{C}$ and 0.25 A/cm^2 current density comes from the investigations by Hacket et al. [99], who performed tests under methane-free syngas. Compared with operation under tar-free syngas, the initial performance under naphthalene-bearing fuel was lower (kept unaddressed by authors) while the degradation rate was higher. While at 100 ppm naphthalene the voltage decline was limited, a clear increase of the polarization resistance at 1000 Hz was observed. At 500 ppm naphthalene the voltage decline was larger, and in this case the impedance spectroscopy data indicated predominantly an increase of the polarization resistance at 100 Hz. As for the tests performed under benzene containing syngas, post mortem analysis revealed no presence of carbon, but clear changes in the nickel microstructure was observed after exposure to naphthalene, which the authors speculated to be related to the formation of an amorphous solution of carbon with nickel.

In a recent publication from Jeong et al. the results are reported from a 4-cell stack test with Ni-3YSZ anode supported cells at $715 \text{ }^\circ\text{C}$ connected to a gasifier with additional deep tar cleaning. While stable performance was obtained under tar free gasifier-gas the performance under tar-laden gas (total tar load 3.5 g/Nm^3) was problematic, the fuel cell experienced a rapid increase of the

pressure drop over a time period of 5 hours, while a comparative test where deep tar cleaning was maintained did not show this problem. Post mortem analysis revealed heavy carbon deposition on all four cells of the tar-exposed stack, in particular at the fuel inlet manifold, the cell inlet and on the nickel current collecting mesh at the fuel inlet, indicating that the tars were responsible for the carbon. SEM-EDX revealed that the carbon on the anode was mostly present as fibers, often with a nickel particle on the fiber tip, while carbon deposited on the nickel mesh was more disordered, indicating an impact of the nickel particle size on the carbon morphology. In addition, nickel coarsening was observed while the YSZ present in the anode microstructure remained intact [110].

4.2 Exposure to sulphur

Sulphur has long been known for its deleterious effects on the SOFC performance. The first who systematically investigated the impact of sulphur on the electrochemical performance were Matsuzaki et al [113]. In this work it was reported that the poisoning effect with 0.05 to 2 ppm H_2S in hydrogen fuel was dependent on temperature, the equilibrium partial pressure of sulphur and the total sulphur concentration in the fuel. The time needed to achieve a metastable cell voltage after sulphur poisoning was almost independent of the sulphide concentration and was found to increase with decreasing temperature. The authors suggested that the poisoning that they observed was most likely related to an adsorption effect. This was later confirmed by Rasmussen and Hagen [114], who carried out in-plane voltage measurements on an SOFC while sulphur was introduced in the fuel stream and upon recovery, and found that the sulphur poisoning effect was well related to the local gas composition which could only be explained by a fast chemisorption effect. Similar observations were made by Blesznowski et al [115].

It was further found that at increased sulphur concentration irreversible effects were also possible. In this case, the poisoning consisted of more than two steps, i.e. a reversible first voltage fall in a few minutes to a metastable cell voltage, along with progressive and irreversible voltage degradation, which was sometimes followed by fatal performance loss. Sasaki et al. [116] measured irreversible sulphur poisoning at 5 ppm H_2S in H_2 or $\text{H}_2\text{-CO}$, depending on temperature and fuel composition. Zha et al. [117] carried out tests with fuel including 2 and 50 ppm H_2S and measured an initially fast drop in cell performance that is succeeded by a moderate but constant drop in the next 120 h. The sulphur poisoning effect was accumulative and became more severe with increasing H_2S concentration. Hagen [118] found alike considerations. Norheim et al. [119] also measured a voltage decline upon introducing H_2S in the fuel stream but did not measure irreversible degradation, but this was perhaps related to the short exposure time.

Besides the poisoning effect of sulphur on the electrochemical oxidation of hydrogen, its impact on the activity of nickel for equation (7) and the direct steam reforming of hydrocarbons has been investigated. At 750 °C, the addition of 1 ppm H₂S to CO/H₂O fuel led to a complete poisoning of the WGS reaction and a subsequent lack of hydrogen for the electrochemical reaction, while the remaining CO was not electrochemically converted [120]. Kromp et al. [121] revealed that already at 0.5 ppm H₂S, the sulphur poisoned the WGS reaction which inhibited conversion of CO within the fuel. Hagen [118] experienced considerable voltage loss at 2 ppm H₂S in CO/H₂/H₂O fuel at 850 °C and 0.5 A/cm² current density and, after increasing to 8 ppm H₂S, only partial recovery. Similar observations were made at 750 °C and 0.25 A.cm⁻². As the observed tolerance to H₂S was lower than in the case of H₂-H₂O fuel, it was concluded that the WGS reaction was inhibited. Li et al. [122], who performed tests on Ni-YSZ anode operated at 800 °C in humidified syngas with and without the presence of 2 ppm H₂S, on the other hand, revealed by means of exhaust gas analysis, that CO was still converted in the presence of sulphur. Authors suggest that this could be related to the presence of steam. An impedance study by Weber et al. [123] on Ni-YSZ anode worked at 750 °C revealed exhaustive details on the influence of sulphur on the anode processes, from which it follows that sulphur poisoning in H₂/H₂O mixture causes an increase of the polarization contributions at appr. 3 kHz and 100 Hz, which the authors relate to poisoning of active triple phase boundaries in the electrochemically active part of the anode, while poisoning in the presence of methane-free syngas additionally causes an increase of the polarization contributions at 10 Hz and 1 Hz, the latter of which is ascribed to CO/CO₂ diffusion, and thus indicating inhibition of the WGS reaction. Confronting the time-related properties of the polarization opposition of 2 type of anode supported cells, it was further demonstrated that the collected amount of hydrogen sulphide separated through available Ni-surface determine the onset of the degradation.

The first indications that the impact of sulphur impacts the reforming of CH₄ were reported by Bartholomew et al. [124]. Similar effects were reported by Rostrup-Nielsen [125], Smith [126], Hagen et al. [118] and Li et al. [122]. Hagen et al. [118] showed that in the presence of significant amounts of CH₄, the Ni-YSZ anode is severely poisoned at concentrations of 2 ppm H₂S at 850 °C, experiencing a partly irreversible loss because of the losing of percolation of Ni particles close the electrolyte. Further mechanistic explanations on how sulphur interacts with nickel in relation to methane reforming can be found in a paper from Kuhn et al. [127].

The most likely reason behind the dramatic impact of sulphur on the catalytic activity of nickel at low sulphur concentrations appears to be the isosteric heat of adsorption for H₂S on nickel, which esteem is quite higher respect to the heat of formation for bulk nickel sulphide. In other words: the low sticking effect of H₂S on nickel allows the H₂S to quickly reach the anode/electrolyte interface,

where it will adsorb on nickel, hinder the adsorption of other active species and thereby the electrochemical oxidation of hydrogen [128]. Hansen [129] was the first to relate the sulphur coverage of nickel with the impact of sulphur on the electrochemical performance. He did this by using a Temkin isotherm, by which the sulphur coverage was successfully related to the performance drop for Ni-YSZ anodes reported in previous literature.

The irreversible performance drop caused by sulphur was less easy to explain. Some research groups associated it with the agglomeration of Ni particles due to the formation of nickel sulphides [116,117,130–132]. Alternatively, it has been proposed that the adsorbed sulphur species could lead to surface reconstruction of the nickel particles without the formation of secondary phases [114]. Such an effect is looked forward to be barely faster than the surface adsorption process and could produce a quite slower degradation in fuel cell performance by modifying the exposed crystal planes to less active ones [117]. The answer seems to follow from work by Li et al. [133], who exposed Ni-YSZ anode at 800 °C to both dry and humidified hydrogen fuel along with 0.2% H₂S. They found that Ni-YSZ anode operated in dry conditions caused the formation of small nickel sulphide dots on the nickel particles, whereas in presence of 3-10% steam, which alleviated the poisoning effect, these nickel sulphide dots were less clearly visible. The trigger for alteration of the anode microstructure due to sintering, which might be more detrimental than dissolution of sulphur in the nickel bulk, was later suggested to be the result of combined attack of the nickel particles by sulphur and oxygen, the latter of which being the result of high anode overpotential [134].

In addition, it might be that the nature of the oxide that is mixed with nickel to form the anode cermet is important [116]. It is assumed that oxygen spillover from the oxide to the nickel helps to prevent permanent nickel deactivation. Such an effect would become more pronounced as the oxygen ion conductivity of the oxide increases or when the physical contact between the cermet particles becomes more intimate.

It has further been proposed that the presence of sulphur may reduce the risk of coking. Either because sulphur preferentially binds to the nickel sites that are most active for coke formation and steam reforming which leaves only the less active (terrace) sites available for reforming, and these are less prone to coking, or by incorporation of sulphur in the nickel lattice [127]. The downside of all this is that the sulphur potentially deactivates the nickel sites for the electrochemical oxidation of hydrogen and up to now, there is no indication that this can be selectively prevented.

4.3 Exposure to halogens

Chlorine is typically present in the form of HCl in bio-syngas. Li et al. [135] studied, in 2 experiments of 60 minutes, the impact of 8 ppmv of HCl at 850 °C in hydrogen, and then the impact adding 2 ppmv and reducing temperature of 100 °C respect the input date of the first test, and found no observable effect. Blesznowski et al. [115] found that 3 ppm HCl in the supply did not lead to reduction for 2 days experiments, instead 10 ppmv of hydrogen chloride in the supply produced an amendable voltage fall of 10 mV during a 67 h test. . Encouraging results also from Bao et al. [136] and Buchinger et al. [137], who found no observable degradation because of the existence of 40 and 47 ppm of hydrogen chloride, respectively. Marina et al. [138] tested their Ni-YSZ anodes along with 800 ppm HCl and measured a recoverable voltage loss. Kuramoto et al. [139] found that feeding syngas (H₂=70.9 vol%; N₂=23.6 vol%; H₂O=5.5 vol%) with the presence of 10 ppmv HCl does not affect Ni-YSZ cells worked at 900 °C. Instead, Madi et al. [140] revealed quite serious reduction when the SOFC was supplied by hydrogen instead of syngas and they motivated the fact by the diminution in hydrogen chloride elimination thanks to aggressive CO adsorption and oxidation. It was showed a reduction of 3% per 60000 minutes from 10 ppmv of hydrogen chloride in hydrogen.

The mechanism of poisoning by chlorine is proposed to involve adsorption of chlorine on the nickel superficial area, but information about the long-term stability is limited, and thus calls for further investigation.

4.4 Compendium of tolerance level of contaminants compound for SOFC anode and average levels of contaminants in biomass derived syngas

In the literature there is a small amount of published works concerning the tolerance limits of organic and inorganic contaminants for SOFC technology and due to this lack it is not possible to define the exact value of tolerance limits. Referred to the most recent available data, the probable tolerance limits for SOFC anode, at the common operative temperature of 750 °C, are reported in Table 1, in which have been proposed the most stringent limits.

Table 1 - Most probable tolerance limits of organic and inorganic contaminants for SOFC at 750 °C[141–143]

Tar	<10 ^a ppmv
-----	-----------------------

H ₂ S	<1 ppmv
HCl	<1 ppmv
Alkali	<1 ppmv

Then, knowing the tolerance limits of contaminants for SOFC applications, it has to be clear the average composition of syngas. For this purpose, in Figure 4 and in Figure 5 has been reported respectively the main components and the contaminant levels experimentally obtained by the BFB steam gasifier in Güssing [144], that worked at 850 °C and 1 bar at S/B ratio equal to 0.6, for a wide variety of biomass inlet.

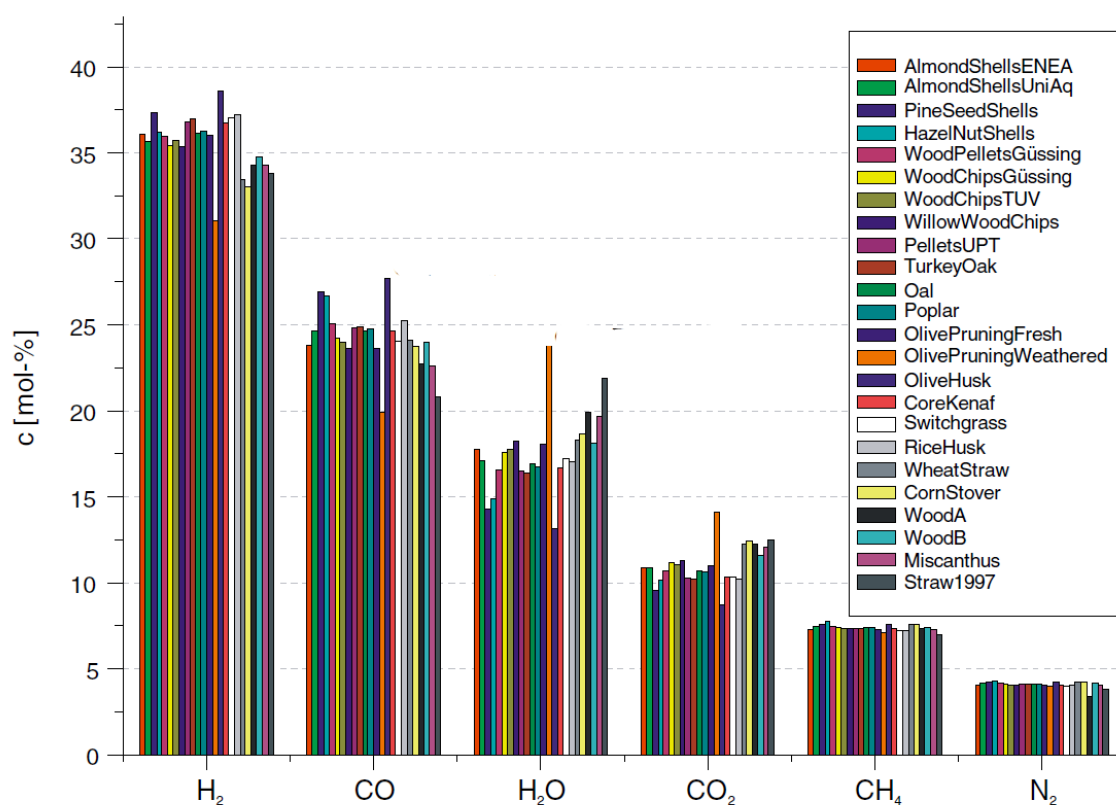


Figure 4 – Prevalent components in the syngas obtained by “Güssing” gasifier considering different biomass sources [145].

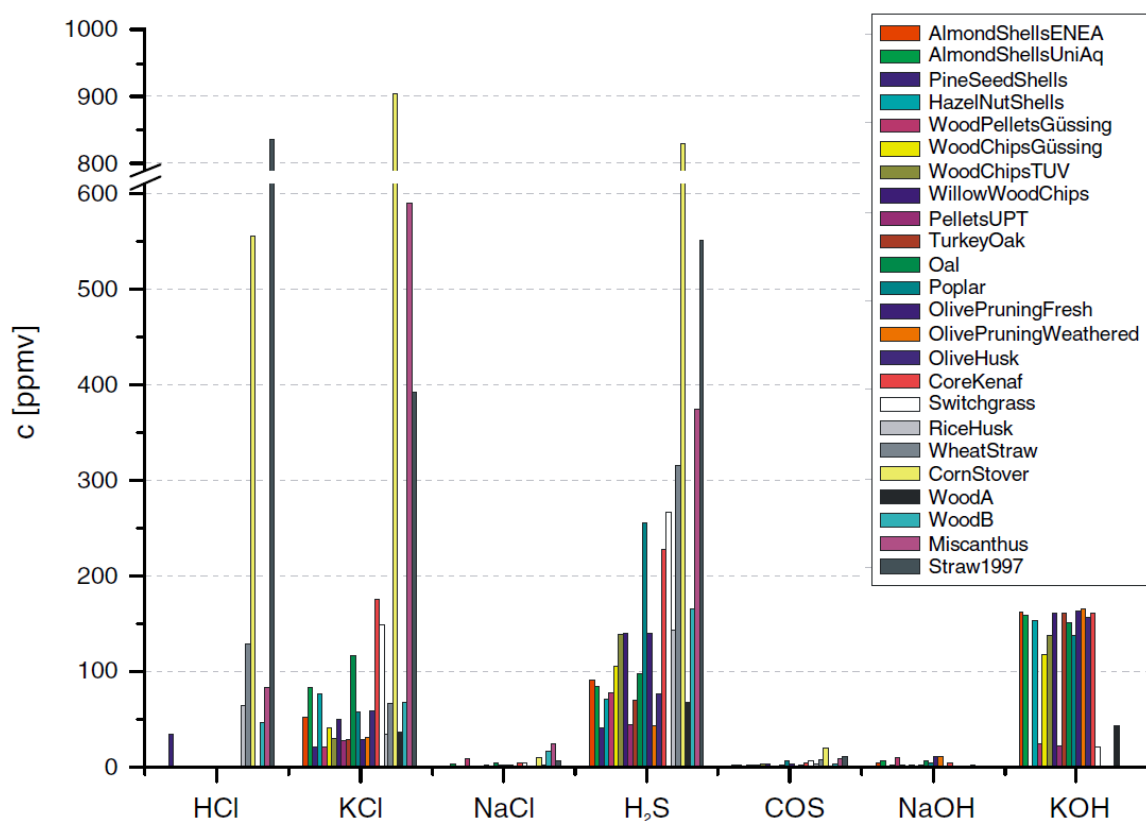


Figure 5 - Predicted inorganic contaminants levels in the “Güssing” gasifier [145].

Considering the previous results reported by Stemmler et al [145], the representative contaminant for halides can be considered HCl, the representative contaminant for sulphur compounds can be considered H₂S and the representative contaminants for alkali can be considered KCl and KOH mainly.

Instead, the average amount of tar in the syngas out of a BFB gasifier is reported in Table 2.

Table 2 - Usual tar levels out of a BFB gasifier, according to different operational conditions.

Biomass Feedstock	Gasification Agent	Bed Material	Gasification Temperature (°C)	Tar Content (g/Nm ³)	Reference
Pine wood chips	Air	Silica sand	780-830	18.0	[146]
Pine wood chips	Steam	Silica sand	750-780	53.0	[146]
Pine wood	Steam/Oxygen	Silica sand	785-830	24.0	[146]

chips					
Forestry residues	Air	n.a.	700-900	3.0	[147]
Pine wood chips	Air	Silica sand + dolomite	700-850	2.0	[148]
Pine wood chips	Steam/Oxygen	Silica sand	780-890	5.0	[149]
Spruce wood pellet	Air/Steam	Quartz, Olivine, Dolomite	780	7.6	[149]
Radiata Pine	Steam	Co/MgO	600	8.4	[150]
Pine wood chips	Steam/Oxygen	Calcined Dolomite	795-830	2.5	[45]
Pine sawdust	Air	Calcined Dolomite	800	13.9	[151]
Bagasse	Air	n.a.	800	14.8	[152]
Wood sawdust	Air	Silica sand	750	0.010	[152]
Almond shell	Steam	Olivine, sand, dolomite	700	6.5	[42]
Almond shell	Steam	Olivine, sand, dolomite	820	1.3	[42]
Pine sawdust	Air	Silica sand	790-810	10.0	[153]
Pine sawdust	Steam	Silica sand + CaO, MgO	780	40.0	[154]
Sawdust	Air	n.a.	780	2.0	[155]

Sawdust	Air	n.a.	857	0.3	[155]
Rice husk	Air	n.a.	750	6.0	[155]
Rice husk	Air	n.a.	940	0.8	[155]

5 Gas cleaning and conditioning technologies

With regard to the producer gas cleaning, there are a lot of applications available to remove contaminants from syngas at different temperatures to achieve the tolerance limits reported in Table 1 for the Ni/YZS anode. Indeed, the tolerance limits for Ni/GDC anode exhibit relatively less challenge (the level of tar admissible for the Ni/GDC anode is near 10 times higher respect to the Ni/YZS shown in Table 1 [40,143]). There are a lot of purification technologies at lower temperatures (around 20 °C), e.g. cyclones, scrubbers and other low temperature applications, ashes can eliminate H₂S, HCl and alkali. However, it has been taken into account that this will affect the heat loss. Hot gas cleaning technologies rise the efficiency of gasification systems by 4% [156] or even more. Moreover, it has been demonstrated that lower temperatures could cause carbon deposition with the consequent need of additional steam to avoid it. The most serious problem that occurs when the system operate at low temperature is tar condensation that generates fouling, clogging and plugging of the apparatus, inhibits catalyst and then produces environmental foul-up. For this reason, tar elimination is strictly suggested at the temperature around the one of the gasification (850 °C), at which ceramic filters are the most obvious choice. The choice of using lower temperature in the gas cleaning step may be done for H₂S removal by comparatively lower-cost and commercially available ZnO sorbent, which works at around 350 °C. In this case, HCl removal must be done before hydrogen sulphide removal with the purpose of elude the deactivation of the sorbent. A particulate filter is suitable to eliminate alkali at 350–400 °C [143].

5.1 Tar removal

Several technologies are suitable for tar removal. Generally, tar removal techniques are categorized into physical methods (e.g. cyclone, scrubbers or filters) and thermo-chemical transformation technologies (converting tar into syngas through catalyst or high temperature), the latter ones allow to convert tar into applicable gas product, increasing the global efficiency of the gasification operation and for this reason have acquired great interest [157]. Among thermochemical conversion methods, the thermal cracking of tar at elevated temperature allows to reduce the big organic molecules into tinier non-condensable gases, but this technique is not very interesting since it needs energies and produces soot [158]. So, the use of catalyst to convert tar into useful gases is more

attractive. Catalytic tar transformation happens mainly by means of these two techniques: conversion inside the gasifier, by fusing of catalyst material and biomass input or conversion outside the gasifier, in a separated reactor downstream. The latter approach has high efficacy in tar removal, but it is difficult for small and medium applications [88,159,160].

5.1.1 Tar removal: catalyst approach

There are a lot of studies focused on catalysts for tar removal. By those researches it is possible to affirm that, for making the choice which catalyst is better to deploy, the characteristics that must be considered are [161–166]:

- The porosity of the material;
- The ability to work in presence of elevated presence of H_2 , CO, CO_2 and H_2O at 650-950 °C;
- The ability to reform methane;
- The ability to provide an appropriate H_2/CO ratio for the process;
- The resistance to deactivation that could be provoked by carbon fouling, sintering and poisoning (especially sulphur poisoning);
- The ability to regenerate easily;
- The price, that has to be as low as possible;
- The resistance to weakening.

A very common catalyst used for tar removal is natural dolomite $CaMg(CO_3)_2$, that is very cheap and allows to achieve 95% or more tar conversion [154,167,168]. Pinto et al. [169] investigated the efficacy of dolomite, olivine, and lime. They showed that dolomite is the most efficacious catalyst to remove tar in syngas. Moreover, in the presence of dolomite the biggest gas yield and bigger heating value (HHV) of syngas have been reached, concluding that it is a very interesting catalyst.

Roche et al. [170] conducted an experiment in a BFB gasifier of dried sludge at 800 °C and at S/B ratio 1 and demonstrated that the effective of dolomite increases when steam is used as oxidising agent, in fact the H_2/CO ratio grew from 1.1 to 2.6 when a combination of dolomite and air-steam were utilized rather than dolomite and pure air.

Several studies from laboratories and pilot plants [148,165,171–175] reported calcined dolomite $CaO-MgO$ as the best solution for tar removal, where both the pore-volume and pore-diameter enhanced the mass transfer.

Pérez et al. [176] reported the tar conversion of 90-95% in a BFB gasifier fed with 10 kg/h of biomass at 800-850 °C where the calcined dolomite is allocated subsequent of the gasification reactor.

Corella et al. [41] proved experimentally that subsequent-dolomite has a slightly bigger efficiency for tar elimination respect to dolomite located in the bed of the reactor, however in-bed dolomite led to issues of elutriation and sintering that have to be taken into account. Following the study of Corella et al. [41] the efficacy of dolomite depending on where it is used in the system could be indicated, as reported in Table 3.

Table 3 - Efficacy of dolomite depending of locations [41]

Gasification with air	Dolomite in the gasifier bed > Dolomite subsequent the gasifier > Without Dolomite
Gasification with steam-oxygen	Dolomite subsequent the gasifier > Dolomite in the gasifier bed > Without Dolomite

Another very common, cheap and used catalyst is natural olivine, $\text{FeMg}(\text{SiO}_4)_2$, which can convert tar lower than dolomite, but it offer a greater opposition to erosion and rip [42]. Courson et al. [177] presented an interesting study carried out at 800 °C using as catalyst pure olivine and they reported that the activity is almost zero as well as CH_4 conversion close to 1% and H_2 yield close to zero. This has been confirmed also by Virginie et al. [178], who analyzed the influence of Fe/olivine in pinewood biomass-gasification at 850 °C with a dual fluidised bed, finding that the catalyst can convert until 65%, moreover it was showed that the transformation of toluene and the production of hydrogen were at least the triple respect to the case in which it was used pure olivine.

Rauch et al. [179] investigated the effectiveness of several olivine catalysts and concluded that their capacity depends on the iron oxide amount. The removal of tar using iron-olivine catalyst was investigated by Rapagnà et al. [180] and was discovered that the mean syngas yield reached 40% when the gasifier was feeding by 10 wt% Fe/olivine; in the meanwhile, tar concentration was lowered by 46%. Moreover, C_{10}H_8 and C_7H_8 were lowered by 48% and 59%, respectively. So, it

can be concluded that iron supported natural olivine can increase the catalytic activity of olivine limiting the tar amount in the gas. Since the iron permeation has moderate price respect to others metals, iron permeation affect modestly the catalyst [181].

Calcined olivine reported high tar conversion respect to normal olivine. In fact, it has been reported that gasification in presence of calcined olivine can have an increase of H₂ content till 7% compared with natural olivine and also a consistent increase in tar reduction (until 40%) due to the mixed oxide created by the calcination process [182–184].

Hu et al. [182] showed experimentally the effect of natural dolomite, calcined dolomite, natural olive and calcined olivine on the gas yield on apricot stones steam-gasification carried out at 800 °C and S/B ratio 1, briefly reported in Figure 6.

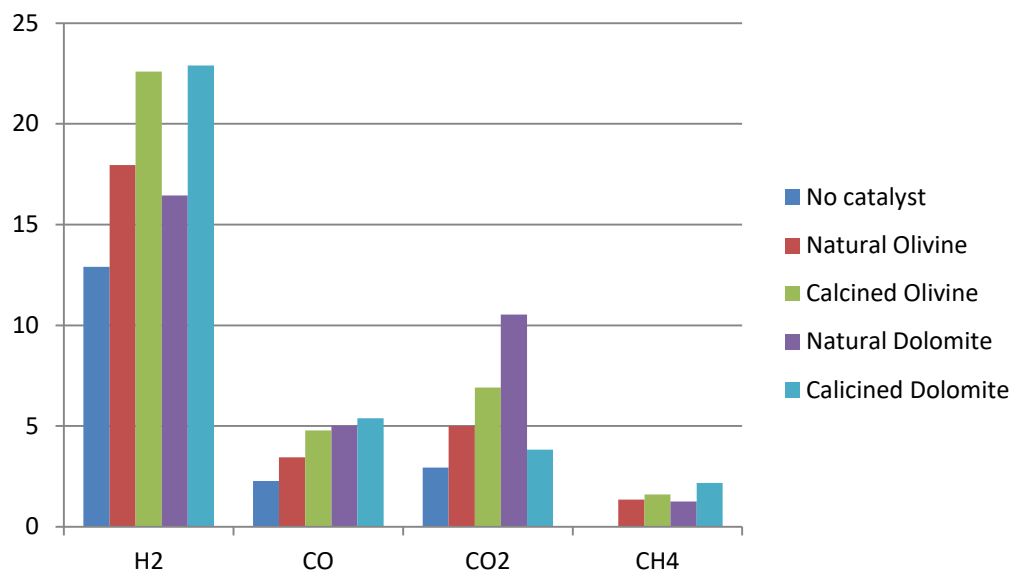


Figure 6 - Impact of olivine and dolomite on gas yield and compound distribution [182]

Simell et al. [185] conducted several experiments in a biomass-BFB air-reactor at 900-910 °C and 1 bar. They found the following order of catalyst regarding the efficacy for decreasing tar: Ni/Al₂O₃ ≈ dolomite ≈ Iron containing dolomite > SiC. However, Ni/Al₂O₃ is not stable and is eventually disabled [186].

Tian et al. [187] analysed the efficacy of different catalyst in a air-steam biomass BFB gasifier at 800-1000 °C, air equivalent ratio (ER) equal to 0.14 and S/B ratio equal to 0.5. They reported the following order position of catalyst in terms of efficacy in reducing tar: dolomite>olivine>lime>no catalyst.

5.1.2 Tar removal: physical approach

Physical cleaning methods can be classified in two typologies: dry cleaning applications and wet cleaning applications. The first one are usually conducted at 200–500 °C and also at 600–800 °C [188,189]. While, the latter are carried out after cooling at around 20–60 °C [161]. In Table 4 and in Table 5 are reported the main dry and wet cleaning methods respectively, with their operational temperature and corresponding tar removal efficiency.

Table 4 – Dry cleaning methods [190]

Technology	Tar removal efficiency (%)	Operational temperature [°C]	References
Cyclonic separator	30-70	100 – 900	[191,192]
Fabric filter	0-50	Up to 600	
Sand bed filter	50-90	20	
Ceramic quartz filter	75-95	650-770	[193]
Adsorbent activated carbon filter	80	20	[194]
Porous catalytic filter disk	77	800	[195]
(2.5%wt Al ₂ O ₃ ; 1.0% wt Ni; 0.5%wt MgO	99	900	
Porous catalytic filter disk	96-98	900	[196]
(1%wt/0.5%wt Ni/ CaO)			

Table 5 – Wet cleaning methods [190]

Technology	Tar removal efficiency (%)	Operational temperature [°C]	References
Impinger	70	50	[197]
Three impinge in series	>95	50	
Washing tower	10-25	50-60	[192]
Wet electrostatic precipitator (ESP)	40-70	20-30	[198]
Venturi scrubber	50-90	20-100	[191,199]
Packed bed scrubber	75	300	[200]
Bio-Oil scrubber	60	50	[194]
Water scrubber	22	20-100	[191,201]

As already explained, tar removal is strictly recommended around the gasification temperature and at such temperatures, ceramic filter candles are one of the most efficient choices. Ceramic filters in the freeboard of the gasification reactor coupled with in-bed gas cleaning by catalyst represents a very effective solution to remove tar [190,202,203].

Rapagnà et al. [204] experimentally proved that using dolomite as sorbent in a BFB reactor near 800 °C, mixed with olivine, the tar amount in the produced syngas reduced from 50% to 80% compared with the corresponding experiments without dolomite. Then, adding a catalytic filter candle in the gasifier freeboard, the syngas produced contained little quantity of tar and it was free of dust.

A very recent and interesting study on this topic is the one of Savuto et al. [205], who investigated a commercially available catalytic filter under three test conditions: not filled candle, candle at 50% filled with catalyst pellets and candle completely filled with catalyst pellets. The tests demonstrated that the theoretical thermodynamic values were almost achieved by the condition of candle filled at the 50%. implying that the catalyst promotes the steam reforming of hydrocarbons. Table 6 summarizes the results from the tar analyses that were carried out on the bench-scale BFB steam gasification tests using olivine sand as the bed material and almond shells as biomass feedstock,

performed by Savuto et al [205]. Considering tests 2-1 to 3-3, it was observed that the catalytic filter caused a considerable reduction in tar concentration. The total tar concentration (including benzene) dropped from 5.8 g/Nm³ to 0.4 g/Nm³ (average value). The cleaned tar consisted of 1-ring compounds (predominantly toluene), the two-ring compound naphthalene (on average 37 mg/Nm³, or 7 ppm), and to a small extent higher-ring tars. A further reduction of the tar concentrations is expected to come from the addition of dolomite to the olivine [168,204]. On the other hand, tar yields in the gasification of almond shells are relatively low. When municipal solid waste is gasified, the tar concentrations are typically 1 to 2 times more elevated compared with using just wood [206,207].

Table 6 - Tar analysis performed during the gasification experiments by Savuto et al. [205]. Test from 2-1 to 3-3 were executed with candle filled at 50% with catalyst pellets. Test from 2-1 to 2-3 and from 3-1 to 3-3 were performed at 820 °C and 780 °C respectively.

	TAR + benzene (mg/Nm ³)							
	Test 1	Test 2-1	Test 2-2	Test 2-3	Test 3-1	Test 3-2	Test 3-3	Test 4
Benzene	2439	130	157	111	75	70	78	–
1-Ring compounds	1711	230	193	199	230	266	230	189
Naphthalene	616	51	16	7	13	113	25	62
2-Ring compounds	479	~0	~0	2	~0	10	3	80
3- and 4-ring compounds	470	49	9	6	78	56	46	57
Phenols	0	0	0	0	0	0	0	0
Total Tar	3276	330	218	214	321	445	304	388
Tar + benzene	5715	460	375	325	396	515	382	–

Furthermore, several experimental applications in fluidized bed gasifiers showed that ceramic candles, with the addition of Ni catalyst, can totally eliminate particulate through their anisotropic porous filtrating design, and then efficaciously limit tar (< 200 mg/Nm³ [202,208–210]).

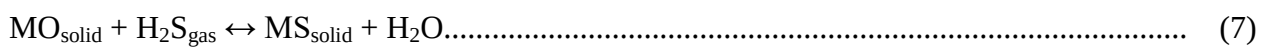
5.2 Sulphur removal

The in-bed catalyst treatments into the gasifier (calling also primary methods) for tar removal, already exposed in paragraph “3.1.1 Tar removal through catalyst approach”, contributes for a first conversion of H₂S: Husmann et al. [211] used different in-bed sorbent in a BFB steam-gasifier demonstrating that dolomite reduces the H₂S-concentration with 60%, while limestone reduces it with 70% and lime reduces it with 55%.

Then, a proper gas cleaning downstream the gasification reactor is needed to reach the tolerance limit for hydrogen sulphide before feeding SOFC system, according to Table 1.

The technologies for gas cleaning can be applied at mid-temperature, from 400 to 600 °C and at high temperature, from 600 to 850 °C, provide very good economic benefits by allowing the gasification process, gas cleaning and conditioning and downstream activities to be processed at close temperatures [21,36]. The ideal desulfurization adsorbent must have the following desired properties: high adsorption capacity (that consequently reduces the required adsorbent amount and process equipment size), fast adsorption kinetics (kinetic of desulfurization has to be first-order dependence in H₂S), high equilibrium constant, affordability, fast and cheap regeneration capability, ideally regenerable [36,142].

The solid-gas reaction that happens among the metal oxide and the contaminant, is:



The reaction (7) concerns H₂S and its equilibrium constant is reported in equation (8):

$$K_{eq,H_2S} = \frac{[\text{H}_2\text{O}][\text{MS}]}{[\text{H}_2\text{S}][\text{MO}]} = \frac{[\text{H}_2\text{O}]}{[\text{H}_2\text{S}]} \quad (8)$$

since that the activity of a pure solid is, by definition, equal to one.

A comparison between the most common metal oxides for desulfurization is reported in Table 7.

Table 7 - Comparison between different metal oxides for desulfurization at Mid to High Temperatures [36,212]

	Zn	Fe	Cu	Mn	Ca
Thermal stability	Acceptable	Not so Acceptable	Acceptable	Acceptable	Acceptable
Reductive stability	Acceptable	Acceptable	Not so Acceptable	Acceptable	Not so Acceptable
Sulfidation performance	Acceptable	Acceptable	Good	Not so Acceptable	Not so Acceptable
Kinetic of desulfurization	First-order dependence in H ₂ S	First-order dependence in H ₂ S	First-order dependence in H ₂ S	First-order dependence in H ₂ S	First-order dependence in H ₂ S

Price	Low	Low	Medium	Medium	Very low
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Nowadays, zinc-based sorbents are considered as the best candidate for H₂S elimination [32,51,213], due to the ability to remove almost totally the H₂S at 400 °C. Higher temperature determinates the de-volatilization of Zn with the consequent reduction of the adsorption capacity. In addition to zinc-based sorbents, only the sorbent based on cerium or copper are able to reduce H₂S below 1 ppm [32,40,213,214]. Generally, the H₂S cleaning capacity of different oxides is: Stannum<Nichel<Iron<Manganese<Molybdenum<Cobalt<Zinc<Copper and Cerium [40] and is illustrated in Figure 7.

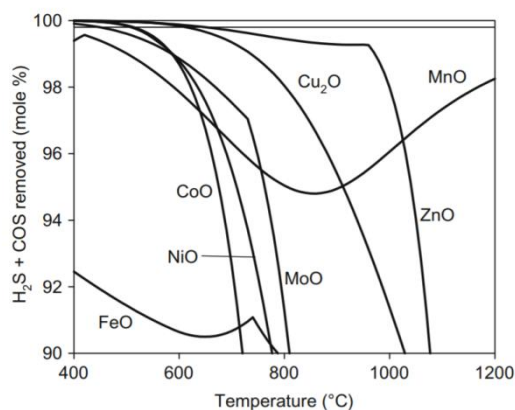


Figure 7 - Adsorption of metal oxides at their thermodynamic equilibrium [215]

In Table 8 are reported some characteristics of the most common metal oxides for H₂S removal.

Table 8 – Properties of metal oxides for H₂S elimination [216–218]

Sorbent	Chemical formula	Theoretical sorption capacity (g S/g sorbent)	Temperature range (°C)	Price (USD/kg)
Cerium oxide	Ce ₂ O ₃	0.093	500-700	5.9
Copper oxide	Cu ₂ O	0.224	540-700	5.8

Zinc oxide	ZnO	0.395	450-650	2.6
Manganese oxide	MnO	0.400	400-900	4.2
Iron oxide	FeO	0.245	450-700	1.4

Slimane and Abbasian [219] created CuO sorbents drugged with several Cu and Mn content, they could achieved a very good desulfurization efficiency (H_2S concentration under 1 ppmv.) at 500-600 °C for the sorbent IGTSS-179 and at 450–600 °C for the sorbent IGTSS-326A.

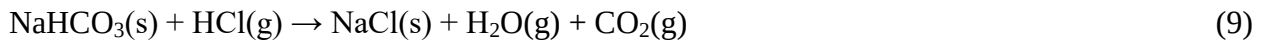
Zeng et al. [220] investigated the main operative conditions on desulfurization capacity of the reduced cerium oxide. CeO_n ($n < 2$) showed superior desulfurization capacity respect to CeO_2 and the H_2S amount next to desulfurization at 850 °C and 700 °C was reduced to 10 ppmv and 1 ppmv, respectively. Elemental sulphur was produced directly during the regeneration of the sulphied product, Ce_2O_2S , with SO_2 . Producing directly elemental sulphur avoids the issue of ultimate sulphur control from dilute SO_2 regeneration product gas associated with zinc-based sorbents.

Ikenaga et al. [221] utilized carbon materials (activated carbon, activated carbon filter and Yallourn coal) as support of zinc ferrite ($ZnFe_2O_4$). In the test with the support of zinc ferrite it is was demonstrated that the adsorption capacity was considerable higher compared to the test with no support, and the concentration of H_2S dropped from 4000 ppmv under 1 ppmv at 500 °C. These sorbent can be regenerated by 50 vol% O_2 /Air gas mix at 450 °C for 30 minutes with a narrow drop in sulphur activity.

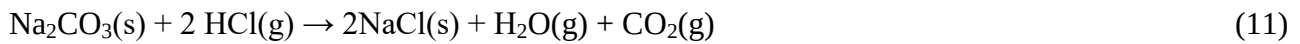
5.3 Hydrogen chloride removal

A very favourable technology for HCl elimination includes alkali-based sorbents, mainly sodium and potassium species [222–225]. Investigations on CaO or $CaCO_3$ sorbents are usually conducted for the applications above 500 °C [226–228]. Verdone et al. [229] confirmed that HCl removal efficiency of Na_2CO_3 sorbent achieves the highest values at 400-500 °C. Ohtsuka et al. [230] tested $NaAlO_2$ as HCl sorbent and demonstrated it removed HCl in a simulated syngas from 200 ppm to below 1ppm at 400 °C. Moreover, they indicated that the HCl capture efficiency of $NaAlO_2$ was better than that of Na_2CO_3 . Both $NaAlO_2$ and Na_2CO_3 were able to capture HCl under the presence of H_2S . Krishnan et al. [231] evaluated nahcolite ($NaHCO_3$), which is a natural carbonate mineral and transformed to porous Na_2CO_3 over 150 °C. The nahcolite-based sorbent lowered HCl concentration from 1750 ppm to below 1 ppm at 400-600 C. Dou et. al [232] showed that nahcolite

(NaHCO₃) is one of the most suitable alkali-based sorbents, due to its ability to limit the concentration of HCl under 1 ppmv at 526-650 °C. The next reaction happens using nahcolite:



Moreover, it must be considered that raising the temperature of until to 550 °C, water molecules are divided, following reaction (11). Next, NaHCO₃ decomposes to Na₂CO₃(s), which reacts with HCl to produce NaCl, following reaction (11)



Experimental results demonstrate that the temperature of NaHCO₃ has to be around 550 °C to reduce HCl concentration under 1 ppmv.

Ren et al. [223] experimentally investigated the adsorption capacity of a alkali-based potassium carbonate sorbent for HCl and showed a reduction of 54%, 51%, and 32% at 500 °C, 300 °C and 20 °C each. The adsorption of hydrogen chloride by Na₂CO₃(s) is thermodynamically favourable at moderate temperatures; but, higher temperatures are kinetically favourable until the alkali chloride salt decomposition limit.

Baek et al. [224] analyzed the performance of the unprocessed and of the processed potassium-based CO₂ sorbents to remove HCl by means of a micro fluidized-bed reactor and by means of a bench-scale bubbling fluidized-bed reactor, which works respectively at 300 and 540 °C and 20 bar. They showed that the concentration of HCl decreased from 150-900 ppmv to 5 ppmv and from 130-390 ppmv to 1 ppmv.

6 Materials and Methods

6.1 Biomass characteristics

Using biomass waste from agricultural means zero costs for the feedstock, avoiding fuel vs. food competition and having less life cycle impacts. In order to select the most suitable biomass waste to feed the gasifier, the following criteria have to be taken into account [1]:

- Availability of biomass on a significant scale (tons/year);
- Low heat value (LHV), that has to be high, so biomass with lower humidity is preferable;
- Chemical composition, that has to be low of sulphur, chlorine and ash.
- Size and shape of biomass, that have to be uniform in order to ensure homogeneous and efficient gasification and so bulk density, that has to be comparable with that of the gasifier bed, even if the latter can be adjusted via pretreatment and feeding systems.

Following the previous criteria, among the different agricultural biomass waste, hazelnut shells, which represent an abundant agricultural sub-product in regions of moderate climate [233,234], have been selected for this study. The characteristics of hazelnut shells are reported in Table 9.

Table 9. Physical and chemical properties of hazelnut shells [235].

Bulk density (kg/m ³)		Moisture content (% _{wt})			
319.14		7.90			
Proximate analysis (% _{wt} , dry basis)					
Ash		Volatile matter		Fixed carbon	
1.16		72.45		26.39	
Ultimate analysis (% _{wt} , dry basis)					

C	H	N	O	Cl	S
50.38	6.03	0.22	42.32	0.38	0.67
Heating values (MJ/kg _{dry})					
HHV			LHV		
20.20			18.85		

6.2 Aspen Plus modelling

The simulation of the biomass gasification process, carried out on Aspen Plus, is based on mass-energy balance and chemical equilibrium among all processes. The following assumptions were considered for the simulation:

- process is steady state and isothermal [236];
- drying and pyrolysis happen instantaneously and volatile products principally consist of H₂, CO, CO₂, CH₄ and H₂O [237];
- char is 100% carbon [238];
- all gases behave ideally;
- the tars considered are toluene (1-ring), naphthalene (2-ring) and benzene;
- the inorganic contaminants considered are hydrogen sulphide, hydrogen chloride and ammonia;
- catalyst is defined as conventional solid;
- uniform SOFC operating temperature and pressure.

In this simulation, the biomass is defined as a nonconventional component, its ultimate and proximate analyses specified according to Table 1. The Peng-Robinson equation, with Boston-Mathias (PR-MB) modification, has been used to evaluate all physical properties of the conventional components in the gasification process. HCOALGEN and DCOALGEN models are selected for the evaluation of the enthalpy and density of both biomass and ash, which are non-conventional components.

6.3 Description of Aspen Plus flow sheet

The Aspen Plus flow sheet of the developed model is shown in Figure 8 while all the units are described in Table 10. The simplified process scheme under investigation is showed in Figure 9 as block diagram

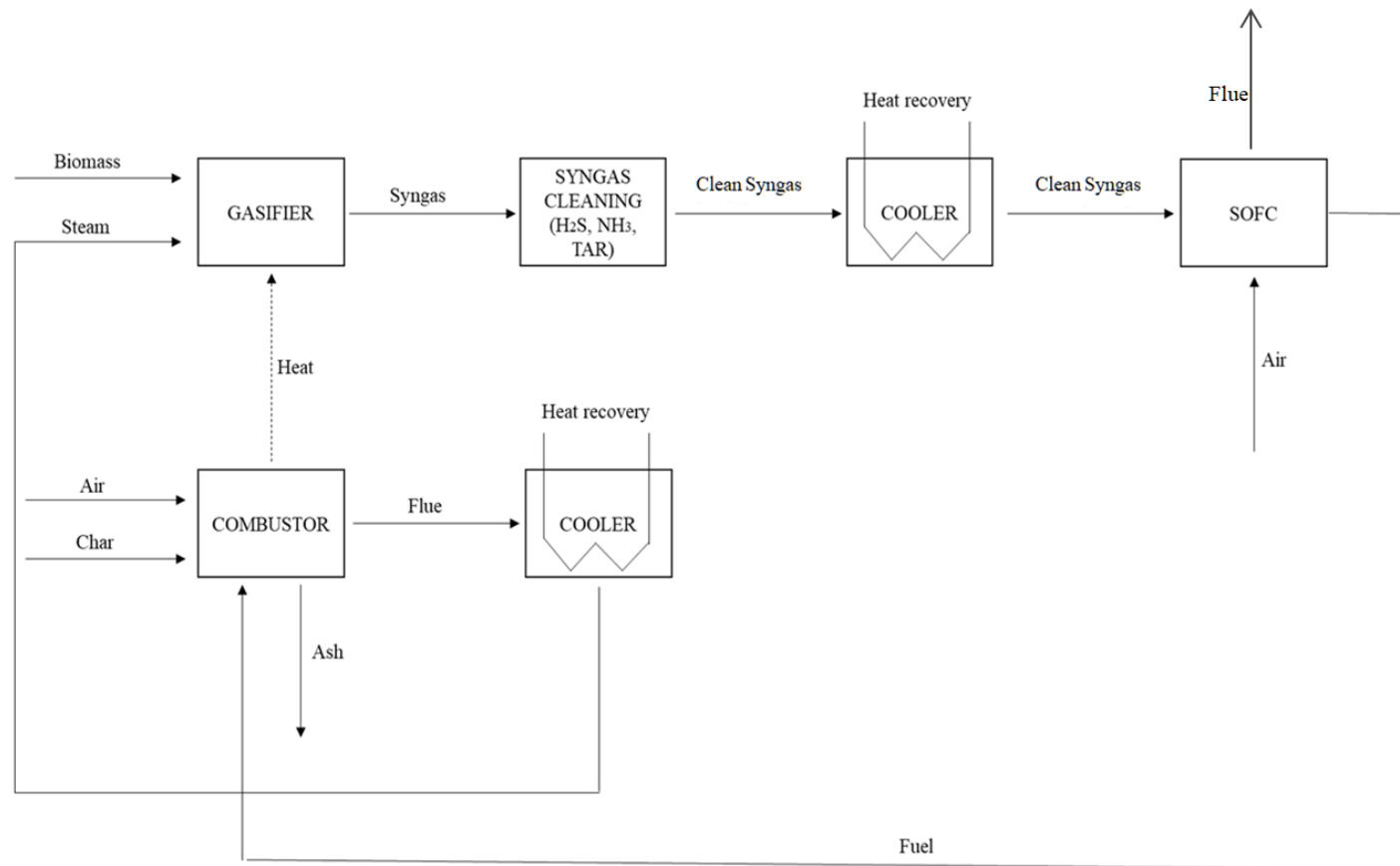


Figure 9 - Simplified block diagram of biomass gasification, syngas cleaning and SOFC system -

The power plant is mostly composed by a gasification reactor producing hazelnut shell-derived syngas. The stream BIOMASS, representing the hazelnut shells feed, goes firstly in the DECOMP block that is a RYield reactor, used to simulate the decomposition of the unconventional feed into its conventional components (carbon, hydrogen, oxygen, sulphur, nitrogen and ash, by specifying the yield distribution according to the biomass ultimate analysis in Table 1). Considering that the DECOMP block creates N, Cl and S as elemental components, which are known to produce principally HCl, NH₃ and H₂S, and the results of experimental fractional conversion model are closer to the experimental data with respect to restricted chemical equilibrium, the product out of DECOMP is moved to the RStoic block to simulate the production of H₂S, HCl and NH₃ by the following reactions [18]:



The fractional conversion considered for S, Cl₂ and N₂ is equal to 1 [70]. Deriving stream S2 goes into a separator SEP, that separates the stream S2 in three sub-streams: volatile part VOLATILE, char part CHAR and a stream composed by HCl, NH₃ and H₂S, called H₂SNH₃. Then, VOLATILE stream is divided in two sub-streams: VOL and H₂, the former, after mixing with the oxidizing fluid, goes into the gasifier, GASIF, and the latter is used to simulate tar production in the RYield block TARPROD; the former, after mixing with the oxidizing fluid, goes into the gasifier, GASIF, and the latter is used to simulate tar production in the RYield block. The block TARPROD is necessary since we are in steady-state conditions and it is not possible to simulate tar formation inside the gasifier GASIF. CHAR stream is split in two sub-streams: TOGASIF that represents the char reacted in the gasifier and S3 that represents the un-reacted char, the latter is then fed to TARPROD where it reacts with hydrogen from the H₂ stream. The tar is assumed to be a formation of toluene, benzene and naphthalene. The quantities of these tars are set in accordance with literature [239] and proportions of about 60%, 20% and 20% for benzene, toluene and naphthalene, respectively, are maintained [240]. The stream S4 is split in two sub-streams that represent the amount of char that moves into the combustor COMBUST and into the gasifier GASIF. The stream S8 is the stream that represents the real output of the gasifier, in fact it is made of the union of GASRAW, H₂SNH₃ and TAR streams. Before going to

the SOFC, syngas S8 needs to be clean, for this reason the following block have been added: a RGibbs reactor DOLOMITH that simulates dolomite reactions at high temperature to lower tar, a RStoic reactor CANDLE that represents the catalytic filter reaction, a REquil reactor ZNOZNS that simulates the reaction of ZnO with H₂S and a RStoic reactor DECLOR that simulates hydrogen chloride removal. The syngas cleaned goes into SOFC system, developed by the use of a REquil ANODE that simulates the anode, a separator CATHODE that simulates the cathode, a RStoic reactor AFTERBURN that simulates the combustion of the fuel and an exchanger EX05. REquil reactor.

The heat recovery is represented by the coolers using in the model simulation. The first recover is made by the exchanger EX01 that uses the heat of the flu from combustor to heat up the air to combustor. The exchanger EX06 follows the EX01 using the remaining heat of the flu to vaporize water and obtain steam to feed the gasifier. The exchanger EX02 heats up the syngas cleaned to anode and cools the syngas out of the candle to the ZNOZNS cleaning block. Then, the exchanger EX03 cools again the syngas to the ZNOZNS block. The exchanger EX04 is part of the SOFC modelling and it heats up air to cathode using in counter-current the stream out of the burner AFTERBUR. The following exchanger EX05 using the residual heat containing in the stream out of the AFTERBUR to heat up the stream WAT.

Table 10. – Description of ASPEN Plus flowsheet unit operation presented in Figure 8.

ASPEN Plus name	Block ID	Description
RYIELD	DECOMP	RYield reactor - converts the non-conventional stream “BIOMASS” into its conventional components
RSTOIC	RSTOIC	RStoic reactor – replicates ammonia and hydrogen sulphide
	CANDLE	RStoic reactor – represents the catalyst filter reaction
	AFTERBUR	RStoic reactor – replicates the 100% combustion of hydrogen and carbon monoxide
	TARPROD	RStoic reactor – represents the production of C ₇ H ₈ and C ₆ H ₆
	COMBUST	RStoic reactor – replicates the combustion of char

	DECLOR	RStoic reactor – simulates the reaction between HCl and nahcolite
SEP	SEP	Separator – divides the biomass in three streams: volatile, char and a stream of NH ₃ and H ₂ S
	SEPH2	Separator – divides a certain part of hydrogen used to produce tar
	CATHODE	Separator – replicates the cathode of the SOFC
	SEPZNS	Separator – separates the ZNS solid fraction
MIXER	MIX1	Mixer – mixes oxidising fluid with combustible fluid
	MIX2	Mixer – unify the product from gasifier with ammonia and hydrogen sulphide
	MIX3	Mixer – unify the stream S3 and H2
	MIX 4	Mixer – unify the product from GASIF with tar
FSPLIT	SPLIT	Splitter – divides char unreacted (S3) from char to burn (S4)
	SPLIT 2	Splitter – divides char to gasifier and to combustor
	SPLIT 3	Splitter – splits fuel to afterburner and to combustor
RGIBBS	GASIF	Gibbs free energy reactor – simulates drying, pyrolysis, partial oxidation and gasification and restricts chemical equilibrium of the specified reactions to set the syngas composition by specifying a temperature approach for individual reactions
	DOLOMITH	Gibbs free energy reactor – simulates the high temperature reaction of dolomite with NH ₃ , H ₂ S and tar
REQUIL	ZNOZNS	REquil reactor – simulates the reaction of ZnO with H ₂ S
	ANODE	REquil reactor – simulates the anode of the SOFC
HeatX	EX01	Heatx – heats up the air to combustor
	EX02	Heatx – cools the stream out of candle and heats the one out of ZNOZNS
	EX04	Heatx – preheats the incoming air to cathode and cools the stream from afterburner
	EX05	Heatx – preheats the water with residual heat of afterburner
	EX06	Heatx – heats the water coming out of the EX05 to steam
Heater	EX03	Heater – cools the stream in input to ZNOZNS

6.4 Gasification model

The reactions considered in the gasification process are reported in Table 11.

Table 11. – Gasification reactions [18].

Reaction	Reaction name	Heat of reaction	Reaction number
Heterogeneous reaction			
$C + 0.5 O_2 \rightarrow CO$	Char partial combustion	$(-111 \text{ MJ kmol}^{-1})$	(15)
$C + H_2O \leftrightarrow CO + H_2$	Water-gas	$(+172 \text{ MJ kmol}^{-1})$	(16)
Homogeneous reactions			
$H_2 + 0.5 O_2 \rightarrow H_2O$	H_2 partial combustion	$(-283 \text{ MJ kmol}^{-1})$	(17)
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water gas-shift	$(-41 \text{ MJ kmol}^{-1})$	(18)
$CH_4 + H_2O \rightarrow CO + 3H_2$	Steam-methane reforming	$(+206 \text{ MJ kmol}^{-1})$	(19)

Equations (15)-(19) of Table 11 are the chemical reactions considered in this work for the gasification process where the oxygen comes from biomass composition, as showed in ultimate analysis, and from air/oxygen stream if air/oxygen gasification is considered. To simulate the gasification process on ASPEN Plus a RGibbs reactor, called GASIF in Figure 1, has been used. This reactor was modelled with the restricted quasi-equilibrium approach, that allows to describe syngas composition more accurately than equilibrium models, as explained in the Introduction paragraph. So, the reactions within the reactor (listed in Table 3) are conducted at their QET, rather than at the actual temperature of the gasifier. In order to be more rigorous, a Data Fit of experimental data (about hazelnut or almond shells, since they have very similar characteristics [18], using steam and/or oxygen or air as gasification agent with a gasification temperature from 600 °C to 870 °C and S/B from 0.33 to 1) has been implemented on Aspen Plus (Table 4). In this way RGibbs gasifier evaluates the chemical equilibrium constant for each reaction at the gasifier temperature and, by that, it provides the equilibrium syngas composition. Since the Data-Fit was made from literature data obtained from experiment carried out with several gasifying agents (steam, air, oxygen

or a mix of these), the model can simulate almost all oxidizing gasification agents (i.e. CO₂ excluded).

Table 12. – Data fit

Test	1 [241]	2 [241]	3 [242]	4 [242]	5 [243]	6 [244]	7 [244]	8 [244]	9 [42]	10 [245]	11 [246]
<i>Operational conditions</i>											
Biomass flow rate (kg/h)	137	177	0.060	0.060	0.904	0.750	0.750	0.750	0.300	0.300	125
Air flow rate (kg/h)	0	0	0	0	0	0	0	0	0	0.650	0
Oxygen flow rate (kg/h)	40	51	0	0	0	0.094	0.188	0.375	0	0	39
Steam flow rate (kg/h)	55	70	0.048	0.048	0.298	0.375	0.375	0.375	0.300	0	55
Gasifier temperature (°C)	825	870	600	750	765	855	855	855	770	900	825
<i>Main variable for analysis</i>											
S/B (steam to biomass ratio)	0.400	0.400	0.800	0.800	0.330	0.500	0.500	0.500	1.000	0	0.440
<i>Gas composition (mole fraction)</i>											
CO (% _{dry})	0.300	0.310	0.217	0.250	0.385	0.242	0.250	0.256	0.332	0.040	0.300
H ₂ (% _{dry})	0.310	0.250	0.367	0.500	0.478	0.322	0.333	0.348	0.436	0.100	0.315
CO ₂ (% _{dry})	0.250	0.260	0.250	0.217	0.076	0.347	0.358	0.340	0.117	0.030	0.245
CH ₄ (% _{dry})	0.110	0.130	0.100	0.067	0.035	0.058	0.055	0.052	0.115	0.070	0.100

6.5 In-bed gas cleaning

The performance of the biomass gasifier is improved by in-bed use of calcined dolomite, simulated in Aspen Plus with a RGibbs reactor DOLOMITH, settled at 800°C and 1 bar. The effect of calcined dolomite (CaO-MgO) in the gasifier bed under stationary conditions is to increase the gas yield by the decrease of tar and inorganic impurities. In the present work, under the assumption of non-considering by-products formed by the reaction of components with calcined dolomite, the conversion rates considered for the tar and inorganic impurities (the dolomite acts as a primary sorbent for ammonia, hydrogen sulphide and hydrogen chloride) are shown in Table 13.

Table 13 - Conversion rate (X) of components that react with dolomite [33,36,168,216,232,247,248]

$X_{C_6H_6}$ (%)	50
$X_{C_{10}H_8}$ (%)	82
$X_{C_7H_8}$ (%)	80
X_{H_2S} (%)	85
X_{HCl} (%)	85
X_{NH_3} (%)	95

6.6 Catalytic filter candles

The catalytic filter candles were simulated by using an isothermal RStoic reactor (called CANDLE). The only compounds considered for the simulation are toluene, benzene and naphthalene. So, the reactions considered in the CANDLE block are:



As regard reaction conversions, data from Savuto et al. [46], experimentally validated for S/B=0.5, were used. Data come from lab-scale gasification tests, thus the behaviour can be replicated in pilot and commercial size gasifiers if the temperature can be maintained constant (as in the case of heat

supply or burn of a little portion of gas) and if it is in agreement with the isothermal model chosen. The conversion rate (X) of components that react in the stoichiometric reactor CANDLE is reported in Table 14.

Table 14 - Conversion rate (X) of components that react in the catalytic candle [46]

	S/B=0.5
X_{CH_4} (%)	90
$X_{C_6H_6}$ (%)	95
$X_{C_7H_8}$ (%)	92
$X_{C_{10}H_8}$ (%)	90

The limits for tar content in the syngas for the main end users are reported in Table 15.

Table 15 – Tar levels in biomass gasification and syngas users limits [40,249]

	Biomass waste gasification	Ammonia production	Gas turbine	SOFC	Methanol synthesis
Tars (mg/Nm ³)	3000-20000	<0.1	<30	<100 ^a	<0.1

^afollowing Aravind et al. [40], for the admissible level of tars in the SOFC three cases could be considered: optimistic case, that assumes tars can be reformed at SOFC anodes and so the inlet concentration of tar could be not taking into account; intermediate case, that assumes a few hundred mg/Nm³ of tars can be tolerated but not full tar loads from biomass gasifier and then conservative case, in which it can be assumed that the tar must be removed to low mg/Nm³ levels for safe SOFC operations. In this work a value between intermediate and conservative case has been selected.

6.7 Sorbent reactor

Since H₂S, NH₃ and HCl are responsible for corrosion and environmental problems, as explained in the Introduction, it's important to take into account, in the gas cleaning chain, a block dedicated to their removal below the desired limits, different for each consequent application. Table 16 reports some values of contaminant limits for different commercialized applications.

Table 16 – Typical H₂S, NH₃ and HCl concentration in biomass waste derived syngas and target level associated syngas applications [33,52,141,164,222,224]

Contaminants (ppm)	Biomass waste gasification	Ammonia production	Gas turbine	SOFC	Methanol synthesis
H ₂ S	20-500	<0.1	<20	<1	<0.5
HCl	30-1000	<1.5	<1.5	<1	<1
NH ₃	20-1000	-	<50	<5000	<10

A multifunctional reactor, able to remove at the same time all the contaminants, is preferable, but it's not practical that a sorbent remove simultaneously multiple contaminants in hot gas cleaning [232] since some contaminants may interfere in the adsorption of others (e.g. HCl inhibit the adsorption of H₂S in many metal oxides) . For this reason, different steps have been developed in order to achieve the desired ppm level for the inorganic impurities considered in the simulation.

6.7.1 Hydrogen sulphide removal

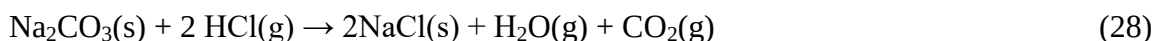
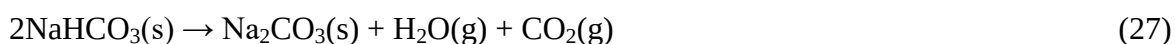
In order to simulate the sorbent reactor, the Aspen Plus model includes a REquil block DESULPH for desulphurization. Equation (7) and (8) point out the effect of a great amount of water concentration on the level of sulphidation of a metal oxide resulting in the possibility for the reaction to goes on only if the sorbent has a very great equilibrium constant for the reaction [52]. In consequence, the amount of steam in the syngas represents an interesting challenge in the material advancement and in the present work a sensitivity analysis on the S/B ratio has been carried out and shown in the Results and Discussion section, paragraph, in order to investigate the impact of steam on the sorbent performance. Another limit of metal oxide sorbents, linked to chemical and mechanical degradation in hot gas cleaning, is their thermal instability at the higher end of the temperature range [250], an aspect that until now has been rarely mentioned in the literature. The metal oxide sorbent must satisfy some criteria: affordability, high equilibrium constant, high adsorption capacity, fast adsorption kinetics, fast and cheapness regeneration capability [36]. According to the previous criteria, zinc-based sorbents are nowadays the leading sorbent competitor for H₂S removal [32,51,213], showing a quasi-total removal of hydrogen sulphide at the operative mid-temperature of 400°C.

6.7.2 Hydrogen chloride removal

The most promising method for HCl removal at mid- and high-temperature involves alkali-based sorbents, mostly sodium and potassium compounds [222]. Dou et. al [232] shew nahcolite (NaHCO_3) as one of the best alkali-based sorbents, since it can remove HCl to concentrations lower than 1 ppm in the temperature range of 526-650°C. Using nahcolite, the following reaction will take place:



However, it has to be taken into account that, when the temperature of nahcolite is raised up 550°C (reaction 27), water molecules are separated. Then, nahcolite disintegrates to sodium carbonate and HCl will react with Na_2CO_3 to form sodium chloride (reaction 28).



Experimental results show that in order to reduce HCl ppm levels until 1 ppm the nahcolite temperature has to be approximately of 550°C. In the Aspen Plus simulation, the removal of HCl is simulated by means of an RGibbs reactor DECLOR, settled at 550°C and 1 bar with the restricted chemical equilibrium option, using the reactions 26-28.

6.8 SOFC model

The SOFC modelling on ASPEN Plus is based on a simplification of the models developed by Doherty et al. and Zhang et al. [82,83], as shown in Figure 8 and explain in paragraph 6.3. The equations involved in the modelling were developed by, described and previously validated [11].

The operative conditions of the plant are reported in Table 17.

Table 17 – The operating conditions of the system.

Thermal power input of the gasifier ($m_{\text{bio}} \cdot \text{HHV}_{\text{bio}}$)	1 MW _{th}
Temperatures	Ambient (biomass, combustion air and water for steam production) 20 °C
	Gasifier/gasification zone – product gas 800 °C

	Gasifier - steam in	400 °C
	Gasifier/combustion zone – exhaust gas	800 °C
	Gasifier/combustion zone – combustion air in	400 °C
	Sorbent reactor for sulphur removal	400 °C
	SOFC anode	910 °C
	Afterburner/combustion zone - exhaust gas	910 °C
	<i>S/B</i> ratio	0.5
	System operating pressure	1 bar

7 Results and discussions

7.1 Analysis of the developed gasification model

Considering only the developed gasification model (the green part of Figure 8), in order to demonstrate the feasibility of this model with different mix of oxidizing agents, several comparisons with experimental data have been conducted. The maximum discrepancy value obtained for hydrogen, with respect to experimental data, is of 8% and all the other values reached by the developed simulations, considering both organic and inorganic compounds, are in good agreement with literature data. The gas yield reached by the developed simulation is in the range of 1.1-1.3 Nm³/kg.

7.1.1 Steam gasification results and model validation

The developed simulation model has been validated using experimental data of Rapagnà and Latif [242] and Karatas and Akgun [251] for steam gasification. Rapagnà and Latif used a lab-scale fluidized-bed reactor as gasifier, at 1 bar and 800 °C and hazelnut shells as biomass feedstock. The lab-scale reactor used by Karatas and Akgun was a fluidized-bed , at 1 bar and 800 °C and the biomass feedstock used was walnut shells, that have very similar characteristics with respect to hazelnut shells. The comparison of the operative conditions and results of the present model simulation and literature data are reported in Table 18. The discrepancy of the simulative results against experimental values is shown in Table 19.

Table 18. - Comparison of operating conditions and steam gasification results (stream S8) of the present study with literature data.

	Case 1		Case 2	
	Model simulation	Literature data [242]	Model simulation	Literature data [252]
Gasifier type	Fluidized-bed	Fluidized-bed	Fluidized-bed	Fluidized-bed
Bed-material	Silica sand	Silica sand	Silica sand	Silica sand
Biomass	Hazelnut shells	Hazelnut shells	Hazelnut shells	Walnut shells

feedstock				
Biomass flow rate (kg/h)	0.06	0.06	0.898	0.898
Gasification pressure (bar)	1	1	1	1
Gasification temperature (°C)	800	800	770	770
Oxidising agent	Steam	Steam	Steam	Steam
S/B ratio	0.8	0.8	0.4	0.4
H ₂ (%dry mole fraction)	44.2	45.0	31.8	35
CO (%dry mole fraction)	16.7	26.7	20.4	22
CO ₂ (%dry mole fraction)	22.1	20	20	15
CH ₄ (%dry mole fraction)	5.3	6.0	7.6	8
NH ₃ (ppm)	1112.2	Not evaluated	1961.0	Not evaluated
H ₂ S (ppm)	1479.1	Not evaluated	2609.5	Not evaluated
HCl (ppm)	1001.3	Not evaluated	1798.0	Not evaluated
Toluene (g/Nm ³)	4.5	Not evaluated	5.3	Not evaluated
Benzene (g/Nm ³)	10.6	Not evaluated	12.4	Not evaluated
Naphthalene (g/Nm ³)	4.5	Not evaluated	7.4	Not evaluated
LHV (MJ/Kg)	9.5	Not evaluated	11.7	10.1
Gas yield (Nm ³ /kg)	1.3	1.5	1.6	Not evaluated

Table 19. – Discrepancy of simulative results against experimental data

	Case 1	Case 2
H ₂ (%dry mole fraction)	1.7%	9.1%
CO (%dry mole fraction)	37.4%	7.2%
CO ₂ (%dry mole fraction)	10.5%	33%

The comparison of the resulting composition values with the literature ones, reported in Table 18, shows a comparable product syngas composition (the difference is below 10% for the main gas, i.e. H₂, below 38% for CO and CO₂ and below 15% for CH₄). The under or the over prediction of CH₄ is an ordinary issue in the simulative modelling since tar is not considered in the equilibrium models and it is simulated apart from the gasifier block. The underproduction of CO and the overproduction of CO₂ is due to the negligence in the simulation of steam kinetic factors (steam lowering the gas speed, causes an increase in residence time and it favors the dissociation of H₂O) that favor the conversion of char and heavy hydrocarbons into light ones (i.e. CO). The production of tar and inorganic contaminants is not evaluated by Rapagnà and Latif and Karatas and Akgun, however the results obtained for toluene, benzene and naphthalene agree with other literature experimental sources [235,239,253]. Zhou et al. reported that the concentration of NH₃ in the gasification product is between 500 to 30000 ppm, depending on the nitrogen content of the biomass feedstock and the gasifier conditions [254]. The concentration of H₂S reported in literature ranges from 1000 to 14000 ppm in the raw syngas [250] and the concentration of HCl is around 750 ppm [250].

7.1.2 Effect of steam to biomass (S/B) ratio

A sensitivity analysis is carried out in order to evaluate the effect of the S/B ratio on the hazelnut shells-derived syngas composition that comes from the gasifier at the fixed temperature of 800 °C. In Figure 10 the trend of the dry molar fraction of each component is reported against S/B ratio. The concentration of H₂ and CO₂ rises with the rise of S/B ratio and the concentrations of CO and CH₄ decrease with S/B ratio. Increasing steam favors the water-gas reaction and steam methane reforming reactions resulting in an increase of H₂ and CO concentrations; however, the CO concentration decreases with increasing S/B ratio due to the water-gas shift reaction which reduces CO reacting with steam and increases H₂ and CO₂ concentrations. Similar trends were reported in literature references [58,255].

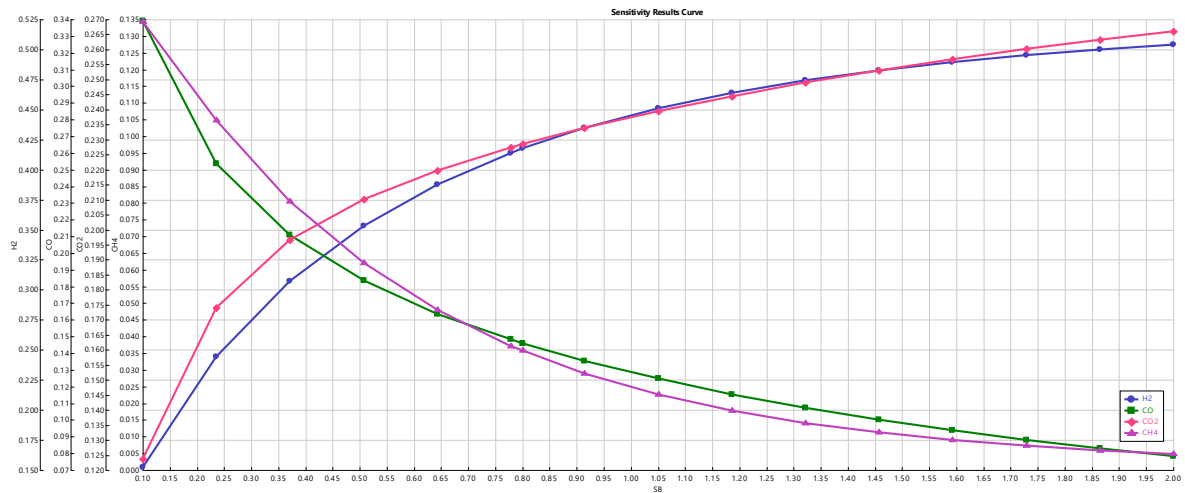


Figure 10. – Effect of S/B ratio on syngas composition.

7.1.3 Effect of gasification temperature on syngas composition

A sensitivity analysis is carried out in order to evaluate the effect of the gasification temperature on the hazelnut shells-derived syngas composition, keeping the S/B ratio fixed at 0.8. In Figure 11 is shown the trend of the syngas composition as a function of the temperature in the range 770-880°C. It can be observed that H₂ and CO concentrations increase with the increase of temperature, due to the endothermic reactions 16 (Water gas) and 19 (Steam methane reforming). On the other hand, the increase of temperature causes the decrease of CO₂, CH₄ and H₂O. The decrease of CO₂ production depends on reaction 18 (Water gas shift) that is exothermic, being favored at low temperatures, and for this reason the higher temperature means the higher CO and the lower CO₂ production. Similar trends were observed by [18,55].

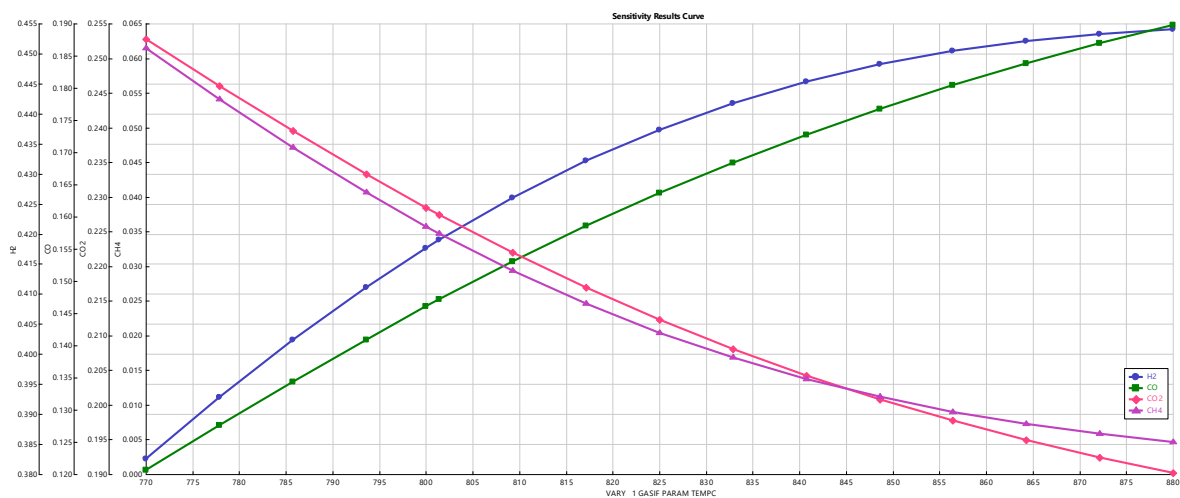


Figure 11. – Effect of temperature on syngas composition.

7.1.4 Air-steam gasification results and model validation

The developed simulation model has been validated using experimental data of Lv et al. [256] for air-steam gasification. The experimental set-up was a fluidized-bed reactor, operated at 1 bar and 800 °C and the biomass feedstock used was pine sawdust, that presents very similar characteristics with respect to hazelnut shells, except for the inorganics that are not considered. The comparison of the operative conditions and results of the present model simulation and literature data are reported in Table 20. The discrepancy of the simulative results against experimental values is shown in Table 21.

Table 20. - Comparison of operating conditions and air-steam gasification results (stream S8) of the present study with literature.

	Model simulation	Literature data [256]
Gasifier type	Fluidized-bed	Fluidized-bed
Bed-material	Silica sand	Silica sand
Biomass feedstock	Hazelnut shells	Pine sawdust
Biomass flow rate (kg/h)	0.445	0.445
Gasification pressure (bar)	1	1
Gasification temperature (°C)	800	800
Oxidising agent	Steam and air	Steam and air
S/B ratio	0.5	0.5
ER	0.2	0.2
H ₂ (%dry mole fraction)	35.0	33.0
CO (%dry mole fraction)	18.0	17.0
CO ₂ (%dry mole fraction)	34.6	42.0
CH ₄ (%dry mole fraction)	1.2	5.5
NH ₃ (ppm)	2095.1	Not evaluated
H ₂ S (ppm)	2787.1	Not evaluated

HCl (ppm)	1621.3	Not evaluated
Toluene (g/Nm ³)	6.5	Not evaluated
Benzene (g/Nm ³)	15.3	Not evaluated
Naphthalene (g/Nm ³)	9.4	Not evaluated
LHV (MJ/Kg)	5	6
Gas yield (Nm ³ /kg)	1.2	2

Table 21. – Discrepancy of simulative results against experimental data

H ₂ (%dry mole fraction)	6.0%
CO (%dry mole fraction)	5.8%
CO ₂ (%dry mole fraction)	17.6%
CH ₄ (%dry mole fraction)	78.0%

The comparison of the resulting composition values with the literature ones, reported in Table 20, shows a comparable product syngas composition (the difference is 6% for the main gas, i.e. H₂, below 18% for CO and CO₂ and 80% for CH₄; but, it has already been mentioned previously that CH₄ is under or over-predicted). Tar production was not evaluated by Lv et al., but as for the case mentioned previously in the text, the results obtained for toluene, benzene and naphthalene agree with other literature experimental sources [235,239,257] and the same for the inorganic compounds concentration.

7.1.5 Steam-oxygen gasification results and model validation

Experimental data is rarer regarding steam-oxygen, therefore the developed simulation model has been validated using experimental data of Barisano et al. [258] for Steam-Oxygen gasification that used olivine instead of silica sand as bed material and almond instead of hazelnut shells as biomass. Almond shells have very similar characteristics respect to the hazelnut shells and the olivine is well known to have a WGS catalyst effect (so the H₂ and CO₂ contents will be higher meanwhile CO lower). The experimental set-up used by Barisano et al. was a fluidized-bed reactor, worked at 1 bar and 850 °C. The comparison of the operative conditions and results of the present model simulation and literature data are reported in Table 21. The discrepancy of the simulative results against experimental values is shown in Table 22.

Table 21. - Comparison of operating conditions and steam-oxygen gasification results (stream S8) of the present study with literature.

	Model simulation	Literature data [258]
Gasifier type	Fluidized-bed	Fluidized-bed
Bed-material	Silica sand	Olivine
Biomass feedstock	Hazelnut shells	Almond shells
Biomass flow rate (kg/h)	122	122
Gasification pressure (bar)	1	1
Gasification temperature (°C)	850	850
Oxidising agent	Steam and oxygen	Steam and oxygen
S/B ratio	0.4	0.4
Oxygen flow rate (kg/h)	44.0	44.0
H ₂ (%dry mole fraction)	24.2	28.9
CO (%dry mole fraction)	25.1	21.7
CO ₂ (%dry mole fraction)	28.7	31.8
CH ₄ (%dry mole fraction)	4.0	9.5
NH ₃ (ppm)	2357.1	Not evaluated
H ₂ S (ppm)	3136.1	Not evaluated
HCl (ppm)	1790.3	Not evaluated
Toluene (g/Nm ³)	7.2	Not evaluated
Benzene (g/Nm ³)	17.0	Not evaluated
Naphthalene (g/Nm ³)	10.0	Not evaluated
LHV (MJ/Kg)	14.83	15.0
Gas yield (Nm ³ /kg)	1.1	1.1

Table 22. – Discrepancy of simulative results against experimental data

H ₂ (%dry mole fraction)	16.3%
CO (%dry mole fraction)	15.6%
CO ₂ (%dry mole fraction)	9.7%

The comparison of the resulting composition values with the literature ones, reported in Table 20, shows a comparable product syngas composition (the difference is 16% for the main gas, i.e. H₂, below 16% for CO and CO₂ and 58% for CH₄; but it has already been mentioned previously that CH₄ is under or over-predicted). Thus, even if olivine was used as bed material, the difference of H₂, CO and CO₂ are similar to the previous ones. Tar production was not evaluated by Barisano et al., but as for the case mentioned previously in the text, the results obtained for toluene, benzene and naphthalene agree with other literature experimental sources [235,239,257] and the same is for the inorganic contaminants concentration.

7.2 Comparison of the developed quasi-equilibrium gasification model with a kinetic literature model

In order to better understand the differences and the applicability range of the 0-D thermodynamic developed gasification model, it has been compared with a 1-D kinetic gasification model developed in MATLAB by Di Carlo et al. [7], combining hydrodynamics and reaction kinetics according to the geometry of reactor.

The comparison was carried on considering the same biomass and operating conditions (and no catalysts and/or sorbents addition except for the bed material in the kinetic model). The aim of the work is to evaluate gasification model's discrepancy from real values within different conditions in order to highlight possible improvements and in which case one model is more suitable than the other. After a comparison of the results of the models against experimental data at two S/B ratios, a sensitivity analysis for a wide range of S/B ratios has been performed. The experimental comparison and sensitivity analysis shows that the two models provide sufficiently similar data in terms of the main components of the syngas although the thermodynamic model shows, with increasing S/B, a greater increase of H_2 and CO_2 and lower decrease of CH_4 and CO respect to the kinetic one and the experimental data. Thus, the thermodynamic model, despite being calibrated by experimental data, can be used mainly to analyze global plant performance due to the reduced importance of the discrepancy from a global energy and plant perspective. Meanwhile, the more complex kinetic model should be used when a more precise gas composition is needed and, of course, for reactor design.

7.2.1 Brief description of the MATLAB gasification model

Details of the model can be found in Di Carlo et al. [7]. It is a semi-empirical model for steam gasification which implements a 1-D resolution of the mass and energy balance along the axis of the cylinder in order to calculate the syngas composition. In this model, the pyrolysis reactions were considered instantaneous, because the operating temperature is quite high in the gasifier where biomass is fed. For this reason, the de-volatilization time was considered negligible, assuming that biomass is instantaneously converted in its de-volatilization products. In order to obtain realistic values for the pyrolysis products and to validate the biomass steam gasification model, experimental tests on a bench scale fluidized bed reactor were used [259]. A hydrodynamic model according to Kunii and Levenspiel [260] (Geldart group B powder) was used to describe the bubble and

emulsion phases and their interaction in the fluidized bed. The rates of the gasification reactions (heterogeneous and homogeneous reactions, including one-ring tar reforming) have been implemented using literature kinetic correlations [11]. In Figure 12 the MATLAB algorithm flow chart is illustrated, more details of the model can be found in the works of Di Carlo et al. [7,261].

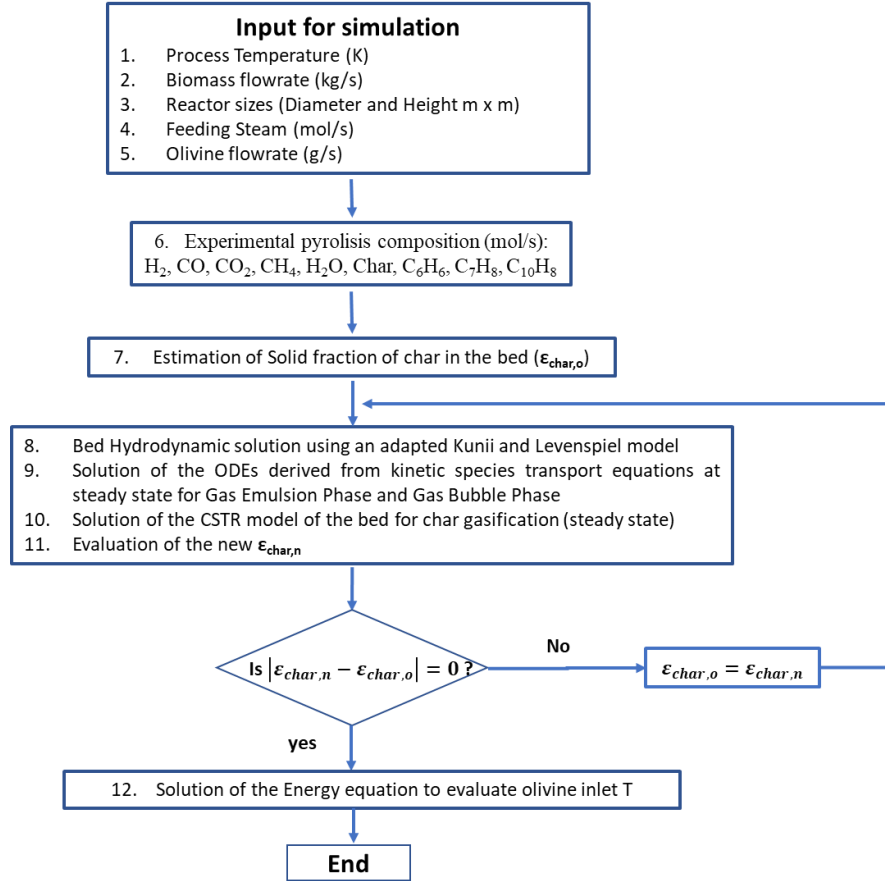
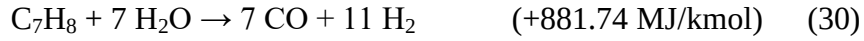


Figure 12 -MATLAB model algorithm flow chart

The LHV of the produced syngas can be calculated from the standard low calorific values (MJ/kg) of the combustible components of the syngas (120 MJ/kg, 10 MJ/kg and 50 MJ/kg for H₂, CO and CH₄ respectively) considering their mass-based concentrations in the total gas mixture. The thermal balance of the gasifier determines the temperature drop of the circulating bed material (olivine), considering a fixed ratio of 50 kg_{olivine}/kg_{biomass} as heat transfer media between the gasifier and the combustor. The specific heat of the olivine is fixed at 750 kJ/(kg·K). Using olivine as bed material also provides a moderate catalytic effect for the heterogeneous reactions in the MATLAB model [7], modifying the syngas composition. The model has been tuned and validated using the experimental results obtained in a bench scale fluidized bed gasifier [261]. The reactions considered in the model are the same of the Aspen Plus (which are reported in Table 1) plus the Boudouard reaction (R6) and the tar reforming (R7), shown below, which were not considered in the Aspen Plus model due to the fact that they are very far from thermodynamic equilibrium. Adding such

reactions would lead to inaccurate results respect to the experimental ones (i.e., more CO and H₂ and no toluene).



7.2.2 Model comparison

The operation conditions, of the Aspen Plus model developed and the MATLAB model previously described, are reported in Table 23.

Table 23. - Common operating conditions of Aspen Plus and MATLAB models.

Thermal Power Input of the Gasifier ($m_{\text{bio}} \cdot \text{LHV}_{\text{bio}}$) 350 kW_{th}	
Temperature	850 °C
Pressure	1 bar

The size of 350 kW_{th} (kilowatt-thermal) has been chosen as a trade-off between the applicability of fluidized bed technology and biomass availability (e.g., hazelnut shells in a hazelnut production plant, i.e., about 500 t/year). Furthermore, a similar scale gasifier is suitable to integrate with small-to-medium scale combined heat and power (CHP) end users (as the hazelnut production plants, e.g., few tens of kW_e (kilowatt-electric)). The temperature of 850 °C is used since, as reported in [7,262], it represents a trade-off for syngas composition and characteristics, leading to a reasonable value for both gas yield and LHV (consequently optimizing the cold gas efficiency η_{CG} , following the equation (31)).

$$\eta_{CG} = \frac{\text{LHV}_{\text{syngas}} \cdot m_{\text{syngas}}}{\text{LHV}_{\text{biomass}} \cdot m_{\text{biomass}}} \quad (31)$$

where m is the mass in kg.

Atmospheric pressure is typical for small-to-medium scale plants which do not present criticalities in footprint and occupancy of the balance of plant. Table 24 and Table 25 compare syngas composition, LHV and yield obtained by the two models respect to the literature data,

Fercher et al. [263] and Hofbauer et al. [264], for S/B equal to 0.25 and 0.5 respectively; Table 26 and Table 27 show the absolute and relative error committed by each of the two models respect to the reference literature data. The experimental data are always for steam gasification temperature at 850 °C but, owing to the fact that no experimental data are available in literature for hazelnut shells (at 850 °C and S/B of 0.25 and 0.5), the validation has been done considering wood chips that, as already described, have very similar characteristics within the category of lignocellulosic biomass.

Table 24 - Comparison of syngas composition and characteristics (S/B = 0.25).

$S/B = 0.25 (kg_{steam}/kg_{biomass,dry})$	Literature Data [263,265]	Aspen Plus Model	MATLAB Model
H ₂ (%dry mole fraction)	42.1	34.0	38.7
CO (%dry mole fraction)	16.8	33.5	29.9
CO ₂ (%dry mole fraction)	31.5	20.8	17.2
CH ₄ (%dry mole fraction)	8.8	11.7	14.2
LHV (MJ/kg) _{dry}	13.9-15.1	12.8	15.2
Gas yield $\left(\frac{Nm^3 syngas}{kg biomass}\right)_{dry}$	0.85	1.40	1.25
Cold gas efficiency	0.87–0.96	0.88	0.92

Table 25 - Comparison of syngas composition and characteristics (S/B = 0.5).

$S/B = 0.5 (kg_{steam}/kg_{biomass,dry})$	Literature Data [264,265]	Aspen Plus Model	MATLAB Model
H ₂ (%dry mole fraction)	30–40	43.1	42.2
CO (%dry mole fraction)	20–30	26.0	22.9
CO ₂ (%dry mole fraction)	15–25	24.0	21.8
CH ₄ (%dry mole fraction)	8–12	6.9	13.1
LHV (MJ/kg) _{dry}	14.1–15.2	11.7	14.2
Gas yield $\left(\frac{Nm^3 syngas}{kg biomass}\right)_{dry}$	1	1.60	1.32
Cold gas efficiency	0.89–0.96	0.91	0.95

Table 26 - Validation of syngas composition and characteristics (S/B = 0.25).

Error Analysis	Aspen Model		MATLAB Model	
$S/B = 0.25 (kg_{steam}/kg_{biomass,dry})$	Absolute Error	Relative Error (%dry mole fraction)	Absolute Error	Relative Error (%dry mole fraction)
H ₂ (%dry mole fraction)	−8.1	−19.24	−3.4	−8.08
CO (%dry mole fraction)	+16.7	+99.40	+13.1	+77.98
CO ₂ (%dry mole fraction)	−10.7	−33.97	−14.3	−45.40
CH ₄ (%dry mole fraction)	+2,9	+32.95	+5.4	+61.36
LHV (MJ/kg) _{dry}	−1.7	−11.72	+0.7	+4.8
Gas yield $\left(\frac{Nm^3 syngas}{kg\ biomass}\right)_{dry}$	−0.14	−11.38	+0.02	+1.6
Cold gas efficiency	−0.03	−3.2	+0.01	+1.0

Table 27 - Validation of syngas composition and characteristics (S/B = 0.5).

Error Analysis	Aspen Model		MATLAB Model	
$S/B = 0.5 (kg_{steam}/kg_{biomass,dry})$	Absolute Error	Relative Error (%dry mole fraction)	Absolute Error	Relative Error (%dry mole fraction)
H ₂ (%dry mole fraction)	+8.1	+23.14	+7.2	+20.57
CO (%dry mole fraction)	+1.0	+4.0	−2.1	−8.4
CO ₂ (%dry mole fraction)	+4.0	+20	+1.8	+9.0
CH ₄ (%dry mole fraction)	−3.1	−31	+3.1	+31
LHV (MJ/kg) _{dry}	−2.95	−20.13	−0.45	−3.07
Gas yield $\left(\frac{Nm^3 syngas}{kg\ biomass}\right)_{dry}$	+0.32	+32.0	+0.32	+32.0
Cold gas efficiency	−0.02	−2.1	−0.02	+2.1

For S/B = 0.25 (kg_{steam}/kg_{biomass,dry}) the Aspen Plus and MATLAB values of H₂ and CH₄ are similar and are lower and higher than the reference value, respectively. The AE is within −8 and −3 for H₂ and +3 and +5 CH₄ with a RE within −20% and −8% for H₂ and within +33% and +61% for CH₄ due to its lower values in the syngas. This is due to the presence of olivine used as natural catalytic bed material in the experiments of Hofbauer et al. [264] and Fercher et al. [263] and

Hofbauer et al. that emphasizes the water-gas shift (WGS) reaction (R4) and steam-methane reforming (SMR) reaction (R5), determining in this way the reduction of CO that, vice versa, is higher in the two models (AE +17 and +13 which leads to a RE up to +100%). The MATLAB model, that considers the olivine effect, has fewer differences although the olivine contribution is still lower than what seen in the literature reference. The overestimation of CO consequently shifts the equilibrium of (R4) towards the reagents reducing the CO₂ prediction (AE -10 and -14, RE in the range of -34% and -45%). Despite the differences in gas composition, regarding LHV, yield and cold gas efficiency, the models shows good agreement with the experimental values (Aspen Plus maximum AE 1.7 and RE 12%, MATLAB maximum AE 0.7 and RE 5%), confirming that, for plant analysis also the thermodynamic models can be used meanwhile for specific gas prediction the kinetic models are more suitable.

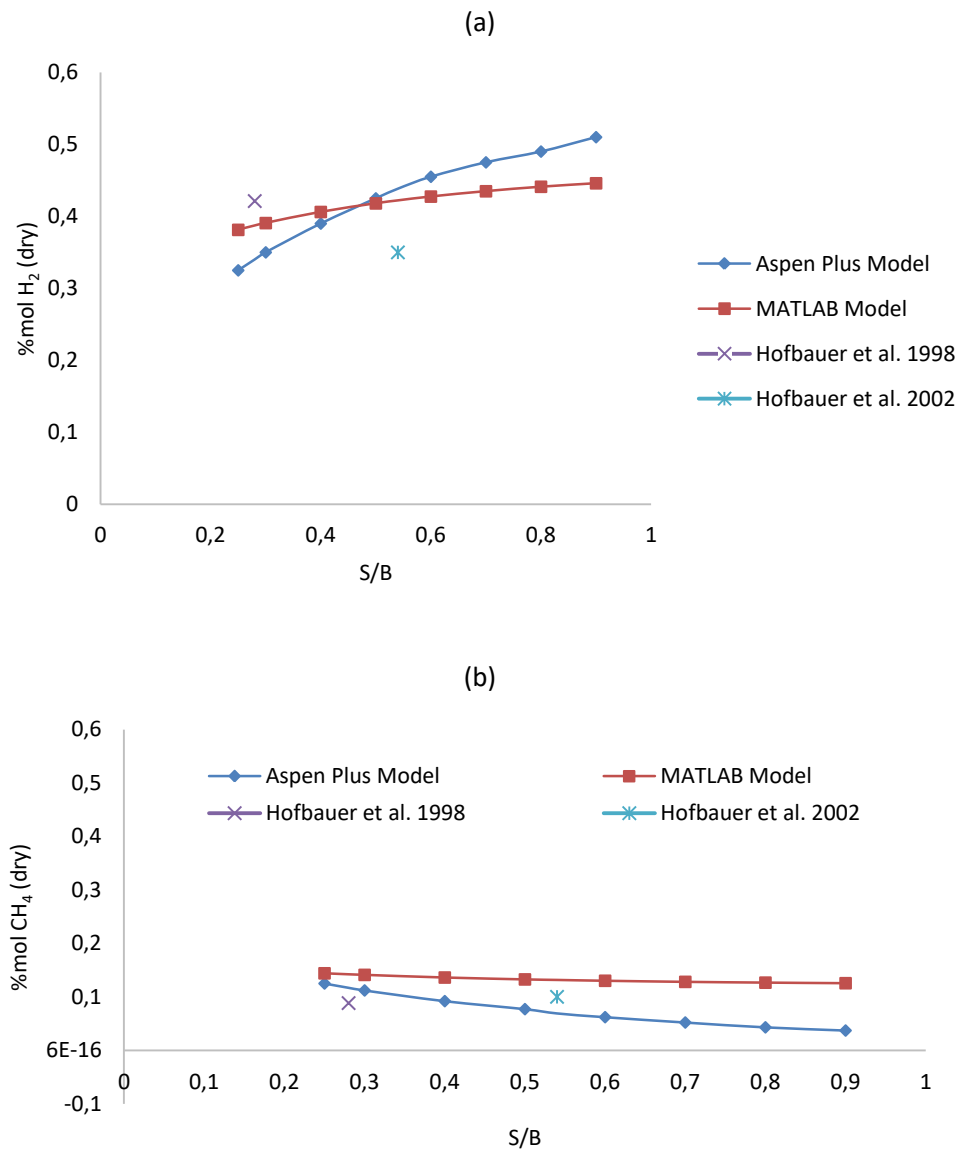
For S/B = 0.5 (kg_{steam}/kg_{biomass,dry}) from the comparison of the experimental values obtained by Hofbauer [264] using 0% of nickel catalyst and quartz as bed material it is possible to observe the good correspondence of the developed models for CH₄, CO and CO₂ (Aspen Plus maximum AE 4 and RE 31%, MATLAB maximum AE 3 and RE 31%). Instead the H₂ is overestimated (Aspen Plus maximum AE 8 and RE 23%, MATLAB maximum AE 7 and RE 21%) mainly because the Aspen Plus model, under equal uncatalyzed conditions, considers equilibrium conditions meanwhile MATLAB overestimates the steam reforming of tars, both factors that increase the H₂ content of the syngas at higher S/B. At S/B 0.5 the LHV, yield and cold gas efficiency are in good agreement (maximum AE -3 and RE +32%), the LHV of the MATLAB model, in this case, is in a better agreement (AE -0.45 and RE -3%) respect to Aspen Plus (AE -2.95 and RE -20.13%) since it considers the reforming of tars.

In order to get the values from Aspen Plus closer to the ones from literature, and reduce the error, it is possible to improve the data-fit of experimental data used for the QET and make a deeper differentiation among the values come from the using of catalyst inside the reactor. Instead, about MATLAB model, in order to reduce the error between simulation values and experimental ones, the key is to improve the data on kinetic constant and residential time, as well as a differentiation among the values come from the using of catalyst inside the reactor.

7.2.3 Sensitivity analysis

Figure 13a–d shows the sensitivity analysis results for each model, varying the S/B ratio from 0.25 to 0.9 and keeping the gasifier temperature fixed at 850 °C. The effect over syngas composition is observed. The absolute and relative error of each of the two models respect to the

reference literature data of Table 26 and Table 27 in S/B equal to 0.25 and 0.5 have been reported in the graphs. A complete analysis of the difference between the Aspen Plus and MATLAB outputs is reported in Table 28.



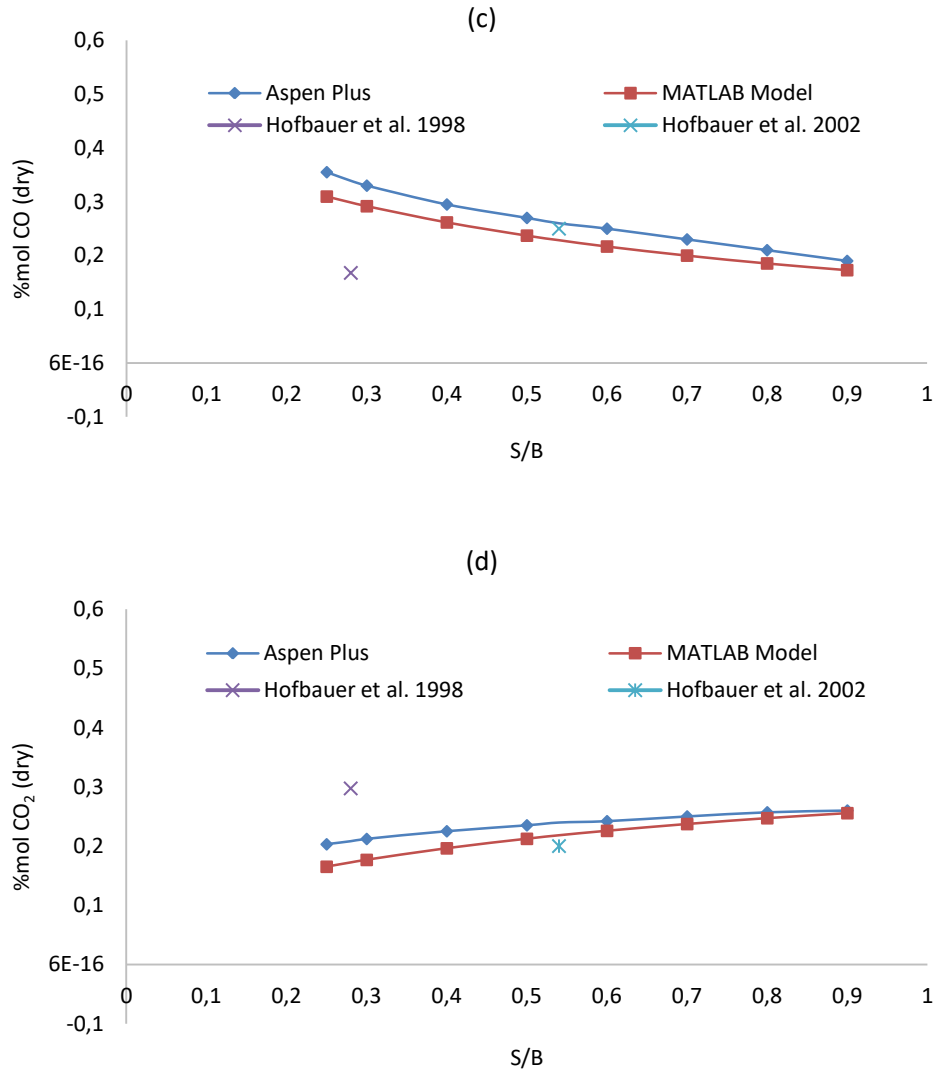


Figure 13 (a–d) - Effect of S/B ratio on syngas **(a)** hydrogen, **(b)** methane, **(c)** carbon monoxide; **(d)** carbon dioxide dry mole fraction.

Table 28 - Absolute error (AE) and Relative Error (RE) between the Aspen Plus and MATLAB model for each S/B operating point. Maximum values (**red**), minimum values (**green**). Mean Absolute Error (MAE) and Mean Relative Error (MRE) over the whole range of S/B.

Error Analysis	AE $ x_{iMATLAB} - x_{iASPEN} $				RE (%) $\frac{ x_{iMATLAB} - x_{iASPEN} }{\bar{x}_{MATLAB,ASPEN}}$			
S/B ($kg_{steam}/kg_{biomass}$)	H ₂	CH ₄	CO	CO ₂	H ₂	CH ₄	CO	CO ₂
0.25	5.63	1.90	4.53	3.79	15.93%	14.13%	13.64%	20.61%

0.3	4.07	2.90	3.82	3.53	10.98%	22.96%	12.30%	18.19%
0.4	1.61	4.41	3.34	2.88	4.04%	38.68%	12.00%	13.68%
0.5	0.70	5.56	3.30	2.28	1.66%	53.04%	13.01%	10.18%
0.6	2.75	6.80	3.32	1.63	6.24%	70.86%	14.23%	6.97%
0.7	4.01	7.60	3.01	1.28	8.81%	84.45%	13.98%	5.27%
0.8	4.89	8.36	2.47	1.00	10.50%	98.57%	12.49%	3.96%
0.9	6.40	8.85	1.72	0.45	13.40%	108.92%	9.46%	1.74%
	MAE				MRE (%)			
<i>S/B (kg_{steam}/kg_{biomass})</i>	H ₂	CH ₄	CO	CO ₂	H ₂	CH ₄	CO	CO ₂
0.25-0.9	3.76	5.80	3.19	2.11	8.95%	61.45%	12.64%	10.07%

The absolute value of the difference between the two outputs is considered since both are modeled quantities and cannot be considered as reference values.

$AE = x_{model} - x_{ref}$; $RE = \frac{x_{model} - x_{ref}}{x_{ref}}$; errors are with sign respect to the median of the reference values.

In order to compare the results of the two models a simple error analysis is taken out evaluating the differences of the estimated syngas composition in relation to the S/B simulated point (Table 28). By comparing only the results of the two models—without a third full reference dataset (which is instead taken out for specific S/B points in Table 26 and Table 27)—the error analysis does not claim to validate the two models for all S/B points, whereas to understand the degree of similarity of the results for the two approaches and, consequently, understand the limits in their applicability in relation to the modelling purpose. The Absolute Error (AE) and Relative Error (RE) between the outputs of the two models in all simulated points are reported in Table 28, together with the mean values of the AE and RE, in order to assess the overall similarity of the datasets along the whole range of the S/B variation.

As shown in Figure 13 (a), the concentration of H₂ increases while steam increases for both models, this is due to the WGS reaction that is favored by the increase of steam. For S/B ratio equal to 0.25, the concentration of H₂ given by the Aspen Plus model is lower than the one given by the MATLAB model, but the yield achieved by Aspen Plus is higher. H₂ grows faster in the Aspen Plus model since it is a thermodynamic model. As shown in Figure 13 (c,d), an increase of the S/B ratio results in an increase of CO₂ and in a decrease of CO, this can be explained by the influence of the WGS reaction that consumes CO and produces CO₂. In fact, even though the WGS is disadvantaged by high temperature respect to the steam-methane reforming (SMR) reaction which is instead

favored at high temperature, we should be considered that the quantity of reagents in the WGS reaction are significantly higher compared to the ones of the SMR reaction. So, it is true that the constant of equilibrium of the WGS reaction is lower than the one of the SMR reaction at 850 °C but, since the quantity of reagents of the WGS reaction are higher, the WGS is the reaction that dominates the trends of CO and CO₂. Figure 13 (b) reports a clear reducing trend of CH₄, as the steam increases, following the SMR reaction. The reduction of the methane in the Aspen Plus model is greater than the one in the MATLAB model with increasing S/B because, being the Aspen Plus a thermodynamic model, it neglects the residence time (more CH₄ is converted). Similar trends were reported in literature references [58,255]. High values of RE for CH₄ can be justified due to its low molar fraction. The maximum Relative Error can reach 108.92% although in that operating point (S/B = 0.9) the CH₄ molar fraction is quite low (0.04 for Aspen Plus and 0.12 for MATLAB) with an AE equal to 0.08, which is acceptable. The overall error analysis shows that the MAE is between 2.11–5.80 for all syngas components. For H₂, CO and CO₂—which present higher molar fractions (>0.15 mol/mol_{syngas})—the MRE is contained between 8.95% and 12.64%. The CH₄ prediction instead is affected by a larger MRE of 61.45% which is however acceptable, for plant analysis purpose, since the absolute molar fraction is low (0.03–0.15 mol_{CH4}/mol_{syngas}).

7.3 Analysis of the developed gas cleaning model

Considered that the stream BIOMASS of Figure 8, made by hazelnut shells, has a constant flow rate (m_{bio}) set to 180 kg/h (1 MWth input size, considering HHV), and considering that the reactor DECLOR and DESULPH are set at 550 and 450 °C respectively, the composition of the syngas out of by the gasifier, the bed gas cleaning reactor , the candle filter and the HCL removal reactor is shown in Table 29.

Table 29 - Composition of the syngas (streams are referred to Figure 8)

Component	Out of the gasifier (stream S8)	Out of the bed gas cleaning DOLOMITH (stream S10)	Out of the candle filter CANDLE (stream S12)	Out of the decholoration DECLOR (stream S27)
H ₂ (%wet mole fraction)	31.3	31	38	42
CO (%wet mole fraction)	15	14	17	18
CO ₂ (%wet mole fraction)	18.5	16.5	15	17
H ₂ O (%wet mole fraction)	30	28	20	22
CH ₄ (%wet mole fraction)	4.6	4.3	4	0.4
NH ₃ (ppm)	1200	50	48	48
H ₂ S (ppm)	2134	290	280	280
HCl (ppm)	976	120	110	0.25
C ₆ H ₆ (g/Nm ³)	13	5.9	0.065	0.065
C ₇ H ₈ (g/Nm ³)	4.5	0.8	0.039	0.039
C ₁₀ H ₈ (g/Nm ³)	6.3	1.2	0.09	0.09

As shown in the last column of Table 29, the only contaminant up to the limit value reported in Table 7 for the most common syngas applications is the H₂S. In fact, toluene, benzene, naphthalene and NH₃ have been reduced to the desired levels in the primary catalyst (block DOLOMITH) by means of dolomite, while HCl has been reduced in the alkali-sorbent based reactor DECLOR. The reduction of the hydrogen sulphide, using the sorbents shown in Table 8, by means of the DESULPH reactor is reported in Table 30 (in which each sorbent is considered at its higher stability temperature). All the values of the other components remain unaltered.

Table 30 – Effect of H₂S adsorption by different sorbents

Sorbent type	Sorbent flow rate (kg/h)	Sorbent temperature (°C)	H ₂ S level (ppm) in the stream S13
Cerium oxide	1.300	600	0.8
Copper oxide	0.530	600	0.8
Manganese oxide	0.299	600	0.8
Zinc oxide	0.289	450	0.8
Iron oxide	0.265	600	0.8

As shown in Table 30, it has been evaluated, from sorption capacity shown in Table 8, the flow rate of each sorbent needed for lower the amount of H₂S under 1 ppm at the reference temperature chose within the temperature range showed in Table 29. In this way, out of the DESULPH block all the contaminants are under the limits.

7.3.1 Effect of steam on sulfidation of a metal oxide

According to equation (10), a higher steam concentration reduces the extent of sulfidation of a metal oxide. This issue, in literature, is rarely studied; there are a lot of publications that focus on sulphur sorbents for dry syngas cleaning, but not so many that involve sorbents for cleaning syngas at high steam concentration. In the present study this aspect has been taken into account and in Figure 4 the sensitivity analysis is shown that is carried out on zinc oxide (similar trends have been obtained for the other metal oxides under investigation) while varying the steam concentration. The H₂S removal efficiency, reported in the y-axis of Figure 14 and Figure 15, has been evaluated as:

$$H_2S_{removal\ efficiency} = \frac{H_2S\ in\ the\ stream\ S21 - H_2S\ in\ the\ stream\ 13}{H_2S\ in\ the\ stream\ S21} \quad (32)$$

The study demonstrates that the conversion of H₂S lowers with the increase of moisture content and confirm the high steam content of syngas as a compelling challenge in sorbent material advancement.

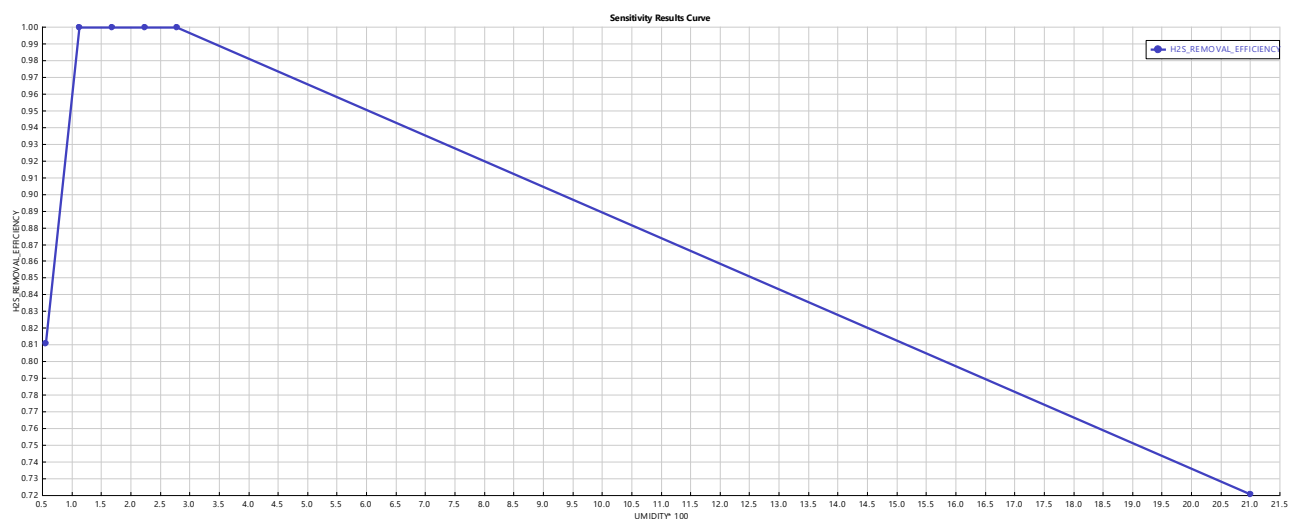


Figure 14 – Result of sensitivity analysis of H₂S concentrations respect to steam content in syngas

In the case of zinc oxide, it has been shown that it is able to reach close to 100% H₂S removal for syngas containing steam between 1.5% and 3%.

7.3.2 Effect of temperature on sulfidation of a metal oxide

A sensitivity analysis, on the influence of temperature on the sorbent capacity to adsorb hydrogen sulphide, has been carried out. The analysis reveals similar trends for each sorbent considered in this paper and it has been chosen to report only the behaviour of zinc oxide (in its temperature range) as representative. The result is shown in Figure 5 and demonstrates that the temperature has a negative impact on the H₂S conversion.

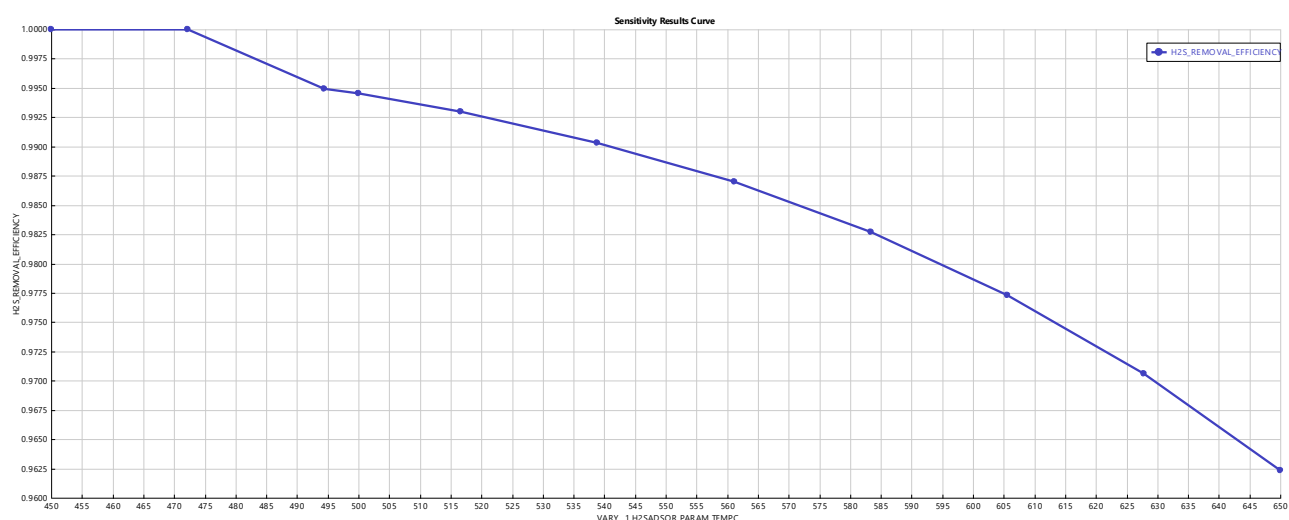


Figure 15 - Result of sensitivity analysis of H₂S concentrations respect to temperature

In the case of zinc oxide, the maximum conversion of H_2S is achieved at temperatures between 450° and 470°C . The trend is in line with the expected results, since $K_{eq, \text{H}_2\text{S}}$ decreases with the increase of temperature and both chemical and mechanical degradation disrupt the thermal stability of metal oxides at the higher end of the temperature ranges [232].

7.4 Analysis of the developed SOFC model

The cold gas efficiency η_{CG} of the whole system is evaluated as

$$\eta_{CG} = \frac{LHV_{syngas} \cdot m_{syngas}}{LHV_{biomass} \cdot m_{biomass}} \quad (33)$$

and it's equal to 0.79.

The thermal energy balance reveals that the power heat needed by the combustor is 367 kW, so a *Design Specs* has built in order to split the stream S25 and provide the required power heat to the COMBUST by means of the stream S26.

7.4.1 Effect of S/B ratio

Figure 16 shows the effect of the *S/B* ratio on the electrical efficiency of the SOFC and Figure 17 shows the effect of *S/B* ratio on the current density (A/m^2) j_{cell} . Increasing steam to biomass ratio affects negatively the efficiency and increases the current density, thanks to the modification in anode temperature and gaseous component partial pressure, which reduces the Nerst voltage and rises the voltage losses. For this reason, is preferable to operate at low *S/B* ratio. The cell voltage is calculated using the Nerst equation. i_{cell} is the current (A) that is calculated by $i_{cell} = 4 \cdot F \cdot n_{O_2,required}$. j_{cell} is the current density (A/m^2) $j_{cell} = \frac{i_{cell}}{A_{cell}}$. Power density is given by the multiplication of V and j_{cell} . The cell electrical efficiency is then calculated according to

$$\eta_{el} = \frac{\text{Current (A)} \cdot V \text{ (V)}}{n_{syngas}(\text{mol/s}) \cdot LHV_{syngas} \text{ (J/mol)}} \quad (34)$$

$n_{syngas} \left(\frac{mol}{s} \right)$ and $LHV_{syngas} \left(\frac{J}{mol} \right)$ are the input flow rate and LHV of the syngas feeding the SOFC.

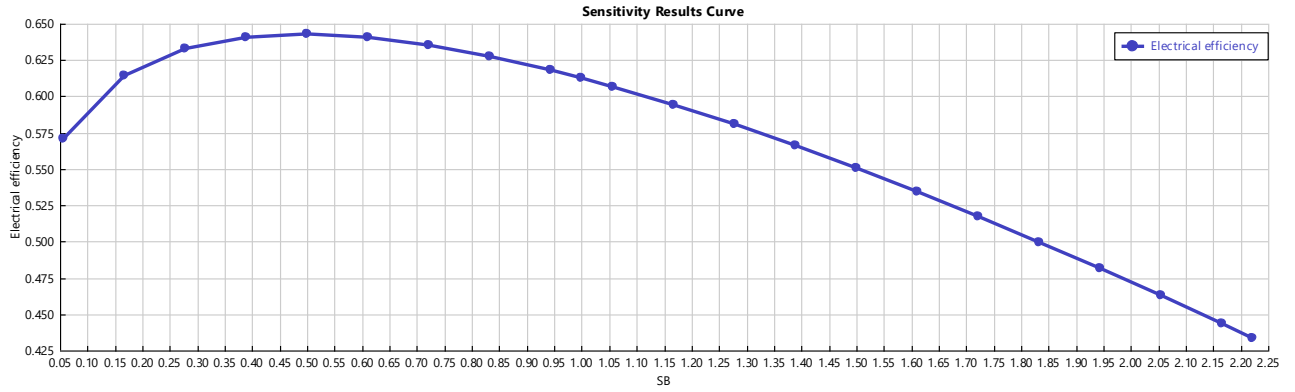


Figure 16 – Effect of S/B ratio on electrical efficiency

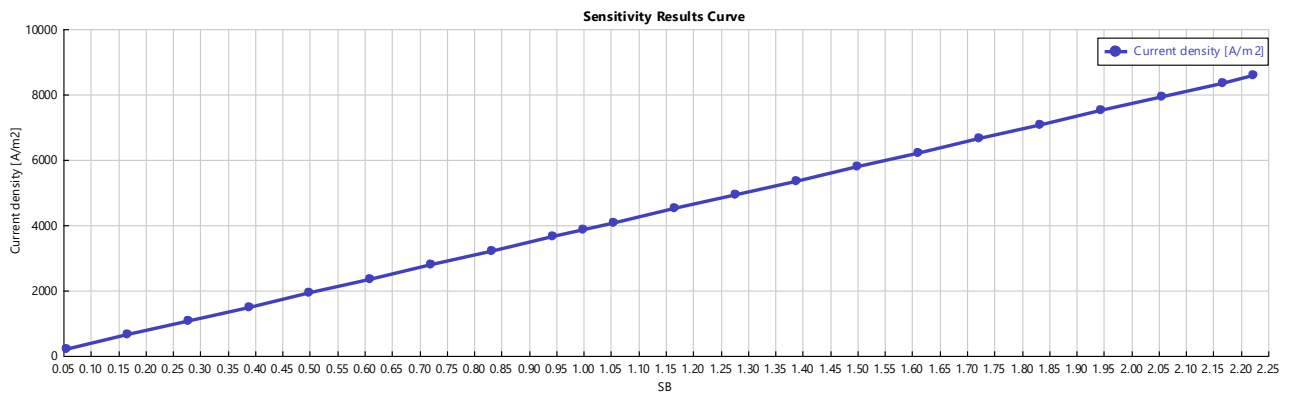


Figure 17 – Effect of S/B ratio in current density.

At the S/B ratio using for the simulation ($S/B=0.5$), the electrical efficiency achieves with the SOFC is 63%.

7.4.2 Effect of current density

Figure 18, Figure 19 and Figure 20 show the effects of varying current density j_{cell} on the system. Increasing j_{cell} decreases voltage and electrical efficiency but increases power until a peak, then power decreases. The descending trend of the cell voltage showed in Figure 6 is due to higher voltage losses (ohmic, activation and concentration). The reduction of the electrical efficiency with current density is shown in Figure 20. The trends obtained from the sensitivity analysis are in good agreement with literature ones [82,83].

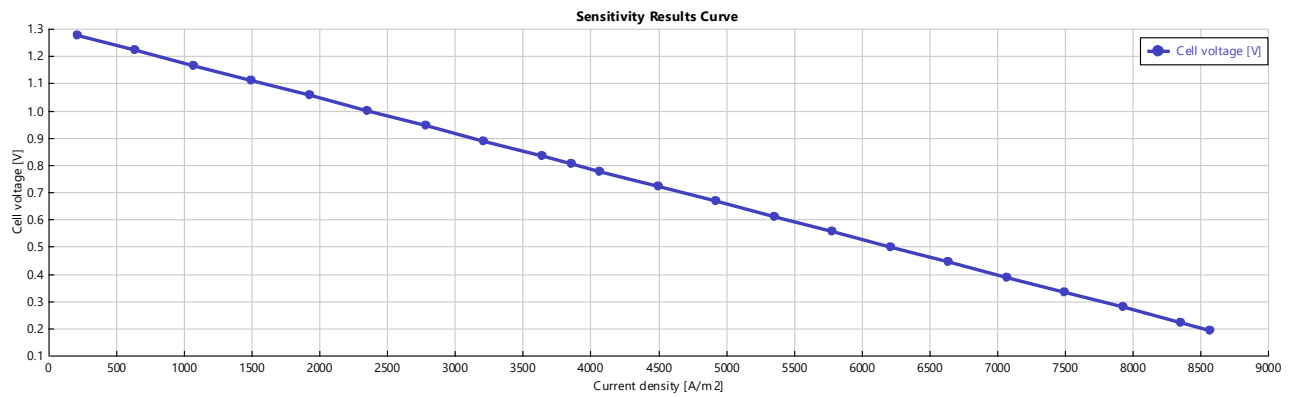


Figure 18 – Effect of current density on cell voltage

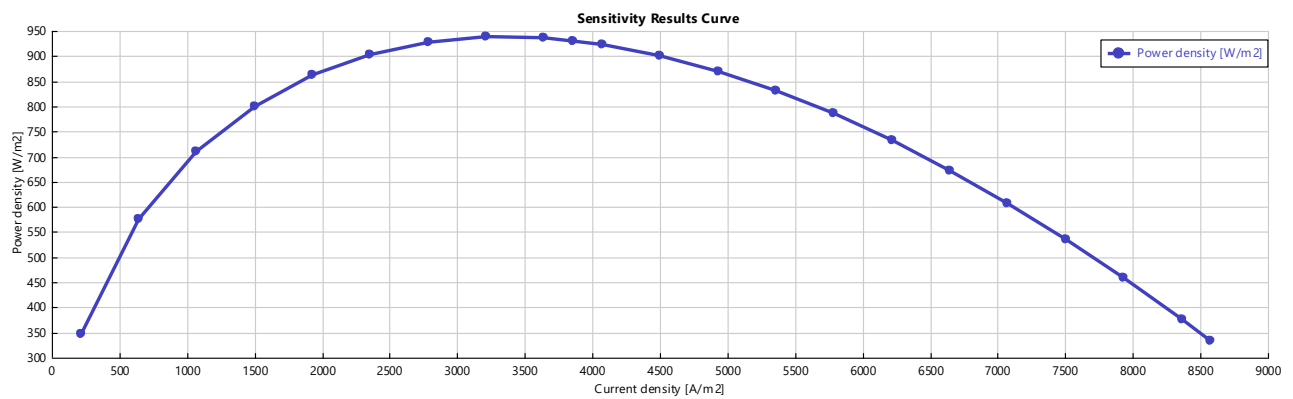


Figure 19 - Effect of current density on power density

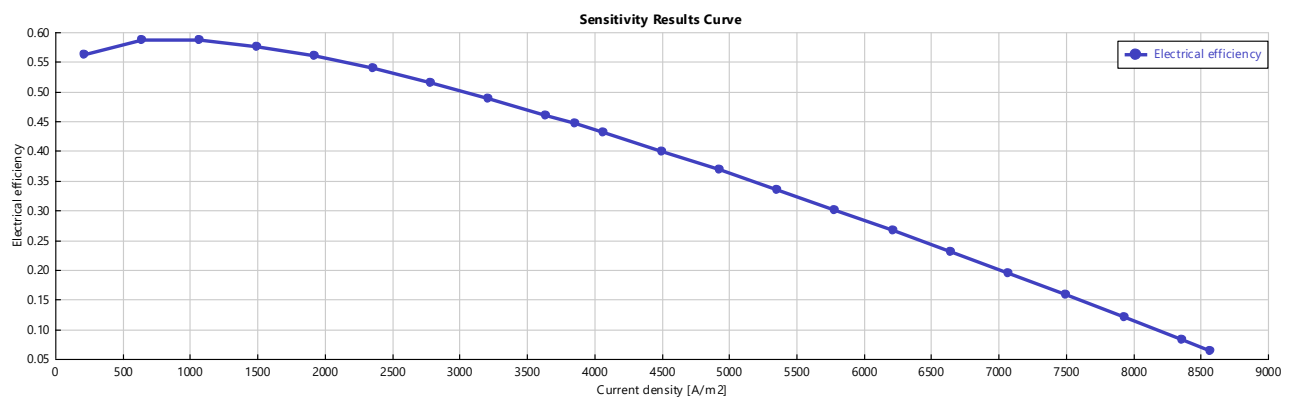


Figure 20 – Effect of current density on electrical efficiency

A typical operating current density range is 1800-2000 A/m² [266], corresponding to a cell voltage of 1.1 V a power of 850 W/m² and an electrical efficiency of 57%.

7.4.3 Influence of CO concentration and air flow rate on SOFC power production

A sensitivity analysis on the SOFC power production, varying the inlet air and the mole fraction of CO inlet to the ANODE block, is carried out. As shown in Figure 21 increasing the concentration of CO allows to increase the SOFC power (Q-net SOFC, in the y-axis) produced. In fact, according to equation (16) more CO favours the water-gas shift reaction, that is an exothermic one. This means that the cell requires less heat duty and can give more.

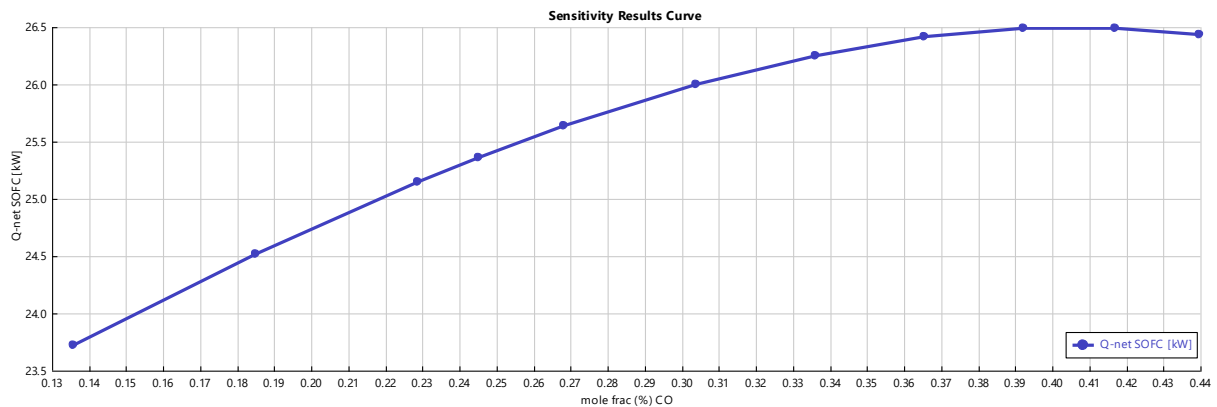


Figure 21 – Influence of CO concentration on SOFC power production

In Figure 22 is reported the trend of SOFC power production respect to the mass flow of air to the cathode. The increasing in air mass flow corresponds to an increase in power production.

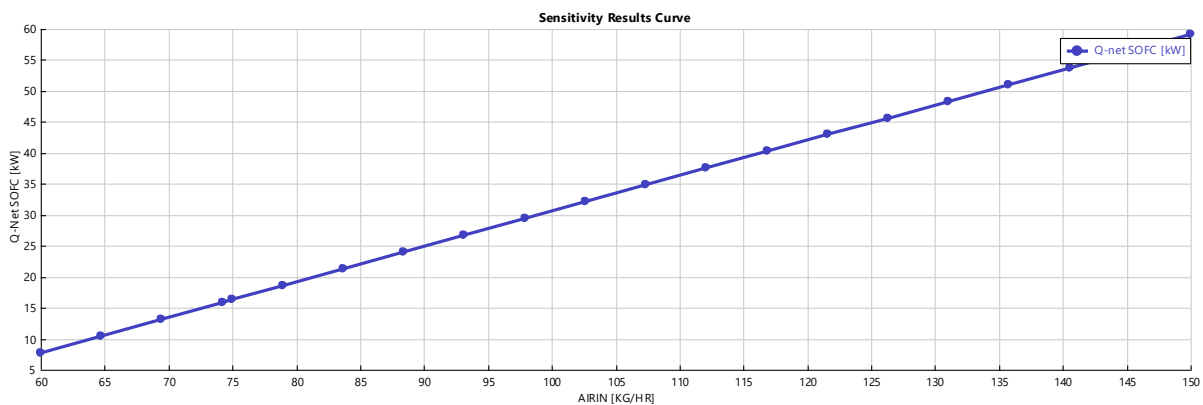


Figure 22 - Influence of air flow rate to the cathode on SOFC power production

Considering concentration of CO equals to 20% (see Table 10) and flow rate of 90 kg/h for the air into the cathode, the SOFC power production is around 25 kW.

8 Other applications

The developed gasification and gas cleaning model can be used coupled to a huge variety of system, not only with SOFC, as deeply investigated until now in this thesis. In fact, the gas cleaning chain developed is able to low the contaminants under the limits for the most common applications (see Table 15 and Table 16).

So, in order to demonstrate the feasibility of the model, in this chapter, it is coupled with a Steam Inject micro Gas Turbine (SImGT) and with an Organic Rankin Cycle (ORC).

8.1 Materials and Methods

The subsystems are modelled considering the practical requirements and characteristics of the main components, which results in a realistic calculation of the net performance of the integrated system: (i) a 600 kWth of biomass input gasifier; (ii) a Turbec T-100 mGT with nominal electric power and thermal output of 100 kWel and 155 kWth respectively; and (iii) a regenerative ORC unit with a nominal rated power of 10 kWel/100 kWth. The purified syngas is then burnt in the combustion chamber of the mGT, and the flue gas expands in the turbine to produce electricity. Eventually, the flue gas of the mGT unit is mixed together with those from the gasifier combustor and recovered in the evaporator of the ORC system to produce additional electric power. Figure 23 shows the schematic configuration of the integrated system together with the main design temperature and pressure values that are inputs to the model.

flow rate of the input water corresponds to the sum of the of process steam mass flow rate calculated based on the steam-to-biomass ratio (S/B) and the mass flow rate of the steam that is injected into the combustion chamber. Therefore, depending on the working conditions of the gasifier and the SImGT unit, the mass flow rate of the water is varied leading to fluctuations of temperatures of the flue gas streams. In turn, these fluctuations affect the thermal and electrical power production of the mGT and the bottom ORC unit.

8.1.1 SImGT and HRSG unit

To include the realistic performance of the mGT unit, Turbec_T100 is considered as mGT unit. and the following main components included into the model: (i) a centrifugal compressor; (ii) a single-shaft radial turbine; (iii) a regenerator; and (iv) a combustion chamber. Table 31 below reports the nominal performance of the mGT unit fuelled by natural gas (NG) [267,268].

Table 31 – Nominal performance of Turbec_T100 fuelled by NG*

Net Electrical Power	100 kW $\pm$ 3 kW	Turbine inlet temperature	950 oC
Thermal Power	155 kW $\pm$ 5 kW	Turbine outlet temperature	650 oC
Fuel consumption (NG, LHV = 49 MJ/kg)	24.5 kg/h	Exhaust gas temperature	270 oC
Electrical Efficiency	30 % $\pm$ 1 %	Compressor outlet temperature	214 oC
Nominal mass flow rate	0.8 kg/s	Shaft rotational speed	70000 RPM
Turbine efficiency	0.826	Pressure in combustion chamber	4.5 bar
Compressor efficiency	0.768	NOx and CO emissions	<15 ppmv at 15 % O ₂

*Data based on ISO standard conditions of ambient pressure and temperature and relative humidity of 101.3 kPa and 15 oC and 60 % respectively, neglecting pressure drops at the inlet and exhaust.

In this study, the mGT is supposed to be fuelled by the syngas produced by the gasifier unit while steam injection is considered to improve the overall electric power production of the system. In

order to include the off-design behavior of the mGT in the simulation, the performance curves of the compressor and the turbine have been taken from the mathematical models developed by Wang and Cai [269], as carried out also in other studies [7,270]. More precisely, Figure 24 shows the characteristic curves, in terms of reduced pressure ratio $\dot{\pi} = \pi/\pi_0$ and reduced efficiency $\dot{\eta} = \eta/\eta_0$, of both the compressor and the turbine with reduced mass flow rate $\dot{G} = (G\sqrt{T_{in}/P_{in}})/(G_0\sqrt{T_{in,0}/P_{in,0}})$, for different reduced rotational speeds $\dot{N} = (N/\sqrt{T_{in}})/(N_0/\sqrt{T_{in,0}})$ (where 0 indicates the design values presented in Table 31). On the contrary, the mechanical efficiency of the turbine is fixed to 95% for all the operating conditions.

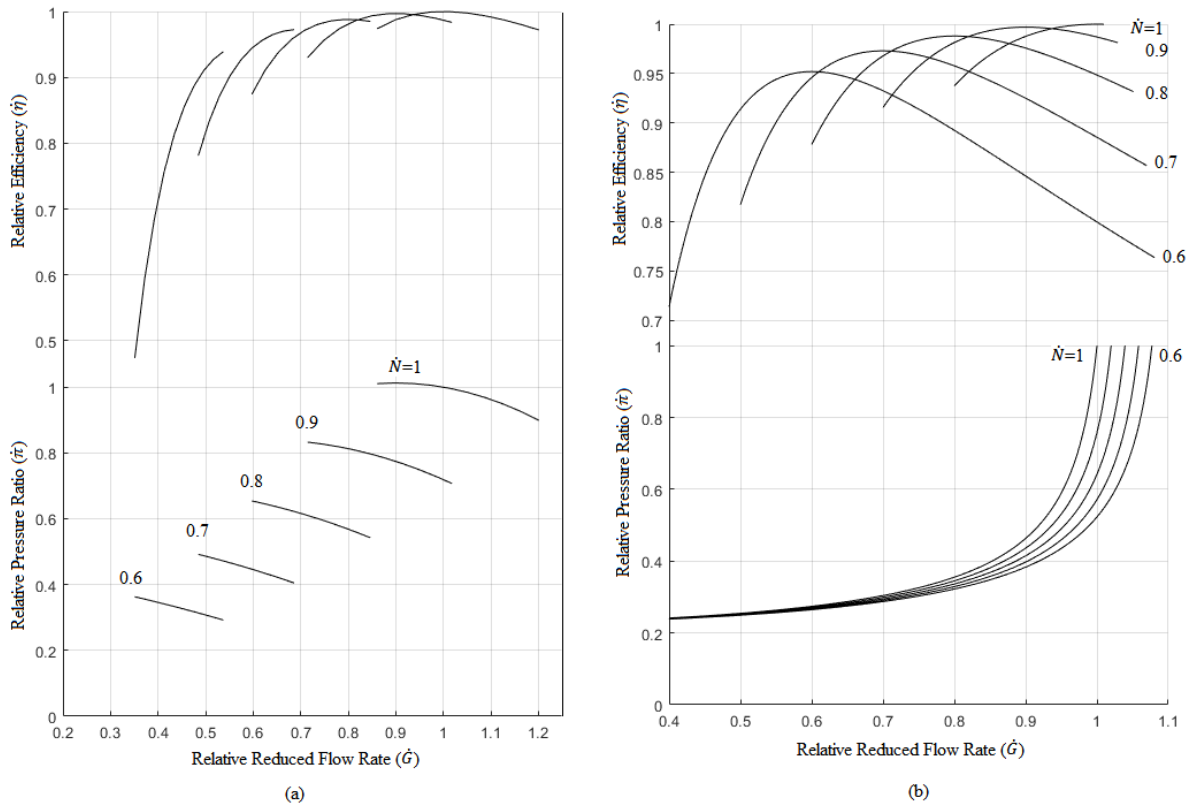


Figure 24 - Characteristics curves of a) compressor, b) turbine

In a Steam Injected micro Gas Turbine (SImGT) the total inlet mass flow rate to the turbine is equal to the sum of the compressed air, the injected steam and the fuel mass flow rates. As it is evident from Fig. 2, at nominal operating conditions the turbine works close to the choking condition; as a consequence, in a SImGT, the inlet mass flow rate at the compressor is reduced to avoid a choked flow in the turbine. On the other hand, this reduction needs to be limited to prevent compressor surge.

More precisely, in the present model for a given mass flow rate of the injected steam, the mass flow rate of the fuel (syngas) is calculated by keeping fixed the inlet temperature of the turbine (outlet temperature of the combustion chamber) at 950 °C.

In addition, in order to predict the effect of the injected steam on the overall emissions of the mGT, the most relevant reactions in the combustion chamber have been included into the model. However, such emissions do not depend only on the relative mass flow rate of the steam and of the syngas, but also on many other parameters such as: the LHV of the syngas, the geometry of the combustion chamber, the turbulence effects, the interaction between the steam and the fuel-air mixture and the local position of the steam injectors with respect to the flame [271]. As a consequence, zero-dimensional models are not able to properly predict the impact of steam injection on the mGT emissions. Therefore in this study the results of the 1-D model of the syngas-fueled combustion chamber of the same mGT unit proposed by Renzi et al. [271] are considered thus taking into account the influence of the steam on the overall system emissions.

Eventually, as regards the fuel compressor, its isentropic and mechanical efficiencies are assumed equal to 85% and 95% respectively, whilst the power consumption of the water pump is neglected.

8.1.2 Organic Rankin Cycle

According to Clemente et al. [272], who investigated the performance of an ORC system coupled with a 100 kW_{el} mGT with different working fluids, Isopentane, Isobutane and R245fa revealed to be the most suitable fluids. Moreover, in a previous study Vera et al. [72] proved that Isopentane allows to achieve the maximum thermal efficiency and electricity production in case an ORC unit is used as the bottom power cycle of a syngas fueled gas turbine. However, this fluid is a highly flammable, and the performance of the ORC system does not reduce so much when R245fa is adopted. Therefore, in this study, R245fa has been considered as the working fluid considering its widespread adoption in small-scale low-temperature ORC systems.

As regards the proposed ORC unit, it works according to regenerative cycle at pressure lower than 20 bars. In particular, the mass flow rate of the working fluid is adjusted according to the mass flow rate and the inlet and outlet temperatures of the hot stream (the flue gas from the mGT unit) at the evaporator. The minimum outlet temperature of this flue gas is fixed to 110°C to prevent any condensation of the water and corrosion issues at the exhaust. Hence, any change in the mass flow rate of the water in the HRSG unit results in variations of the mass flow rate and the performance of the bottom ORC unit.

Table 32 represents the main design parameters of the ORC unit. To protect the pump from two-phase flow, a sub-cooling of 5 °C is considered at the condenser. Moreover, a temperature difference between the cooling water inlet and the saturation temperature of R245fa at the condenser is considered equal to 30 °C, which because of thermodynamic properties of R245fa, it results in a pressurized condenser that is advantageous for its operation.

Table 32 – Design parameters of the ORC system

Organic Fluid	R245fa	Expander isentropic efficiency	60 %
Regeneration efficiency	67 %	Pumps (for organic fluid and water) isentropic efficiency	70 %
Super-heating at the turbine inlet	10°C	Expanders and pumps mechanical efficiency	90 %
Sub-cooling at the pump inlet	5 °C	Maximum pressure	20 bar

8.2 Results and discussion

Figure 25 shows the trend of the net work and efficiency of the integrated system and the produced thermal load in the condenser of the ORC unit (CHP) with varying S/B ratio for 15 g/s mass flow rate of injected steam. As can be seen, both the net work and the efficiency reduce slightly at higher values of S/B (>0.75), while the available thermal power for CHP decreases significantly. Indeed, at higher values of the S/B ratio, the reduction of the system overall performance is caused by the higher thermal energy consumption for steam production. Therefore, higher mass flow rate of the process steam is negative for the performance of the integrated system, and it should be fixed to the minimum amount required by the gasification process.

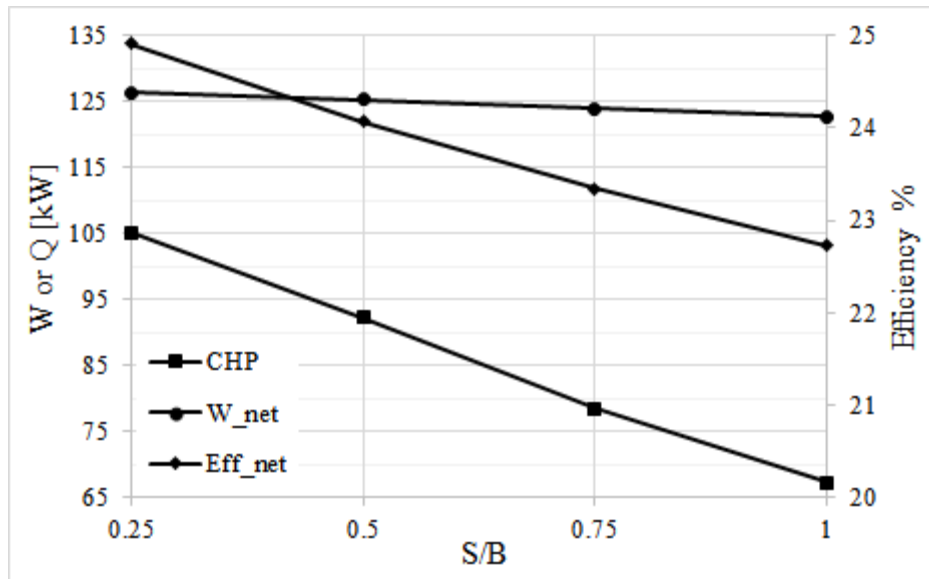


Figure 25 - Performance of the integrated system fed by syngas at different S/B with constant mass flow rate of the injected steam at 15 g/s

The main advantage of higher S/B values is the less tar content in the raw syngas that is very important feature of any biomass fed power system. Indeed, tar is one the most critical issues of a gasification system since it can clog the equipment of the system thus causing its shutdown. Therefore, the optimum value of the S/B depends on many different parameters such as the biomass type, the gasification agent and gasifier type.

Figure 26 shows the variations of the mass flow rate of air (in the main compressor) and of the fuel (biomass) with the mass flow rate of the injected steam into the combustion chamber. In the range of the mass flow rate of the injected steam reported in the Figure 8, the reduction of the air mass flow rate in the compressor does not cause its surge, so the rotational speed of the compressor (and also of the turbine) can be kept at nominal values (about 70,000 RPM). On the contrary with the mass flow rate of air, the mass flow rate of fuel is increased to maintain the inlet temperature of the turbine at the design value. Figure 26 also shows that the mass flow rate of the turbine is almost constant thus proving that the turbine works close to the choked conditions very similar to its nominal operation.

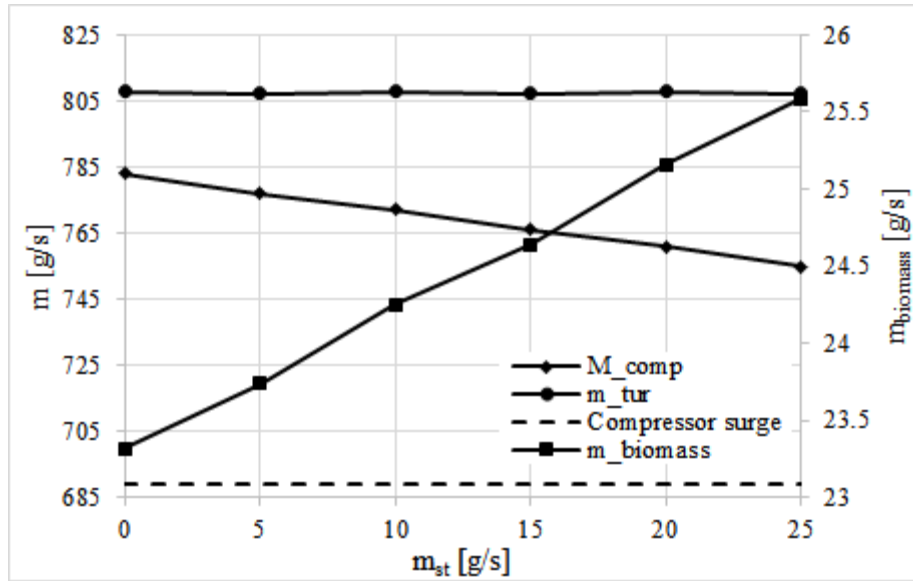


Figure 26 - Mass flow rate of compressor, turbine and the syngas via the mass flow rate of the injected steam at $S/B = 0.5$

Figure 27 presents the performance of the integrated system and its sub-units for $S/B = 0.5$ with varying mass flow rate of the injected steam in terms of net output power of the mGT (W_{mGT}), of the ORC unit (W_{ORC}), of the mGT+ORC (W_{net}), the thermal power output from the ORC unit (CHP), and the overall efficiency of the whole system. It is evident that steam injection increases the net power of the mGT because of the higher mass flow rate in the turbine and the lower mass flow rate in the compressor compared to the standard operation of the mGT. However, the net efficiency of the system is penalized because of the increase of the mass flow rate of the fuel. Furthermore, the available CHP power is decreased revealing the fact that steam generation reduces the available energy at the bottom ORC unit. In summary, steam injection increases the net power production with minor degradation of the net efficiency, and significant drop of the CHP thermal output.

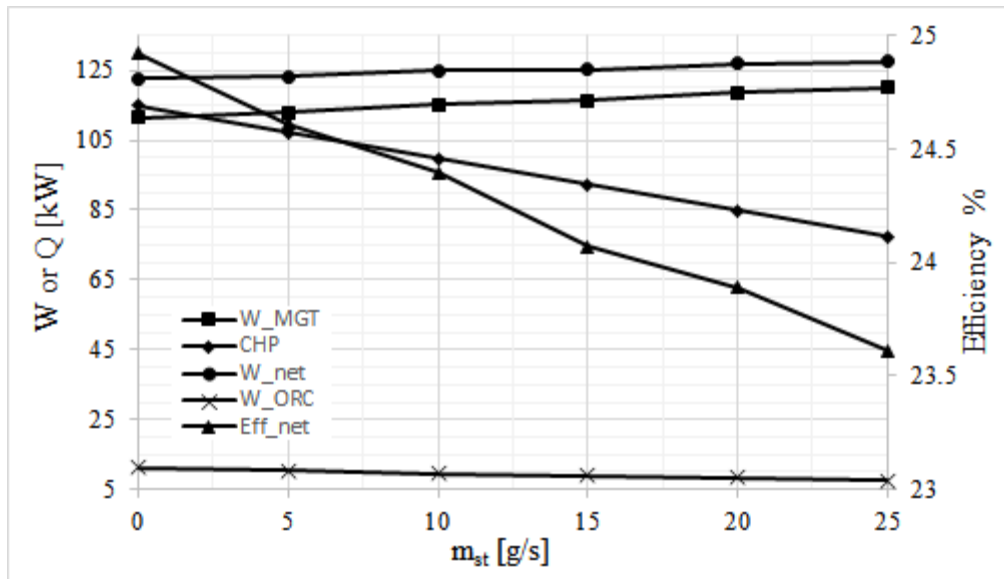


Figure 27 - Performance of the integrated system fed by syngas at different mass flow rates of the injected steam at $S/B = 0.5$

The integrated system is simulated when it is fuelled by NG to investigate the effect of the fuel type on its performance. Trends of the mass flow rates are similar in both cases by comparing Figure 28 and 30. Furthermore, even though the mass flow rate of air is decreased more with biomass fuel than with NG, the compressor does not meet the surge line in neither cases and the rotational speed of the shaft is remained at the nominal values of about 70000 RPM for all the operating conditions.

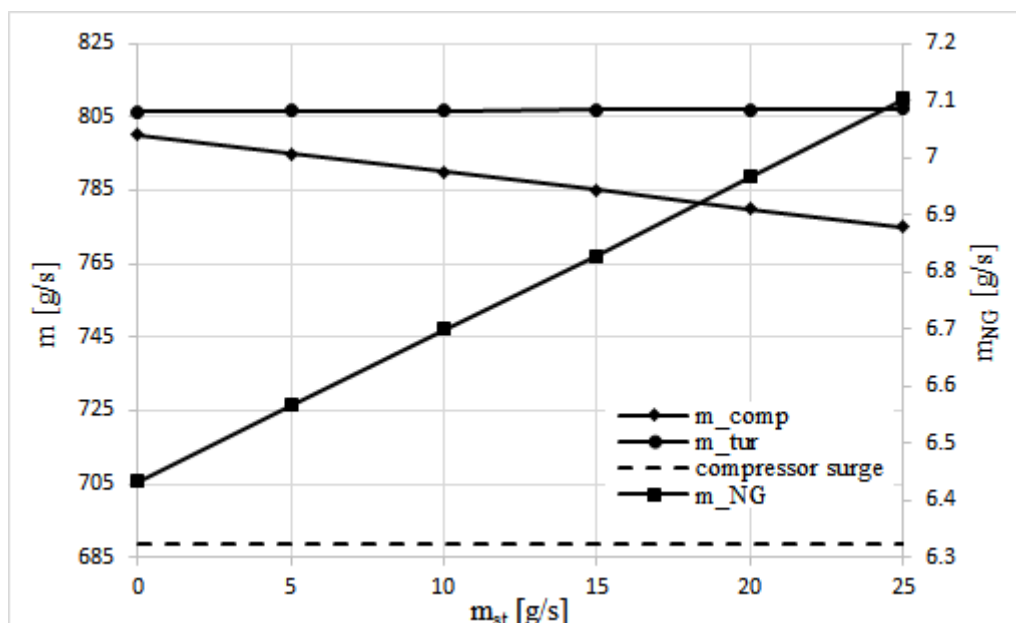


Figure 30 - Mass flow rate of compressor, turbine and NG via the mass flow rate of the injected steam

Performance of the system fuelled by NG is shown in Figure 31. It can be noticed that the performances of the biomass-fuelled SImGT, especially the overall electric efficiency, are reduced compared to the SImGT fed by NG. However, the role of the bottom ORC unit becomes more important when syngas is the fuel because of the increase of both the net work of the ORC unit and thermal power of the CHP.

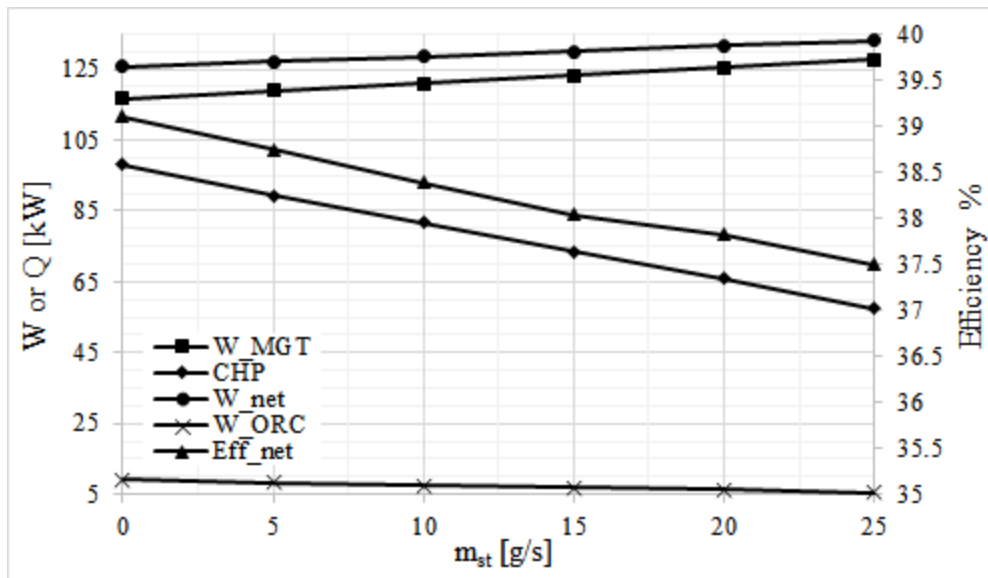


Figure 31 - Performance of the integrated system fed by NG at different mass flow rates of the injected steam

By comparing the performances of the proposed integrated system with those of similar systems reported in literature it can be observed that, despite the absence of a bottom ORC unit, Renzi et al [271] reached an overall electrical efficiency higher than those reported in other works. In their study, authors used the exhausts from the turbine to only produce the steam for the mGT. In this work, instead, also the auxiliary fuel consumption that is required by the gasifier and the fuel booster energy consumption are included in the calculation of the efficiency. Furthermore, Renzi et al [271] considered a more than double (56 g/s) mass flow rate of the injected steam, and do not clearly report the type of the gasifier and the LHV of the biomass used in their calculations.

As regards the adoption of the bottom ORC unit, its positive impact is more appreciable in other works. This is mainly due to the small-size of the top mGT system considered in this study compared to the other integrated systems. Table 33 reports a summary of the performances comparison of the proposed system with those of similar works reported in literature.

Table 33 – Comparison of the performance of the system in this study with relevant systems in literature

Performance parameters	Gasifier + SImGT ORC (present work)	Gasifier + EFGT ORC [72]	Gasifier + ICE cascade ORC [273]	Gasifier + ORC [274]	Gasifier + SImGT [271]
Gasifier type	Fluidized bed	downdraft	downdraft	Biomass furnace (direct combustion)	n.a.
Biomass type	Hazelnut shell	Olive tree pruning	Spruce chips	n.a.	Forestry residual
LHV of biomass (MJ/kg, dry)	18.727	16-18	n.a.	n.a	n.a.
Biomass consumption (kg/h)	92	217	250.1	3600	n.a.
Top cycle net power (kW)	120.12	150.2	298.3	1383	–
ORC net power (kW)	7.5	57.1	40 ^a , 31 ^b	700	–
Net power (kW)	127.6	207.3	369	2083	129.4
Exhaust temperature (°C)	110	290	527.6 ^a	400	–
ORC working fluid	R245fa	Isopentane	R123 ^a , R245fa ^b	Toluene	–
ORC efficiency (%)	8.7	20.4	14.6 ^a , 5.8 ^b	19	–
Overall efficiency (%)	23.6	20.7	28.3	23	28.5
Overall efficiency without ORC cycle (%)	22.2	15.3	22.9	15.3	–

^a upper cycle of the cascade

^b lower cycle of the cascade

9 Conclusions

In the last decades, biomass gasification technology has been established as a viable technique for the conversion of many solid biomass residues in valuable syngas that can generate electricity and heat via cogeneration devices as combustion engines, turbines or fuel cells, or produce biofuels or chemicals. In order to optimize gasifier design and its operation with minimal temporal and costs, models that do not require specific information on the dimensions, capacity and structure of the reactor, but at the same time, that can give accurate descriptions of syngas composition are needed. Quasi-Equilibrium Temperature models seem to provide an answer to this problem, but there is no model in literature that encompasses air/steam/oxygen gasification including inorganic (hydrogen sulphide, hydrogen chloride and ammonia) and organic (toluene, benzene and naphthalene) contaminants. In order to develop a model that can be applied to almost all the combination of oxidizing agents a Data-Fit of experimental data carried out with several gasifying agents (steam, air, oxygen or a mix of these) has been taken from literature. The model has been validated using the most abundant lignocellulosic waste (here hazelnut shell) and the most used oxidizing agents (S/B ratio at 0.4 and 0.8; steam at 0.5 and ER at 0.2; S/B ratio at 0.4 and oxygen to biomass ratio at 0.36) showing good correlation between simulative and experimental data. The maximum value of discrepancy for the hydrogen concentration, that is the main component of the gasification gas, is of 16.3%. Also, the sensitivity analysis has showed similar trends to the ones reported in literature. Thus, the model can be used to simulate composition and contaminants of different gasification processes without taking into account specific information on the dimensions, capacity and structure of the reactor but, nevertheless, being able to have results not too much different from experimental ones. Then, models to predict the behaviour of an innovative hot gas cleaning and conditioning system, constituted by a combination of catalyst sorbent inside the gasifier reactor and catalysts in the freeboard for tar removal and a subsequent sorbent reactor for H_2S and HCl removal have been developed. The main purpose was to study the performance of this innovative system, able to remove contaminants such as tars, H_2S , NH_3 and HCl from syngas through catalytic methods, varying operative conditions, such as temperature and steam content to find the best combination. The developed simulation model allows for obtaining, for each contaminant, values below the limit for the main commercialized applications. More attention had been paid to hydrogen sulphide removal, the most utilizing metal oxide sorbents had been introduced and their amount for the removal of the H_2S and trend respect to steam content and

temperature was studied. For the zinc oxide, the best configuration calculated, that allows to removal near the 100% of H_2S , is around 2% of humidity and 460°C .

Then, a SOFC model has been coupled to the model utilizing existing ASPEN Plus functions and unit operation blocks without using external subroutines, this allowed to reduce complexity and ensure short computational times. A sensitivity analysis was carried out in order to evaluate the influence of current density and steam to biomass ratio on the system. Investigation revealed that is preferable to work at low S/B ratio in order to inhibit CO_2 formation in the exhausted gas and to have higher electrical efficiency. Then, there must be a trade-off between voltage, power and electrical efficiency with respect to the current density. Considering a value of j_{cell} between 1800 and 2000 A/m^2 the values obtained for voltage, power and electrical efficiency are respectively 1.1 V, 850 W/m^2 and 57%. Finally, we showed that increasing concentration of CO and air inlet to the SOFC increases the SOFC power production

In order to show the feasibility of the gasification model united to the gas cleaning model, the SOFC system has been replaced with a 100 kW_e mGT and an ORC unit, as the bottom cycle. The integrated system operates with higher net electric power than its nominal operation thanks to the bottom ORC unit and steam injection in the combustion chamber. However, results have shown that the overall electric efficiency is penalized slightly by adopting the wet cycle. The syngas-fuelled system, at its maximum electric power, produces the net power of 127.6 kW_{el} with 23.6 % overall electric efficiency using 25 g/s steam injected into the combustion chamber. Moreover, results confirm the reduction of performance of the integrated system especially the overall electric efficiency when the mGT is fuelled with syngas instead of its nominal fuel, NG. Nevertheless, the produced thermal power in the condenser of the ORC unit is increased showing the ability of the integrated system to meet higher users' thermal demands.

The SImGT configuration entails also environmental benefits in terms of NO_x and CO significant emission reduction. However, adoption of steam injected combustion in micro-scales has also some limitations and it should be adopted with cautions because of the risk of compressor surge. In addition, further implications should be considered when a low LHV fuel such as syngas is injected in the combustion chamber since the steam injection can negatively affect the combustion process. Nevertheless, the performed thermodynamic analysis proved the integration of different energy conversion systems could results in significant energy and environmental benefits thus potentially contributing to a more sustainable development and diffusion of distributed generation technologies.

The developed thermodynamic quasi-equilibrium gasification model has been also compared against a 1-D kinetic model found in literature and realized by MATLAB. The composition and characteristics of the product gas given by the models has been compared at 850 °C and atmospheric pressure over a full range of S/B and validated against experimental data at S/B ratio equal to 0.25 and 0.5. As a general conclusion it can be said that the two models provide sufficiently similar data in terms of the main components of the syngas composition at the outlet of the gasifier. Mean Absolute Error is within 2.11 and 5.80 for all syngas component gases. The Mean Relative Error is acceptable between 8.95% and 12.64% for H₂, CO and CO₂ gases while for CH₄ it is equal to 61.45%. Such high value can be justified by the fact that the contribution of CH₄ in the syngas composition is low (<0.15) which affects the overall syngas composition prediction less significantly with an AE of 0.08. The influence of the steam to biomass ratio on the syngas composition of both models was investigated. The concentration of H₂ increases while steam increases for both models, due to the WGS reaction, and it grows faster in the Aspen Plus model since it is a thermodynamic model. The values obtained from the simulation by Aspen Plus, as far as the system parameters (LHV, yield, cold gas efficiency and gas composition) are concerned, have a higher error, compared to the literature values, than those of MATLAB. However, this error does is acceptable for what regards system simulation because it is within an error range of 10-20%. For this reason, if the objective of the process modelling is to investigate system coupling and/or integration thermodynamic models seem to be more suitable than kinetic ones due to their enhanced simplicity and generalized approach while at the same time assessing with sufficient accuracy the overall mass and energy balance of the plant. On the other hand, if the objective is to predict specific gas composition and design and/or optimize an actual gasifier system, a kinetic model is needed, providing the trends and distributions of the analysed quantities along the axis of reactor and useful design data regarding the thermal balance and the hydrodynamics of the system.

References

- [1] Villarini, M., Marcantonio, V., Colantoni, A., Bocci, E., Villarini, M., Marcantonio, V., Colantoni, A., and Bocci, E., 2019, "Sensitivity Analysis of Different Parameters on the Performance of a CHP Internal Combustion Engine System Fed by a Biomass Waste Gasifier," *Energies*, **12**(4), p. 688.
- [2] Colantoni, A., Villarini, M., Marcantonio, V., Gallucci, F., Cecchini, M., Colantoni, A., Villarini, M., Marcantonio, V., Gallucci, F., and Cecchini, M., 2019, "Performance Analysis of a Small-Scale ORC Trigeneration System Powered by the Combustion of Olive Pomace," *Energies*, **12**(12), p. 2279.
- [3] Pala, L. P. R., Wang, Q., Kolb, G., and Hessel, V., 2017, "Steam Gasification of Biomass with Subsequent Syngas Adjustment Using Shift Reaction for Syngas Production: An Aspen Plus Model," *Renew. Energy*, **101**, pp. 484–492.
- [4] Bocci, E., Sisinni, M., Moneti, M., Vecchione, L., Di Carlo, A., and Villarini, M., 2014, "State of Art of Small Scale Biomass Gasification Power Systems: A Review of the Different Typologies," *Energy Procedia*, **45**, pp. 247–256.
- [5] Thapa, S., Bhoi, P. R., Kumar, A., and Huhnke, R. L., 2017, "Effects of Syngas Cooling and Biomass Filter Medium on Tar Removal," *Energies*, **10**(3).
- [6] "Biomass for Power Generation and CHP – Analysis - IEA" [Online]. Available: <https://www.iea.org/reports/biomass-for-power-generation-and-chp>. [Accessed: 20-Sep-2020].
- [7] Di Carlo, A., Borello, D., and Bocci, E., 2013, "Process Simulation of a Hybrid SOFC/MGT and Enriched Air/Steam Fluidized Bed Gasifier Power Plant," *Int. J. Hydrogen Energy*, **38**(14), pp. 5857–5874.
- [8] Thakkar, M., Mohanty, P., Shah, M., and Singh, V., 2018, "An Overview of Biomass Gasification," *Recent Adv. Biofuels Bioenergy Util.*, pp. 147–156.
- [9] Sikarwar, V. S., Zhao, M., Clough, P., Yao, J., Zhong, X., Memon, M. Z., Shah, N., Anthony, E. J., and Fennell, P. S., 2016, "An Overview of Advances in Biomass Gasification," *Energy Environ. Sci.*, **9**(10), pp. 2939–2977.

- [10] Sarangi, P., Nanda, S., and Mohanty, P., 2018, “Recent Advancements in Biofuels and Bioenergy Utilization.”
- [11] Di Carlo, A., Bocci, E., and Naso, V., 2013, “Process Simulation of a SOFC and Double Bubbling Fluidized Bed Gasifier Power Plant,” *Int. J. Hydrogen Energy*, **38**(1), pp. 532–542.
- [12] “Impact Assessment on the Energy Efficiency Directive Review, European Commission, 2014.”
- [13] “(No Title)” [Online]. Available: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52014DC0330&from=EN>. [Accessed: 22-Sep-2020].
- [14] Bocci, E., Luca, ;, Zotto, D., Monforti, A., 1, F., Marcantonio, V., Carlo, A. Di, Alessandro, ;, Giuliano, D., Elisa, ;, 4, S., Barisano, D., Stephen, ;, Phail, M., Massimiliano, ;, Pietra, D., Pumiglia, D., Cocchi, M., Jan, ;, Ouweltjes, P., Ligang, ;, 9, W., and Van Herle, J., 2019, *FIRST RESULTS OF THE H2020-LC-SC3-RES-11 BLAZE PROJECT: BIOMASS LOW COST ADVANCED ZERO EMISSION SMALL-TO-MEDIUM SCALE INTEGRATED GASIFIER FUEL CELL COMBINED HEAT AND POWER PLAN*.
- [15] European Commission, 2018, *SET Plan Delivering Results : The Implementation Plans*.
- [16] Qi, T., Lei, T., Yan, B., Chen, G., Li, Z., Fatehi, H., Wang, Z., and Bai, X.-S., 2019, “Biomass Steam Gasification in Bubbling Fluidized Bed for Higher-H₂ Syngas: CFD Simulation with Coarse Grain Model,” *Int. J. Hydrogen Energy*, **44**(13), pp. 6448–6460.
- [17] Tian, T., Li, Q., He, R., Tan, Z., and Zhang, Y., 2017, “Effects of Biochemical Composition on Hydrogen Production by Biomass Gasification,” *Int. J. Hydrogen Energy*, **42**(31), pp. 19723–19732.
- [18] Marcantonio, V., De Falco, M., Capocelli, M., Bocci, E., Colantoni, A., and Villarini, M., 2019, “Process Analysis of Hydrogen Production from Biomass Gasification in Fluidized Bed Reactor with Different Separation Systems,” *Int. J. Hydrogen Energy*, **44**(21), pp. 10350–10360.
- [19] Li, X. T., Grace, J. R., Lim, C. J., Watkinson, A. P., Chen, H. P., and Kim, J. R., 2004, “Biomass Gasification in a Circulating Fluidized Bed,” *Biomass and Bioenergy*, **26**(2), pp. 171–193.

- [20] Fremaux, S., Beheshti, S.-M., Ghassemi, H., and Shahsavan-Markadeh, R., 2015, "An Experimental Study on Hydrogen-Rich Gas Production via Steam Gasification of Biomass in a Research-Scale Fluidized Bed," *Energy Convers. Manag.*, **91**, pp. 427–432.
- [21] Ngoc Lan Thao, N. T., Chiang, K.-Y., Wan, H.-P., Hung, W.-C., and Liu, C.-F., 2019, "Enhanced Trace Pollutants Removal Efficiency and Hydrogen Production in Rice Straw Gasification Using Hot Gas Cleaning System," *Int. J. Hydrogen Energy*, **44**(6), pp. 3363–3372.
- [22] Puig-Arnavat, M., Bruno, J. C., and Coronas, A., 2010, "Review and Analysis of Biomass Gasification Models," *Renew. Sustain. Energy Rev.*, **14**(9), pp. 2841–2851.
- [23] An, H., Song, T., Shen, L., Qin, C., Yin, J., and Feng, B., 2012, "Coal Gasification with in Situ CO₂ Capture by the Synthetic CaO Sorbent in a 1 KWth Dual Fluidised-Bed Reactor," *Int. J. Hydrogen Energy*, **37**(19), pp. 14195–14204.
- [24] Ahmed, T. Y., Ahmad, M. M., Yusup, S., Inayat, A., and Khan, Z., 2012, "Mathematical and Computational Approaches for Design of Biomass Gasification for Hydrogen Production: A Review," *Renew. Sustain. Energy Rev.*, **16**(4), pp. 2304–2315.
- [25] Doherty, W., Reynolds, A., Kennedy, D., Doherty, W., Reynolds, A., and Kennedy, D., *Aspen Plus Simulation of Biomass Gasification in a Steam Blown Dual Fluidised Bed Recommended Citation Aspen plus Simulation of Biomass Gasification in a Steam Blown Dual Fluidised Bed*.
- [26] Patra, T. K., and Sheth, P. N., 2015, "Biomass Gasification Models for Downdraft Gasifier: A State-of-the-Art Review," *Renew. Sustain. Energy Rev.*, **50**, pp. 583–593.
- [27] Nikoo, M. B., and Mahinpey, N., 2008, "Simulation of Biomass Gasification in Fluidized Bed Reactor Using ASPEN PLUS," *Biomass and Bioenergy*, **32**(12), pp. 1245–1254.
- [28] Basu, P., 2010, *Biomass Gasification and Pyrolysis: Practical Design and Theory*, Academic Press.
- [29] Ahmed, A. M. A., Salmiaton, A., Choong, T. S. Y., and Azlina, W. A. K. G. W., 2015, "Review of Kinetic and Equilibrium Concepts for Biomass Tar Modeling by Using Aspen Plus," *Renew. Sustain. Energy Rev.*, **52**, pp. 1623–1644.

- [30] Marcantonio, V., Monarca, D., Colantoni, A., and Cecchini, M., 2019, "Ultrasonic Waves for Materials Evaluation in Fatigue, Thermal and Corrosion Damage: A Review," *Mech. Syst. Signal Process.*, **120**.
- [31] Wang, J., Zhang, Y., Han, L., Chang, L., and Bao, W., 2013, "Simultaneous Removal of Hydrogen Sulfide and Mercury from Simulated Syngas by Iron-Based Sorbents," *Fuel*, **103**, pp. 73–79.
- [32] Gupta, R. P., and O'Brien, W. S., 2000, "Desulfurization of Hot Syngas Containing Hydrogen Chloride Vapors Using Zinc Titanate Sorbents," *Ind. Eng. Chem. Res.*, **39**(3), pp. 610–619.
- [33] Xu, C. (Charles), Donald, J., Byambajav, E., and Ohtsuka, Y., 2010, "Recent Advances in Catalysts for Hot-Gas Removal of Tar and NH₃ from Biomass Gasification," *Fuel*, **89**(8), pp. 1784–1795.
- [34] Liu, Y., Yu, H., Liu, J., and Chen, D., 2019, "Catalytic Characteristics of Innovative Ni/Slag Catalysts for Syngas Production and Tar Removal from Biomass Pyrolysis," *Int. J. Hydrogen Energy*, **44**(23), pp. 11848–11860.
- [35] Rhyner, U., Edinger, P., Schildhauer, T. J., and Biollaz, S. M. A., 2014, "Experimental Study on High Temperature Catalytic Conversion of Tars and Organic Sulfur Compounds," *Int. J. Hydrogen Energy*, **39**(10), pp. 4926–4937.
- [36] Cheah, S., Carpenter, D. L., and Magrini-Bair, K. A., 2009, "Review of Mid- to High-Temperature Sulfur Sorbents for Desulfurization of Biomass- and Coal-Derived Syngas," *Energy and Fuels*, **23**(11), pp. 5291–5307.
- [37] Sharma, S. D., Dolan, M., Park, D., Morpeth, L., Ilyushechkin, A., McLennan, K., Harris, D. J., and Thambimuthu, K. V., 2008, "A Critical Review of Syngas Cleaning Technologies - Fundamental Limitations and Practical Problems," *Powder Technol.*, **180**(1–2), pp. 115–121.
- [38] Epikhin, A. N., Krylov, I. O., Somov, A. A., Suchkov, S. I., Timashkov, K. V., Stokov, A. A., and Ligovskaya, I. G., 2012, "Prospects for the Use of Natural Ferromanganese Sorbents of Hydrogen Sulfide for High-Temperature Cleaning of Syngas," *Power Technol. Eng.*, **46**(2), pp. 143–148.
- [39] Ptasinski, K. J., 2008, "Thermodynamic Efficiency of Biomass Gasification and Biofuels

Conversion,” *Biofuels, Bioprod. Biorefining*, **2**(3), pp. 239–253.

- [40] Aravind, P. V, and De Jong, W., 2012, “Review Evaluation of High Temperature Gas Cleaning Options for Biomass Gasification Product Gas for Solid Oxide Fuel Cells,” *Prog. Energy Combust. Sci.*, **38**, pp. 737–764.
- [41] Corella, J., Aznar, M. P., Gil, J., and Caballero, M. A., 1999, “Biomass Gasification in Fluidized Bed: Where to Locate the Dolomite to Improve Gasification?,” *Energy and Fuels*, **13**(6), pp. 1122–1127.
- [42] Rapagnà, S., Jand, N., Kiennemann, A., and Foscolo, P. U., 2000, “Steam-Gasification of Biomass in a Fluidised-Bed of Olivine Particles,” *Biomass and Bioenergy*, **19**(3), pp. 187–197.
- [43] Corella, J., Toledo, J. M., and Molina, G., 2008, “Performance of CaO and MgO for the Hot Gas Clean up in Gasification of a Chlorine-Containing (RDF) Feedstock,” *Bioresour. Technol.*, **99**(16), pp. 7539–7544.
- [44] Tan, R. S., Tuan Abdullah, T. A., Mahmud, S. A., Md Zin, R., and Md Isa, K., 2019, “Catalytic Steam Reforming of Complex Gasified Biomass Tar Model toward Hydrogen over Dolomite Promoted Nickel Catalysts,” *Int. J. Hydrogen Energy*, **44**(39), pp. 21303–21314.
- [45] Olivares, A., Aznar, M. P., Caballero, M. A., Gil, J., Francés, E., and Corella, J., 1997, “Biomass Gasification: Produced Gas Upgrading by In-Bed Use of Dolomite,” *Ind. Eng. Chem. Res.*, **36**(12), pp. 5220–5226.
- [46] Savuto, E., Di Carlo, A., Steele, A., Heidenreich, S., Gallucci, K., and Rapagnà, S., 2018, “Syngas Conditioning by Ceramic Filter Candles Filled with Catalyst Pellets, Placed inside the Freeboard of a Fluidized Bed Steam Gasifier,” To be Submitt.
- [47] Moneti, M., Di Carlo, A., Bocci, E., Foscolo, P. U., Villarini, M., and Carlini, M., 2016, “Influence of the Main Gasifier Parameters on a Real System for Hydrogen Production from Biomass,” *Int. J. Hydrogen Energy*, **41**(28), pp. 11965–11973.
- [48] Rupesh, S., Muraleedharan, C., and Arun, P., 2016, “ASPEN plus Modelling of Air–Steam Gasification of Biomass with Sorbent Enabled CO₂ Capture,” *Resour. Technol.*, **2**(2), pp. 94–103.

- [49] Herce, C., Cortés, C., and Stendardo, S., 2019, “Numerical Simulation of a Bubbling Fluidized Bed Reactor for Sorption-Enhanced Steam Methane Reforming under Industrially Relevant Conditions: Effect of Sorbent (Dolomite and $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and Operational Parameters,” *Fuel Process. Technol.*, **186**(January), pp. 137–148.
- [50] Cheng, B., Cao, Z., Bai, Y., and Zhang, D., 2010, “Preparation and Selection of Fe-Cu Sorbent for COS Removal in Syngas,” *Front. Chem. Eng. China*, **4**(4), pp. 441–444.
- [51] Chomiak, M., Trawczyński, J., Blok, Z., and Babiński, P., 2016, “Monolithic Zn-Co-Ti Based Sorbents for Hot Syngas Desulfurization,” *Fuel Process. Technol.*, **144**, pp. 64–70.
- [52] Cheah, S., Parent, Y. O., Jablonski, W. S., Vinzant, T., and Olstad, J. L., 2012, “Manganese and Ceria Sorbents for High Temperature Sulfur Removal from Biomass-Derived Syngas – The Impact of Steam on Capacity and Sorption Mode,” *Fuel*, **97**, pp. 612–620.
- [53] Mandilas, C., Zarvalis, D., Karagiannakis, G., Pagkoura, C., Deloglou, D., and Konstandopoulos, A. G., 2016, “Zinc-Copper Oxide Coated Monolithic Reactors for High Capacity Hydrogen Sulphide Removal from Gaseous Streams,” *Int. J. Hydrogen Energy*, **41**(46), pp. 21251–21260.
- [54] Detchusananard, T., Sharma, S., Maréchal, F., and Arpornwichanop, A., 2019, “Multi-Objective Optimization of Sorption Enhanced Steam Biomass Gasification with Solid Oxide Fuel Cell,” *Energy Convers. Manag.*, **182**(September 2018), pp. 412–429.
- [55] Puig-Gamero, M., Argudo-Santamaria, J., Valverde, J. L., Sánchez, P., and Sanchez-Silva, L., 2018, “Three Integrated Process Simulation Using Aspen Plus®: Pine Gasification, Syngas Cleaning and Methanol Synthesis,” *Energy Convers. Manag.*, **177**, pp. 416–427.
- [56] Liao, C., Summers, M., Seiser, R., Cattolica, R., and Herz, R., 2014, “Simulation of a Pilot-Scale Dual-Fluidized-Bed Gasifier for Biomass,” *Environ. Prog. Sustain. Energy*, **33**(3), pp. 732–736.
- [57] Safarian, S., Unnþórsson, R., and Richter, C., 2019, “A Review of Biomass Gasification Modelling,” *Renew. Sustain. Energy Rev.*, **110**, pp. 378–391.
- [58] Inayat, A., Ahmad, M. M., Yusup, S., Mutalib, M. I. A., Inayat, A., Ahmad, M. M., Yusup, S., and Mutalib, M. I. A., 2010, “Biomass Steam Gasification with In-Situ CO₂ Capture for Enriched Hydrogen Gas Production: A Reaction Kinetics Modelling Approach,” *Energies*,

3(8), pp. 1472–1484.

- [59] Silva, V. B., and Rouboa, A., 2013, “Using a Two-Stage Equilibrium Model to Simulate Oxygen Air Enriched Gasification of Pine Biomass Residues,” *Fuel Process. Technol.*, **109**, pp. 111–117.
- [60] Moradi, R., Marcantonio, V., Cioccolanti, L., and Bocci, E., 2020, “Integrating Biomass Gasification with a Steam-Injected Micro Gas Turbine and an Organic Rankine Cycle Unit for Combined Heat and Power Production,” *Energy Convers. Manag.*, **205**(January).
- [61] W. Gumz, 1950, *Gas Producers and Blast Furnaces*.
- [62] Doherty, W., Reynolds, A., and Kennedy, D., 2009, “The Effect of Air Preheating in a Biomass CFB Gasifier Using ASPEN Plus Simulation,” *Biomass and Bioenergy*, **33**(9), pp. 1158–1167.
- [63] Arteaga-Pérez, L. E., Casas-Ledón, Y., Prins, W., and Radovic, L., 2014, “Thermodynamic Predictions of Performance of a Bagasse Integrated Gasification Combined Cycle under Quasi-Equilibrium Conditions,” *Chem. Eng. J.*, **258**, pp. 402–411.
- [64] Mirmoshtaghi, G., Li, H., Thorin, E., and Dahlquist, E., 2016, “Evaluation of Different Biomass Gasification Modeling Approaches for Fluidized Bed Gasifiers,” *Biomass and Bioenergy*.
- [65] Giuliano, A., Barletta, D., De Bari, I., and Poletto, M., 2018, “Techno-Economic Assessment of a Lignocellulosic Biorefinery Co-Producing Ethanol and Xylitol or Furfural,” *Computer Aided Chemical Engineering*, Elsevier B.V., pp. 585–590.
- [66] Giuliano, A., Cerulli, R., Poletto, M., Raiconi, G., and Barletta, D., 2014, “Optimization of a Multiproduct Lignocellulosic Biorefinery Using a MILP Approximation,” *Comput. Aided Chem. Eng.*, **33**(January), pp. 1423–1428.
- [67] Hosseini, M., Dincer, I., and Rosen, M. A., 2012, “Steam and Air Fed Biomass Gasification: Comparisons Based on Energy and Exergy,” *Int. J. Hydrogen Energy*, **37**(21), pp. 16446–16452.
- [68] Lü, P., Kong, X., Wu, C., Yuan, Z., Ma, L., and Chang, J., 2008, “Modeling and Simulation of Biomass Air-Steam Gasification in a Fluidized Bed,” *Front. Chem. Eng. China*, **2**(2), pp.

- [69] Baruah, D., and Baruah, D. C., 2014, “Modeling of Biomass Gasification: A Review,” *Renew. Sustain. Energy Rev.*, **39**, pp. 806–815.
- [70] Doherty, W., Reynolds, A., and Kennedy, D., 2013, “Aspen Plus Simulation of Biomass Gasification in a Steam Blown Dual Fluidised Bed,” *Book/b. Chapters*.
- [71] Arteaga-Pérez, L. E., Casas-Ledón, Y., Pérez-Bermúdez, R., Peralta, L. M., Dewulf, J., and Prins, W., 2013, “Energy and Exergy Analysis of a Sugar Cane Bagasse Gasifier Integrated to a Solid Oxide Fuel Cell Based on a Quasi-Equilibrium Approach,” *Chem. Eng. J.*
- [72] Vera, D., Jurado, F., Carpio, J., and Kamel, S., 2018, “Biomass Gasification Coupled to an EFGT-ORC Combined System to Maximize the Electrical Energy Generation: A Case Applied to the Olive Oil Industry,” *Energy*, **144**, pp. 41–53.
- [73] Kakaç, S., Pramuanjaroenkij, A., and Yang, X., 2007, “A Review of Numerical Modeling of Solid Oxide Fuel Cells,” **32**, pp. 761–786.
- [74] Chiodo, V., Galvagno, A., Lanzini, A., Papurello, D., Urbani, F., Santarelli, M., and Freni, S., 2015, “Biogas Reforming Process Investigation for SOFC Application,” *Energy Convers. Manag.*, **98**, pp. 252–258.
- [75] Eisavi, B., Chitsaz, A., Hosseinpour, J., and Ranjbar, F., 2018, “Thermo-Environmental and Economic Comparison of Three Different Arrangements of Solid Oxide Fuel Cell-Gas Turbine (SOFC-GT) Hybrid Systems,” *Energy Convers. Manag.*, **168**(April), pp. 343–356.
- [76] Hauck, M., Herrmann, S., and Spliethoff, H., 2017, “ScienceDirect Simulation of a Reversible SOFC with Aspen Plus,” *Int. J. Hydrogen Energy*, **42**(15), pp. 10329–10340.
- [77] Sadhukhan, J., Zhao, Y., Leach, M., Brandon, N. P., and Shah, N., 2010, “Energy Integration and Analysis of Solid Oxide Fuel Cell Based Microcombined Heat and Power Systems and Other Renewable Systems Using Biomass Waste Derived Syngas,” pp. 11506–11516.
- [78] Fung, A. S., 2018, “Performance of Biogas Fueled Hybrid Solid Oxide Fuel Cell (SOFC) and Gas Turbine Cycle,” pp. 1–11.
- [79] Riensche, E., Achenbach, E., Froning, D., Haines, M. ., Heidug, W. ., Lokurlu, A., and von Andrian, S., 2000, “Clean Combined-Cycle SOFC Power Plant — Cell Modelling and

Process Analysis,” J. Power Sources, **86**(1–2), pp. 404–410.

- [80] Palsson, J., Selimovic, A., and Sjunnesson, L., 2000, “Combined Solid Oxide Fuel Cell and Gas Turbine Systems for Efficient Power and Heat Generation,” J. Power Sources, **86**(1–2), pp. 442–448.
- [81] Fuller, T.A.; Chaney L.J.; Wolf, T.L.; Kesseli, J.; Nash, J.; Hatvigsen, J., 2000, “A Novel Cell/Microturbine Combined-Cycle System,” J. Power Sources, **86**.
- [82] Zhang, W., Croiset, E., Douglas, P. L., Fowler, M. W., and Entchev, E., 2005, “Simulation of a Tubular Solid Oxide Fuel Cell Stack Using AspenPlusTM Unit Operation Models,” Energy Convers. Manag., **46**(2), pp. 181–196.
- [83] Doherty, W., Reynolds, A., and Kennedy, D., 2010, “Computer Simulation of a Biomass Gasi Fi Cation-Solid Oxide Fuel Cell Power System Using Aspen Plus,” Energy, **35**(12), pp. 4545–4555.
- [84] Rakesh, N., and Dasappa, S., 2018, “A Critical Assessment of Tar Generated during Biomass Gasification - Formation, Evaluation, Issues and Mitigation Strategies,” Renew. Sustain. Energy Rev., **91**, pp. 1045–1064.
- [85] Kinoshita, C. M., Wang, Y., and Zhou, J., 1994, “Tar Formation under Different Biomass Gasification Conditions,” J. Anal. Appl. Pyrolysis, **29**(2), pp. 169–181.
- [86] Milne, T. A., Evans, R. J., and Abatzoglou, N., *Biomass Gasifier “Tars”: Their Nature, Formation, and Conversion*.
- [87] Maniatis, K., and Beenackers, A. A. C. M., 2000, “Tar Protocols. IEA Bioenergy Gasification Task: Introduction,” Biomass and Bioenergy, **18**(1), pp. 1–4.
- [88] Guan, G., Kaewpanha, M., Hao, X., and Abudula, A., 2016, “Catalytic Steam Reforming of Biomass Tar: Prospects and Challenges,” Renew. Sustain. Energy Rev., **58**, pp. 450–461.
- [89] Devi, L., Ptasiński, K. J., Janssen, F. J. J. G., Van Paasen, S. V. B., Bergman, P. C. A., and Kiel, J. H. A., 2005, “Catalytic Decomposition of Biomass Tars: Use of Dolomite and Untreated Olivine,” Renew. Energy, **30**(4), pp. 565–587.
- [90] Nguyen, H. N. T., Berguerand, N., Schwebel, G. L., and Thunman, H., 2016, “Importance of Decomposition Reactions for Catalytic Conversion of Tar and Light Hydrocarbons: An

Application with an Ilmenite Catalyst,” *Ind. Eng. Chem. Res.*, **55**(46), pp. 11900–11909.

- [91] Trimm, D. L., 1977, “The Formation and Removal of Coke from Nickel Catalyst,” *Catal. Rev.*, **16**(1), pp. 155–189.
- [92] Herrmann, T., Dillig, M., Hauth, M., and Karl, J., 2017, “Conversion of Tars on Solid Oxide Fuel Cell Anodes and Its Impact on Voltages and Current Densities,” *Energy Sci. Eng.*, **5**(4), pp. 194–207.
- [93] Speidel, M., and Fischer, H., 2016, “Steam Reforming of Tars at Low Temperature and Elevated Pressure for Model Tar Component Naphthalene,” *Int. J. Hydrogen Energy*, **41**(30), pp. 12920–12928.
- [94] Singh, D., Hernández-Pacheco, E., Hutton, P. N., Patel, N., and Mann, M. D., 2005, “Carbon Deposition in an SOFC Fueled by Tar-Laden Biomass Gas: A Thermodynamic Analysis,” *J. Power Sources*, **142**(1–2), pp. 194–199.
- [95] Mermelstein, J., Millan, M., and Brandon, N., 2010, “The Impact of Steam and Current Density on Carbon Formation from Biomass Gasification Tar on Ni/YSZ, and Ni/CGO Solid Oxide Fuel Cell Anodes,” *J. Power Sources*, **195**(6), pp. 1657–1666.
- [96] Coll, R., Salvadó, J., Farriol, X., and Montané, D., 2001, “Steam Reforming Model Compounds of Biomass Gasification Tars: Conversion at Different Operating Conditions and Tendency towards Coke Formation,” *Fuel Process. Technol.*, **74**(1), pp. 19–31.
- [97] Jess, A., 1996, “Catalytic Upgrading of Tarry Fuel Gases: A Kinetic Study with Model Components,” *Chem. Eng. Process. Process Intensif.*, **35**(6), pp. 487–494.
- [98] Mermelstein, J., Millan, M., and Brandon, N. P., 2009, “The Impact of Carbon Formation on Ni-YSZ Anodes from Biomass Gasification Model Tars Operating in Dry Conditions,” *Chem. Eng. Sci.*, **64**(3), pp. 492–500.
- [99] Hackett, G. A., Gerdes, K., Chen, Y., Song, X., and Zondlo, J., 2015, “Performance Impact Associated with Ni-Based SOFCs Fueled with Higher Hydrocarbon-Doped Coal Syngas,” *Metall. Mater. Trans. E*, **2**(1), pp. 58–69.
- [100] Lorente, E., Millan, M., and Brandon, N. P., 2012, “Use of Gasification Syngas in SOFC: Impact of Real Tar on Anode Materials,” *Int. J. Hydrogen Energy*, **37**(8), pp. 7271–7278.

- [101] Lorente, E., Berruero, C., Millan, M., and Brandon, N. P., 2013, “Effect of Tar Fractions from Coal Gasification on Nickel-Yttria Stabilized Zirconia and Nickel-Gadolinium Doped Ceria Solid Oxide Fuel Cell Anode Materials,” *J. Power Sources*, **242**, pp. 824–831.
- [102] Liu, M., Millan, M. G., Aravind, P. V., and Brandon, N., 2011, “Influence of Operating Conditions on Carbon Deposition in SOFCs Fuelled by Tar-Containing Biosyngas,” *J. Electrochem. Soc.*, **158**(11), p. B1310.
- [103] Namioka, T., Naruse, T., and Yamane, R., 2011, “Behavior and Mechanisms of Ni/ScSZ Cermet Anode Deterioration by Trace Tar in Wood Gas in a Solid Oxide Fuel Cell,” *Int. J. Hydrogen Energy*, **36**(9), pp. 5581–5588.
- [104] Namioka, T., Nagai, Y., Yoshikawa, K., and Min, T., 2012, “A Tolerance Criterion for Tar Concentration in a Model Wood Gas for a Nickel/Scandia-Stabilized Zirconia Cermet Anode in a Solid Oxide Fuel Cell,” *Int. J. Hydrogen Energy*, **37**(22), pp. 17245–17252.
- [105] Baldinelli, A., Cinti, G., Desideri, U., and Fantozzi, F., 2016, “Biomass Integrated Gasifier-Fuel Cells: Experimental Investigation on Wood Syngas Tars Impact on NiYSZ-Anode Solid Oxide Fuel Cells,” *Energy Convers. Manag.*, **128**, pp. 361–370.
- [106] Pumiglia, D., Vaccaro, S., Masi, A., McPhail, S. J., Falconieri, M., Gagliardi, S., Della Seta, L., and Carlini, M., 2017, “Aggravated Test of Intermediate Temperature Solid Oxide Fuel Cells Fed with Tar-Contaminated Syngas,” *J. Power Sources*, **340**, pp. 150–159.
- [107] Geis, M.; Herrmann, S.; Fendt, S.; Spliethoff, H., 2016, “Fuels, Degradation of the SOFC Anode by Contaminants in Biogenic Gaseous,” *12th European SOFC & SOE Forum 2016 5 - 8 July 2016, Lucerne Switzerland*.
- [108] Geis, M., Herrmann, S., Fendt, S., Jeong, H., Lenser, C., Menzler, N. H., and Spliethoff, H., 2018, “Coupling SOFCs to Biomass Gasification - The Influence of Phenol on Cell Degradation in Simulated Bio-Syngas. Part I: Electrochemical Analysis,” *Int. J. Hydrogen Energy*, **43**(45), pp. 20417–20427.
- [109] Jeong, H., Geis, M., Lenser, C., Lobe, S., Herrmann, S., Fendt, S., Menzler, N. H., and Guillon, O., 2018, “Coupling SOFCs to Biomass Gasification – The Influence of Phenol on Cell Degradation in Simulated Bio-Syngas. Part II – Post-Test Analysis,” *Int. J. Hydrogen Energy*, **43**(45), pp. 20911–20920.

- [110] Jeong, H., Hauser, M., Fischer, F., Hauck, M., Lobe, S., Peters, R., Lenser, C., Menzler, N. H., and Guillon, O., 2019, "Utilization of Bio-Syngas in Solid Oxide Fuel Cell Stacks: Effect of Hydrocarbon Reforming," *J. Electrochem. Soc.*, **166**(2), pp. F137–F143.
- [111] Madi, H., Diethelm, S., Ludwig, C., and Van herle, J., 2015, "The Impact of Toluene on the Performance of Anode-Supported Ni-YSZ SOFC Operated on Hydrogen and Biosyngas," *ECS Trans.*, **68**(1), pp. 2811–2818.
- [112] Papurello, D., Lanzini, A., Leone, P., and Santarelli, M., 2016, "The Effect of Heavy Tars (Toluene and Naphthalene) on the Electrochemical Performance of an Anode-Supported SOFC Running on Bio-Syngas," *Renew. Energy*, **99**, pp. 747–753.
- [113] Matsuzaki, Y., and Yasuda, I., 2000, "Poisoning Effect of Sulfur-Containing Impurity Gas on a SOFC Anode: Part I. Dependence on Temperature, Time, and Impurity Concentration," *Solid State Ionics*, **132**(3), pp. 261–269.
- [114] Rasmussen, J. F. B., and Hagen, A., 2009, "The Effect of H₂S on the Performance of Ni-YSZ Anodes in Solid Oxide Fuel Cells," *J. Power Sources*, **191**(2), pp. 534–541.
- [115] Błesznowski, M., Jewulski, J., and Zieleniak, A., 2013, "Determination of H₂S and HCl Concentration Limits in the Fuel for Anode Supported SOFC Operation," *Cent. Eur. J. Chem.*, **11**(6), pp. 960–967.
- [116] Sasaki, K., Susuki, K., Iyoshi, A., Uchimura, M., Imamura, N., Kusaba, H., Teraoka, Y., Fuchino, H., Tsujimoto, K., Uchida, Y., and Jingo, N., 2006, "H₂S Poisoning of Solid Oxide Fuel Cells," *J. Electrochem. Soc.*, **153**(11), p. A2023.
- [117] Zha, S., Cheng, Z., and Liu, M., 2007, "Sulfur Poisoning and Regeneration of Ni-Based Anodes in Solid Oxide Fuel Cells," *J. Electrochem. Soc.*, **154**, pp. 201–206.
- [118] Hagen, A., 2013, "Sulfur Poisoning of the Water Gas Shift Reaction on Anode Supported Solid Oxide Fuel Cells," *J. Electrochem. Soc.*, **160**(2), pp. F111–F118.
- [119] Norheim, A., Wærnhus, I., Broström, M., Hustad, J. E., and Vik, A., 2007, "Experimental Studies on the Influence of H₂S on Solid Oxide Fuel Cell Performance at 800 °C," *Energy and Fuels*, **21**(2), pp. 1098–1101.
- [120] He, H. P., Wood, A., Steedman, D., and Tilleman, M., 2008, "Sulphur Tolerant Shift

Reaction Catalysts for Nickel-Based SOFC Anode,” *Solid State Ionics*, **179**(27–32), pp. 1478–1482.

- [121] Kromp, A., Dierickx, S., Leonide, A., Weber, A., and Ivers-Tiffée, E., 2012, “Electrochemical Analysis of Sulphur-Poisoning in Anode-Supported SOFCs under Reformate Operation,” *ECSTr*, ECS, pp. 161–169.
- [122] Li, T. S., Xu, M., Gao, C., Wang, B., Liu, X., Li, B., and Wang, W. G., 2014, “Investigation into the Effects of Sulfur on Syngas Reforming inside a Solid Oxide Fuel Cell,” *J. Power Sources*, **258**, pp. 1–4.
- [123] Weber, A., Dierickx, S., Kromp, A., and Ivers-Tiffée, E., 2013, “Sulfur Poisoning of Anode-Supported SOFCs under Reformate Operation,” *Fuel Cells*, **13**(4), pp. 487–493.
- [124] Bartholomew, C. H., 1982, “Carbon Deposition in Methanation and Steam Reforming,” *Catal. Rev. Sci. Eng.*, **24**, pp. 67–112.
- [125] Rostrup-Nielsen, J. R., Hansen, J. B., Helveg, S., Christiansen, N., and Jannasch, A. K., 2006, “Sites for Catalysis and Electrochemistry in Solid Oxide Fuel Cell (SOFC) Anode,” *Appl. Phys. A Mater. Sci. Process.*, **85**(4), pp. 427–430.
- [126] Smith, T. R., Wood, A., and Birss, V. I., 2009, “Effect of Hydrogen Sulfide on the Direct Internal Reforming of Methane in Solid Oxide Fuel Cells,” *Appl. Catal. A Gen.*, **354**(1–2), pp. 1–7.
- [127] Kuhn, J. N., Lakshminarayanan, N., and Ozkan, U. S., 2008, “Effect of Hydrogen Sulfide on the Catalytic Activity of Ni-YSZ Cermets,” *J. Mol. Catal. A Chem.*, **282**(1–2), pp. 9–21.
- [128] Gong, M., Liu, X., Trembly, J., and Johnson, C., 2007, “Sulfur-Tolerant Anode Materials for Solid Oxide Fuel Cell Application,” *J. Power Sources*, **168**(2), pp. 289–298.
- [129] Hansen, J. B., 2008, “Correlating Sulfur Poisoning of SOFC Nickel Anodes by a Temkin Isotherm,” *Electrochem. Solid-State Lett.*, **11**(10), pp. B178–B180.
- [130] Braun, R. J., 2008, “Techno-Economic Optimal Design and Application of SOFC Systems for Residential Micro-CHP Applications in the U.S.,” *Proceedings of the 6th International Conference on Fuel Cell Science, Engineering, and Technology*, American Society of Mechanical Engineers Digital Collection, pp. 509–527.

- [131] Mougin, J., Ravel, S., and De Vito, E., 2007, “Influence of Fuel Contaminants on SOFC Operation: Effect on Performance and Degradation Mechanisms MAT4BAT European Project View Project WASTE2WATTS: Unlocking Unused Bio-WASTE Resources with LoW Cost CleAning and Thermal InTegration with Solid Oxide Fuel Cells View Project.”
- [132] Dong, J., Cheng, Z., Zha, S., and Liu, M., 2006, “Identification of Nickel Sulfides on Ni-YSZ Cermet Exposed to H₂ Fuel Containing H₂S Using Raman Spectroscopy,” *J. Power Sources*, **156**(2), pp. 461–465.
- [133] Li, T. S., and Wang, W. G., 2010, “Sulfur-Poisoned Ni-Based Solid Oxide Fuel Cell Anode Characterization by Varying Water Content,” *J. Power Sources*, **196**, pp. 2066–2069.
- [134] Hauch, A., Hagen, A., Hjelm, J., and Ramos, T., 2014, “Sulfur Poisoning of SOFC Anodes: Effect of Overpotential on Long-Term Degradation,” *J. Electrochem. Soc.*, **161**(6), pp. F734–F743.
- [135] Li, T. S., and Wang, W. G., 2011, “The Mechanism of H₂S Poisoning Ni/YSZ Electrode Studied by Impedance Spectroscopy,” *Electrochem. Solid-State Lett.*, **14**(3), p. B35.
- [136] Bao, J. E., Krishnan, G. N., Jayaweera, P., Lau, K. H., and Sanjurjo, A., 2009, “Effect of Various Coal Contaminants on the Performance of Solid Oxide Fuel Cells: Part II. Ppm and Sub-Ppm Level Testing,” *J. Power Sources*, **193**(2), pp. 617–624.
- [137] Buchinger, G., Hinterreiter, P., Raab, T., Griesser, S., Claassen, R., Claassen, D. P., Sitte, W., and Meissner, D., 2006, “Operating Microtubular SOFCS with Hydrogen Chloride and Hydrogen Sulfide Containing Fuels and Synthetic Wood Gas,” *J. Fuel Cell Sci. Technol.*, **3**(3), pp. 280–283.
- [138] Marina, O. A., Pederson, L. R., Thomsen, E. C., Coyle, C. A., and Yoon, K. J., 2010, “Reversible Poisoning of Nickel/Zirconia Solid Oxide Fuel Cell Anodes by Hydrogen Chloride in Coal Gas,” *J. Power Sources*, **195**(20), pp. 7033–7037.
- [139] Kuramoto, K., Hosokai, S., Matsuoka, K., Ishiyama, T., Kishimoto, H., and Yamaji, K., 2017, “Degradation Behaviors of SOFC Due to Chemical Interaction between Ni-YSZ Anode and Trace Gaseous Impurities in Coal Syngas,” *Fuel Process. Technol.*, **160**, pp. 8–18.
- [140] Madi, H., Lanzini, A., Papurello, D., Diethelm, S., Ludwig, C., Santarelli, M., and Van herle,

- J., 2016, “Solid Oxide Fuel Cell Anode Degradation by the Effect of Hydrogen Chloride in Stack and Single Cell Environments,” *J. Power Sources*, **326**, pp. 349–356.
- [141] Cayan, F. N., Zhi, M., Pakalapati, S. R., Celik, I., Wu, N., and Gemmen, R., 2008, “Effects of Coal Syngas Impurities on Anodes of Solid Oxide Fuel Cells,” *J. Power Sources*, **185**(2), pp. 595–602.
- [142] Marcantonio, V., Bocci, E., Ouweltjes, J. P., Del Zotto, L., and Monarca, D., 2020, “Evaluation of Sorbents for High Temperature Removal of Tars, Hydrogen Sulphide, Hydrogen Chloride and Ammonia from Biomass-Derived Syngas by Using Aspen Plus,” *Int. J. Hydrogen Energy*.
- [143] Ud Din, Z., and Zainal, Z. A., 2017, “The Fate of SOFC Anodes under Biomass Producer Gas Contaminants,” *Renew. Sustain. Energy Rev.*, **72**(July 2016), pp. 1050–1066.
- [144] Hermann, H., Reinhard, R., Klaus, B., Koch, R. B., and Kraftwerk, G. G. M. B. H., *Biomass CHP Plant Güssing-A Success Story*.
- [145] Stemmler, M., Tamburro, A., and Müller, M., 2013, “Thermodynamic Modelling of Fate and Removal of Alkali Species and Sour Gases from Biomass Gasification for Production of Biofuels,” *Biomass Convers. Biorefinery*, **3**(3), pp. 187–198.
- [146] Gil, J., Corella, J., Aznar, M. P., and Caballero, M. A., 1999, “Biomass Gasification in Atmospheric and Bubbling Fluidized Bed: Effect of the Type of Gasifying Agent on the Product Distribution,” *Biomass and Bioenergy*, **17**(5), pp. 389–403.
- [147] McKendry, P., 2002, “Energy Production from Biomass (Part 3): Gasification Technologies,” *Bioresour. Technol.*, **83**(1), pp. 55–63.
- [148] Gil, J., Caballero, M. A., Martín, J. A., Aznar, M. P., and Corella, J., 1999, “Biomass Gasification with Air in a Fluidized Bed: Effect of the in-Bed Use of Dolomite under Different Operation Conditions,” *Ind. Eng. Chem. Res.*, **38**(11), pp. 4226–4235.
- [149] Miccio, F., Piriou, B., Ruoppolo, G., and Chirone, R., 2009, “Biomass Gasification in a Catalytic Fluidized Reactor with Beds of Different Materials,” *Chem. Eng. J.*, **154**(1–3), pp. 369–374.
- [150] Tasaka, K., Furusawa, T., and Tsutsumi, A., 2007, “Biomass Gasification in Fluidized Bed

Reactor with Co Catalyst,” *Chem. Eng. Sci.*, **62**(18–20), pp. 5558–5563.

- [151] Lv, P., Yuan, Z., Wu, C., Ma, L., Chen, Y., and Tsubaki, N., 2007, “Bio-Syngas Production from Biomass Catalytic Gasification,” *Energy Convers. Manag.*, **48**(4), pp. 1132–1139.
- [152] Turn, S. Q., Kinoshita, C. M., Ishimura, D. M., and Zhou, J., 1998, “The Fate of Inorganic Constituents of Biomass in Fluidized Bed Gasification,” *Fuel*, **77**(3), pp. 135–146.
- [153] Narváez, I., Orío, A., Aznar, M. P., and Corella, J., 1996, “Biomass Gasification with Air in an Atmospheric Bubbling Fluidized Bed. Effect of Six Operational Variables on the Quality of the Produced Raw Gas,” *Ind. Eng. Chem. Res.*, **35**(7), pp. 2110–2120.
- [154] Delgado, J., Aznar, M. P., and Corella, J., 1997, “Biomass Gasification with Steam in Fluidized Bed: Effectiveness of CaO, MgO, and CaO-MgO for Hot Raw Gas Cleaning,” *Ind. Eng. Chem. Res.*, **36**(5), pp. 1535–1543.
- [155] Chan, F. L., and Tanksale, A., 2014, “Review of Recent Developments in Ni-Based Catalysts for Biomass Gasification,” *Renew. Sustain. Energy Rev.*, **38**, pp. 428–438.
- [156] Klimantos, P., Koukouzas, N., Katsiadakis, A., and Kakaras, E., 2009, “Air-Blown Biomass Gasification Combined Cycles (BGCC): System Analysis and Economic Assessment,” *Energy Convers. Manag.*, **34**(5), pp. 708–714.
- [157] Noichi, H., Uddin, A., and Sasaoka, E., 2010, “Steam Reforming of Naphthalene as Model Biomass Tar over Iron-Aluminum and Iron-Zirconium Oxide Catalyst Catalysts,” *Fuel Process. Technol.*, **91**(11), pp. 1609–1616.
- [158] Sutton, D., Kelleher, B., and Ross, J. R. H., 2001, “Review of Literature on Catalysts for Biomass Gasification,” *Fuel Process. Technol.*, **73**(3), pp. 155–173.
- [159] Nilsson, S., Gómez-Barea, A., Fuentes-Cano, D., and Ollero, P., 2012, “Gasification of Biomass and Waste in a Staged Fluidized Bed Gasifier: Modeling and Comparison with One-Stage Units,” *Fuel*, **97**, pp. 730–740.
- [160] Huang, B. S., Chen, H. Y., Kuo, J. H., Chang, C. H., and Wey, M. Y., 2012, “Catalytic Upgrading of Syngas from Fluidized Bed Air Gasification of Sawdust,” *Bioresour. Technol.*, **110**, pp. 670–675.
- [161] Anis, S., and Zainal, Z. A., 2011, “Tar Reduction in Biomass Producer Gas via Mechanical,

Catalytic and Thermal Methods: A Review,” *Renew. Sustain. Energy Rev.*, **15**(5), pp. 2355–2377.

- [162] Pinto, F., Lopes, H., André, R. N., Gulyurtlu, I., and Cabrita, I., 2007, “Effect of Catalysts in the Quality of Syngas and By-Products Obtained by Co-Gasification of Coal and Wastes. 1. Tars and Nitrogen Compounds Abatement,” *Fuel*, **86**(14 SPEC. ISS.), pp. 2052–2063.
- [163] Asadullah, M., 2014, “Biomass Gasification Gas Cleaning for Downstream Applications: A Comparative Critical Review,” *Renew. Sustain. Energy Rev.*, **40**, pp. 118–132.
- [164] Abdoulmoumine, N., Adhikari, S., Kulkarni, A., and Chattanathan, S., 2015, “A Review on Biomass Gasification Syngas Cleanup,” *Appl. Energy*, **155**, pp. 294–307.
- [165] Richardson, Y., Blin, J., and Julbe, A., 2012, “A Short Overview on Purification and Conditioning of Syngas Produced by Biomass Gasification: Catalytic Strategies, Process Intensification and New Concepts,” *Prog. Energy Combust. Sci.*, **38**(6), pp. 765–781.
- [166] Buentello-Montoya, D., Zhang, X., Li, J., Ranade, V., Marques, S., and Geron, M., 2020, “Performance of Biochar as a Catalyst for Tar Steam Reforming: Effect of the Porous Structure,” *Appl. Energy*, **259**(May), p. 114176.
- [167] Orío, A., Corella, J., and Narváez, I., 1997, “Performance of Different Dolomites on Hot Raw Gas Cleaning from Biomass Gasification with Air,” *Ind. Eng. Chem. Res.*, **36**(9), pp. 3800–3808.
- [168] Pallozzi, V., Di Carlo, A., Bocci, E., and Carlini, M., 2018, “Combined Gas Conditioning and Cleaning for Reduction of Tars in Biomass Gasification,” *Biomass and Bioenergy*, **109**(December 2017), pp. 85–90.
- [169] Pinto, F., André, R. N., Carolino, C., Miranda, M., Abelha, P., Direito, D., Dohrup, J., Sørensen, H. R., and Girio, F., 2015, “Effects of Experimental Conditions and of Addition of Natural Minerals on Syngas Production from Lignin by Oxy-Gasification: Comparison of Bench- and Pilot Scale Gasification,” *Fuel*, **140**, pp. 62–72.
- [170] Roche, E., De Andrés, J. M., Narros, A., and Rodríguez, M. E., 2014, “Air and Air-Steam Gasification of Sewage Sludge. The Influence of Dolomite and Throughput in Tar Production and Composition,” *Fuel*, **115**, pp. 54–61.

- [171] Simell, P. A., Leppälahti, J. K., and Bredenberg, J. B. so., 1992, "Catalytic Purification of Tarry Fuel Gas with Carbonate Rocks and Ferrous Materials," *Fuel*, **71**(2), pp. 211–218.
- [172] Taralas, G., Vassilatos, V., Sjöström, K., and Delgado, J., 1991, "Thermal and Catalytic Cracking of *n* -Heptane in Presence of CaO, MgO and Calcined Dolomites," *Can. J. Chem. Eng.*, **69**(6), pp. 1413–1419.
- [173] Taralas, G., 1996, "Catalytic Steam Cracking of N-Heptane with Special Reference to the Effect of Calcined Dolomite," *Ind. Eng. Chem. Res.*, **35**(7), pp. 2121–2126.
- [174] Orío, A., Corella, J., and Narváez, I., 1997, "Characterization and Activity of Different Dolomites for Hot Gas Cleaning in Biomass Gasification," *Developments in Thermochemical Biomass Conversion*, Springer Netherlands, pp. 1144–1157.
- [175] Narváez, I., Orío, A., Aznar, M. P., and Corella, J., 1996, "Biomass Gasification with Air in an Atmospheric Bubbling Fluidized Bed. Effect of Six Operational Variables on the Quality of the Produced Raw Gas," *Ind. Eng. Chem. Res.*, **35**(7), pp. 2110–2120.
- [176] Pérez, P., Aznar, P. M., Caballero, M. A., Gil, J., Martín, J. A., and Corella, J., 1997, "Hot Gas Cleaning and Upgrading with a Calcined Dolomite Located Downstream a Biomass Fluidized Bed Gasifier Operating with Steam-Oxygen Mixtures," *Energy and Fuels*, **11**(6), pp. 1194–1197.
- [177] Courson, C., Makaga, E., Petit, C., and Kiennemann, A., 2000, "Development of Ni Catalysts for Gas Production from Biomass Gasification. Reactivity in Steam- and Dry-Reforming," *Catal. Today*, **63**(2–4), pp. 427–437.
- [178] Virginie, M., Adánez, J., Courson, C., de Diego, L. F., García-Labiano, F., Niznansky, D., Kiennemann, A., Gayán, P., and Abad, A., "Effect of Fe–Olivine on the Tar Content during Biomass Gasification in a Dual Fluidized Bed," *Appl. Catal. B Environ.*, **121–122**, pp. 214–222.
- [179] Rauch, R., Bosch, K., Hofbauer, H., Świerczyński, D., Courson, C., and Kiennemann, A., *Comparison of Different Olivines for Biomass Steam Gasification*.
- [180] Rapagnà, S., Virginie, M., Gallucci, K., Courson, C., Di Marcello, M., Kiennemann, A., and Foscolo, P. U., 2011, "Fe/Olivine Catalyst for Biomass Steam Gasification: Preparation, Characterization and Testing at Real Process Conditions," *Catalysis Today*, Elsevier, pp.

163–168.

- [181] Guan, G., Chen, G., Kasai, Y., Lim, E. W. C., Hao, X., Kaewpanha, M., Abuliti, A., Fushimi, C., and Tsutsumi, A., 2012, “Catalytic Steam Reforming of Biomass Tar over Iron- or Nickel-Based Catalyst Supported on Calcined Scallop Shell,” *Appl. Catal. B Environ.*, **115–116**, pp. 159–168.
- [182] Hu, G., Xu, S., Li, S., Xiao, C., and Liu, S., 2006, “Steam Gasification of Apricot Stones with Olivine and Dolomite as Downstream Catalysts,” *Fuel Process. Technol.*, **87**(5), pp. 375–382.
- [183] Islam, M. W., 2020, “A Review of Dolomite Catalyst for Biomass Gasification Tar Removal,” *Fuel*, **267**(October 2019), p. 117095.
- [184] Christodoulou, C., Grimekis, D., Panopoulos, K. D., Pachatouridou, E. P., Iliopoulou, E. F., and Kakaras, E., 2014, “Comparing Calcined and Un-Treated Olivine as Bed Materials for Tar Reduction in Fluidized Bed Gasification,” *Fuel Process. Technol.*, **124**, pp. 275–285.
- [185] Simell, P., Kurkela, E., Ståhlberg, P., and Hepola, J., 1996, “Catalytic Hot Gas Cleaning of Gasification Gas,” *Catal. Today*, **27**(1–2), pp. 55–62.
- [186] Srinakruang, J., Sato, K., Vitidsant, T., and Fujimoto, K., 2006, “Highly Efficient Sulfur and Coking Resistance Catalysts for Tar Gasification with Steam,” *Fuel*, **85**(17–18), pp. 2419–2426.
- [187] Tian, Y., Zhou, X., Lin, S., Ji, X., Bai, J., and Xu, M., 2018, “Syngas Production from Air-Steam Gasification of Biomass with Natural Catalysts,” *Sci. Total Environ.*, **645**, pp. 518–523.
- [188] Simeone, E., Siedlecki, M., Nacken, M., Heidenreich, S., and de Jong, W., 2013, “High Temperature Gas Filtration with Ceramic Candles and Ashes Characterisation during Steam–Oxygen Blown Gasification of Biomass,” *Fuel*, **108**, pp. 99–111.
- [189] Tuomi, S., Kurkela, E., Simell, P., and Reinikainen, M., 2015, “Behaviour of Tars on the Filter in High Temperature Filtration of Biomass-Based Gasification Gas,” *Fuel*, **139**, pp. 220–231.
- [190] Valderrama Rios, M. L., González, A. M., Lora, E. E. S., and Almazán del Olmo, O. A.,

- 2018, “Reduction of Tar Generated during Biomass Gasification: A Review,” *Biomass and Bioenergy*, **108**(November 2017), pp. 345–370.
- [191] Prabhansu, Karmakar, M. K., Chandra, P., and Chatterjee, P. K., 2015, “A Review on the Fuel Gas Cleaning Technologies in Gasification Process,” *J. Environ. Chem. Eng.*, **3**(2), pp. 689–702.
- [192] Hasler, P., and Nussbaumer, T., 1999, “Gas Cleaning for IC Engine Applications from Fixed Bed Biomass Gasification,” *Biomass and Bioenergy*, **16**(6), pp. 385–395.
- [193] De Jong, W., Ünal, Ö., Andries, J., Hein, K. R. G., and Spliethoff, H., 2003, “Biomass and Fossil Fuel Conversion by Pressurised Fluidised Bed Gasification Using Hot Gas Ceramic Filters as Gas Cleaning,” *Biomass and Bioenergy*, **25**(1), pp. 59–83.
- [194] Nakamura, S., Kitano, S., and Yoshikawa, K., 2016, “Biomass Gasification Process with the Tar Removal Technologies Utilizing Bio-Oil Scrubber and Char Bed,” *Appl. Energy*, **170**, pp. 186–192.
- [195] Ma, L., Verelst, H., and Baron, G. V., 2005, “Integrated High Temperature Gas Cleaning: Tar Removal in Biomass Gasification with a Catalytic Filter,” *Catalysis Today*, Elsevier, pp. 729–734.
- [196] Engelen, K., Zhang, Y., Draelants, D. J., and Baron, G. V., 2003, “A Novel Catalytic Filter for Tar Removal from Biomass Gasification Gas: Improvement of the Catalytic Activity in Presence of H₂S,” *Chem. Eng. Sci.*, **58**(3–6), pp. 665–670.
- [197] Khummongkol, D., and Tangsathitkulchai, C., 1989, “A Model for Tar-Removal Efficiency from Biomass-Produced Gas Impinging on a Water Surface,” *Energy*, **14**(3), pp. 113–121.
- [198] van Paasen, S. V. B. ., Rabou, L. P. L. M. ., and Bär, R., “TAR REMOVAL WITH A WET ELECTROSTATIC PRECIPITATOR (ESP); A PARAMETRIC STUDY,” *Exhibition, Presented at “The 2nd World Conference and Technology on Biomass for Energy, Industry and Climate Protection” in Rome, Italy, 10-14 May 2004.*
- [199] Han, J., and Kim, H., 2008, “The Reduction and Control Technology of Tar during Biomass Gasification/Pyrolysis: An Overview,” *Renew. Sustain. Energy Rev.*, **12**(2), pp. 397–416.
- [200] Bhawe, A. G., Vyas, D. K., and Patel, J. B., 2008, “A Wet Packed Bed Scrubber-Based

Producer Gas Cooling-Cleaning System,” *Renew. Energy*, **33**(7), pp. 1716–1720.

- [201] Ahmad, N. A., and Zainal, Z. A., 2016, “Performance and Chemical Composition of Waste Palm Cooking Oil as Scrubbing Medium for Tar Removal from Biomass Producer Gas,” *J. Nat. Gas Sci. Eng.*, **32**, pp. 256–261.
- [202] Rapagnà, S., Gallucci, K., di Marcello, M., Matt, M., Nacken, M., Heidenreich, S., and Foscolo, P. U., 2010, “Gas Cleaning, Gas Conditioning and Tar Abatement by Means of a Catalytic Filter Candle in a Biomass Fluidized-Bed Gasifier,” *Bioresour. Technol.*, **101**(18), pp. 7123–7130.
- [203] García-Labiano, F., Gayán, P., de Diego, L. F., Abad, A., Mendiara, T., Adánez, J., Nacken, M., and Heidenreich, S., 2016, “Tar Abatement in a Fixed Bed Catalytic Filter Candle during Biomass Gasification in a Dual Fluidized Bed,” *Appl. Catal. B Environ.*, **188**, pp. 198–206.
- [204] Rapagnà, S., Gallucci, K., and Foscolo, P. U., 2018, “Olivine, Dolomite and Ceramic Filters in One Vessel to Produce Clean Gas from Biomass,” *Waste Manag.*, **71**, pp. 792–800.
- [205] Savuto, E., Carlo, A. Di, Steele, A., Heidenreich, S., Gallucci, K., and Rapagnà, S., 2019, “Syngas Conditioning by Ceramic Filter Candles Filled with Catalyst Pellets and Placed inside the Freeboard of a Fluidized Bed Steam Gasifier,” *Fuel Process. Technol.*, **191**, pp. 44–53.
- [206] Wilk, V., and Hofbauer, H., 2013, “Co-Gasification of Plastics and Biomass in a Dual Fluidized-Bed Steam Gasifier: Possible Interactions of Fuels,” *Energy and Fuels*, **27**(6), pp. 3261–3273.
- [207] Campoy, M., Gómez-Barea, A., Ollero, P., and Nilsson, S., 2014, “Gasification of Wastes in a Pilot Fluidized Bed Gasifier,” *Fuel Process. Technol.*, **121**, pp. 63–69.
- [208] D’Orazio, A., Rapagnà, S., Foscolo, P. U., Gallucci, K., Nacken, M., Heidenreich, S., Di Carlo, A., and Dell’Era, A., 2015, “Gas Conditioning in H₂ Rich Syngas Production by Biomass Steam Gasification: Experimental Comparison between Three Innovative Ceramic Filter Candles,” *Int. J. Hydrogen Energy*, **40**(23), pp. 7282–7290.
- [209] Rapagnà, S., Gallucci, K., Di Marcello, M., Foscolo, P. U., Nacken, M., Heidenreich, S., and Matt, M., 2012, “First Al₂O₃ Based Catalytic Filter Candles Operating in the Fluidized Bed Gasifier Freeboard,” *Fuel*, **97**, pp. 718–724.

- [210] Nacken, M., Baron, G. V., Heidenreich, S., Rapagnà, S., D’Orazio, A., Gallucci, K., Denayer, J. F. M., and Foscolo, P. U., 2015, “New DeTar Catalytic Filter with Integrated Catalytic Ceramic Foam: Catalytic Activity under Model and Real Bio Syngas Conditions,” *Fuel Process. Technol.*, **134**, pp. 98–106.
- [211] Husmann, M., Zuber, C., Maitz, V., Kienberger, T., and Hochenauer, C., 2016, “Comparison of Dolomite and Lime as Sorbents for In-Situ H₂S Removal with Respect to Gasification Parameters in Biomass Gasification,” *Fuel*, **181**, pp. 131–138.
- [212] Frilund, C., Simell, P., Kaisalo, N., Kurkela, E., and Koskinen-Soivi, M.-L., 2020, “Desulfurization of Biomass Syngas Using ZnO-Based Adsorbents: Long-Term Hydrogen Sulfide Breakthrough Experiments,” *Energy & Fuels*, **34**(3), pp. 3316–3325.
- [213] Cui, H., Turn, S. Q., Keffer, V., Evans, D., Tran, T., and Foley, M., 2010, “Contaminant Estimates and Removal in Product Gas from Biomass Steam Gasification,” *Energy & Fuels*, **24**(2), pp. 1222–1233.
- [214] Rodriguez, J. A., and Maiti, A., 2000, “Adsorption and Decomposition of H₂S on MgO(100), NiMgO(100), and ZnO(0001) Surfaces: A First-Principles Density Functional Study,” *J. Phys. Chem. B*, **104**(15), pp. 3630–3638.
- [215] Sharma, S. D., Dolan, M., Ilyushechkin, A. Y., McLennan, K. G., Nguyen, T., and Chase, D., 2010, “Recent Developments in Dry Hot Syngas Cleaning Processes,” *Fuel*, **89**(4), pp. 817–826.
- [216] Meng, X., De Jong, W., Pal, R., and Verkooyen, A. H. M., 2010, “In Bed and Downstream Hot Gas Desulphurization during Solid Fuel Gasification: A Review,” *Fuel Process. Technol.*, **91**(8), pp. 964–981.
- [217] “<https://www.statista.com/>” [Online]. Available: <https://www.statista.com/>.
- [218] “<https://markets.businessinsider.com/commodities>” [Online]. Available: <https://markets.businessinsider.com/commodities>.
- [219] Slimane, R. B., and Abbasian, J., 2000, “Copper-Based Sorbents for Coal Gas Desulfurization at Moderate Temperatures,” *Ind. Eng. Chem. Res.*, **39**(5), pp. 1338–1344.
- [220] Zeng, Y., Kaytakoglu, S., and Harrison, D. P., 2000, “Reduced Cerium Oxide as an Efficient

and Durable High Temperature Desulfurization Sorbent,” *Chem. Eng. Sci.*, **55**(21), pp. 4893–4900.

- [221] Ikenaga, N. O., Ohgaito, Y., Matsushima, H., and Suzuki, T., 2004, “Preparation of Zinc Ferrite in the Presence of Carbon Material and Its Application to Hot-Gas Cleaning,” *Fuel*, Elsevier, pp. 661–669.
- [222] Ephraïm, A., Ngo, L. D., Pham Minh, D., Lebonnois, D., Peregrina, C., Sharrock, P., and Nzihou, A., 2018, “Valorization of Waste-Derived Inorganic Sorbents for the Removal of HCl in Syngas,” *Waste and Biomass Valorization*, **0**(0), pp. 1–12.
- [223] Ren, X., Rokni, E., Liu, Y., and Levendis, Y. A., 2018, “Reduction of HCl Emissions from Combustion of Biomass by Alkali Carbonate Sorbents or by Thermal Pretreatment,” *J. Energy Eng.*, **144**(4).
- [224] Baek, J. I., Eom, T. H., Lee, J. B., Jegarl, S., Ryu, C. K., Park, Y. C., and Jo, S. H., 2015, “Cleaning of Gaseous Hydrogen Chloride in a Syngas by Spray-Dried Potassium-Based Solid Sorbents,” *Korean J. Chem. Eng.*, **32**(5), pp. 845–851.
- [225] Dou, B., Wang, C., Chen, H., Song, Y., Xie, B., Xu, Y., Tan, C., Wan, W., Engvall, K., Yang, W., Cavalli, A., Kunze, M., Aravind, P. V., Lee, Y. J., Choi, J. W., Park, J. H., Namkung, H., Song, G. S., Park, S. J., Lee, D. W., Kim, J. G., Jeon, C. H., Choi, Y. C., Ren, X., Rokni, E., Liu, Y., Levendis, Y. A., Tsvetkov, M. V., Polianczyk, E. V., and Zaichenko, A. Y., 2018, “HCl Neutralization by Alkaline Sorbents in the Gasification of Chloride-Containing Fuel in the Filtration Combustion Mode,” *ACS Sustain. Chem. Eng.*, **6**(10), pp. 13056–13065.
- [226] Partanen, J., Backman, P., Backman, R., and Hupa, M., 2005, “Absorption of HCl by Limestone in Hot Flue Gases. Part II: Importance of Calcium Hydroxychloride,” *Fuel*, **84**(12–13), pp. 1674–1684.
- [227] Chyang, C. S., Han, Y. L., and Zhong, Z. C., 2009, “Study of HCl Absorption by CaO at High Temperature,” *Energy and Fuels*, **23**(8), pp. 3948–3953.
- [228] Beatrice Coda, *,†, Martti Aho, ‡, Roland Berger, † and, and Hein†, K. R. G., 2001, “Behavior of Chlorine and Enrichment of Risky Elements in Bubbling Fluidized Bed Combustion of Biomass and Waste Assisted by Additives.”

- [229] Verdone, N., and De Filippis, P., 2006, “Reaction Kinetics of Hydrogen Chloride with Sodium Carbonate,” *Chem. Eng. Sci.*, **61**(22), pp. 7487–7496.
- [230] Ohtsuka, Y., Tsubouchi, N., Kikuchi, T., and Hashimoto, H., 2009, “Recent Progress in Japan on Hot Gas Cleanup of Hydrogen Chloride, Hydrogen Sulfide and Ammonia in Coal-Derived Fuel Gas,” *Powder Technol.*, **190**(3), pp. 340–347.
- [231] Krishnan, G. N., Canizales, A., Gupta, R., and Ayala, R., 1996, *Development of Disposable Sorbents for Chloride Removal from High-Temperature Coal-Derived Gases*, Pittsburgh, PA, and Morgantown, WV.
- [232] Dou, B., Wang, C., Chen, H., Song, Y., Xie, B., Xu, Y., and Tan, C., 2012, “Research Progress of Hot Gas Filtration, Desulphurization and HCl Removal in Coal-Derived Fuel Gas: A Review,” *Chem. Eng. Res. Des.*, **90**(11), pp. 1901–1917.
- [233] Monarca, D., Colantoni, A., Cecchini, M., Longo, L., Vecchione, L., Carlini, M., and Manzo, A., 2012, “Energy Characterization and Gasification of Biomass Derived by Hazelnut Cultivation: Analysis of Produced Syngas by Gas Chromatography,” *Math. Probl. Eng.*, **2012**, pp. 1–9.
- [234] Monarca, D., Cecchini, M., Guerrieri, M., and Colantoni, A., 2009, “CONVENTIONAL AND ALTERNATIVE USE OF BIOMASSES DERIVED BY HAZELNUT CULTIVATION AND PROCESSING,” *Acta Hortic.*, (845), pp. 627–634.
- [235] Di Carlo, A., Borello, D., Sisinni, M., Savuto, E., Venturini, P., Bocci, E., and Kuramoto, K., 2015, “Reforming of Tar Contained in a Raw Fuel Gas from Biomass Gasification Using Nickel-Mayenite Catalyst,” *Int. J. Hydrogen Energy*, **40**(30), pp. 9088–9095.
- [236] Ye, G., Xie, D., Qiao, W., Grace, J. R., and Lim, C. J., 2009, “Modeling of Fluidized Bed Membrane Reactors for Hydrogen Production from Steam Methane Reforming with Aspen Plus,” *Int. J. Hydrogen Energy*, **34**(11), pp. 4755–4762.
- [237] Sadaka, S. S., Ghaly, A. E., and Sabbah, M. A., 2002, “Two Phase Biomass Air-Steam Gasification Model for Fluidized Bed Reactors: Part I—Model Development,” *Biomass and Bioenergy*, **22**(6), pp. 439–462.
- [238] Demirbaş, A., 2001, “Carbonization Ranking of Selected Biomass for Charcoal, Liquid and Gaseous Products,” *Energy Convers. Manag.*, **42**(10), pp. 1229–1238.

- [239] Rapagnà, S., Orazio, A. D., Gallucci, K., and Ugo, P., 2014, "Hydrogen Rich Gas from Catalytic Steam Gasification of Biomass in a Fluidized Bed Containing Catalytic Filters," *Chem. Eng. Trans.*, **37**, pp. 157–162.
- [240] Damartzis, T., Michailos, S., and Zabaniotou, A., 2012, "Energetic Assessment of a Combined Heat and Power Integrated Biomass Gasification-Internal Combustion Engine System by Using Aspen Plus®," *Fuel Process. Technol.*, **95**, pp. 37–44.
- [241] Canneto, G.; Nanna, F.; Alvino, E.; Pinto, G.; Villone, A.; Carnevale, M.; Valerio, V.; Battafarano, A.; Corrado, M.; Barisano, D., "Deliverable 5.1: Test Campaign with the 1 MWth Prototype Gasifier Operation of the Gasifier in the Basic Configuration and Conversion into the Advanced One."
- [242] Serigio, R., and Ajmal, L., 1997, "Steam Gasification of Almond Shells in a Fluidised Bed Reactor: The Influence of Temperature and Particle Size on Product Yield and Distribution," *Biomass and Bioenergy*, **12**(4), pp. 281–288.
- [243] Karatas, H., Olgun, H., and Akgun, F., 2013, "Experimental Results of Gasification of Cotton Stalk and Hazelnut Shell in a Bubbling Fluidized Bed Gasifier under Air and Steam Atmospheres," *Fuel*, **112**, pp. 494–501.
- [244] Barisano, D., Canneto, G., Nanna, F., Villone, A., Alvino, E., Carnevale, M., and Pinto, G., 2014, "Production of Gaseous Carriers via Biomass Gasification for Energy Purposes," *Energy Procedia*, **45**, pp. 2–11.
- [245] Esfahani, R. M., Wan Ab Karim Ghani, W. A., Mohd Salleh, M. A., and Ali, S., 2012, "Hydrogen-Rich Gas Production from Palm Kernel Shell by Applying Air Gasification in Fluidized Bed Reactor," *Energy & Fuels*, **26**(2), pp. 1185–1191.
- [246] Barisano, D., Canneto, G., Nanna, F., Alvino, E., Pinto, G., Villone, A., Carnevale, M., Valerio, V., Battafarano, A., and Braccio, G., 2016, "Steam/Oxygen Biomass Gasification at Pilot Scale in an Internally Circulating Bubbling Fluidized Bed Reactor," *Fuel Process. Technol.*, **141**, pp. 74–81.
- [247] Bjoerkman, E., and Sjoestroem, K., 1991, "Decomposition of Ammonia over Dolomite and Related Compounds," *Energy & Fuels*, **5**(5), pp. 753–760.
- [248] Din, Z. U., and Zainal, Z. A., 2016, "Biomass Integrated Gasification-SOFC Systems:

Technology Overview,” *Renew. Sustain. Energy Rev.*, **53**, pp. 1356–1376.

- [249] Torres, W., Pansare, S. S., and Goodwin, J. G., 2007, “Hot Gas Removal of Tars, Ammonia, and Hydrogen Sulfide from Biomass Gasification Gas,” *Catal. Rev.*, **49**(4), pp. 407–456.
- [250] Dou, B., Wang, C., Chen, H., Song, Y., Xie, B., Xu, Y., and Tan, C., 2012, “Research Progress of Hot Gas Filtration, Desulphurization and HCl Removal in Coal-Derived Fuel Gas: A Review,” *Chem. Eng. Res. Des.*, **90**(11), pp. 1901–1917.
- [251] Karatas, H., and Akgun, F., 2018, “Experimental Results of Gasification of Walnut Shell and Pistachio Shell in a Bubbling Fluidized Bed Gasifier under Air and Steam Atmospheres,” *Fuel*, **214**(June 2017), pp. 285–292.
- [252] Karatas, H., and Akgun, F., 2018, “Experimental Results of Gasification of Walnut Shell and Pistachio Shell in a Bubbling Fluidized Bed Gasifier under Air and Steam Atmospheres,” *Fuel*, **214**(June 2017), pp. 285–292.
- [253] Savuto, E., Di Carlo, A., Bocci, E., D’Orazio, A., Villarini, M., Carlini, M., and Foscolo, P. U., 2015, “Development of a CFD Model for the Simulation of Tar and Methane Steam Reforming through a Ceramic Catalytic Filter,” *Int. J. Hydrogen Energy*, **40**(25), pp. 7991–8004.
- [254] Zhou, L., Yang, Z., Tang, A., Huang, H., Wei, D., Yu, E., and Lu, W., 2019, “Steam-Gasification of Biomass with CaO as Catalyst for Hydrogen-Rich Syngas Production,” *J. Energy Inst.*
- [255] Florin, N. H., and Harris, A. T., 2007, “Hydrogen Production from Biomass Coupled with Carbon Dioxide Capture: The Implications of Thermodynamic Equilibrium,” *Int. J. Hydrogen Energy*, **32**(17), pp. 4119–4134.
- [256] Lv, P. ., Xiong, Z. ., Chang, J., Wu, C. ., Chen, Y., and Zhu, J. ., 2004, “An Experimental Study on Biomass Air–Steam Gasification in a Fluidized Bed,” *Bioresour. Technol.*, **95**(1), pp. 95–101.
- [257] Savuto, E., Di Carlo, A., Bocci, E., D’Orazio, A., Villarini, M., Carlini, M., and Foscolo, P. U., 2015, “Development of a CFD Model for the Simulation of Tar and Methane Steam Reforming through a Ceramic Catalytic Filter,” *Int. J. Hydrogen Energy*, **40**(25), pp. 7991–8004.

- [258] Barisano, Donatella; Canneto, Giuseppe; Rep, M., “Deliverable 5.2: UNiFHY 1000 Long Term Tests and Further Hardware Modifications.”
- [259] Jand, N., and Foscolo, P. U., 2005, “Decomposition of Wood Particles in Fluidized Beds,” *Ind. Eng. Chem. Res.*, **44**(14), pp. 5079–5089.
- [260] Kunii, D., and Levenspiel, O., 1990, “Fluidized Reactor Models. 1. For Bubbling Beds of Fine, Intermediate, and Large Particles. 2. For the Lean Phase: Freeboard and Fast Fluidization,” *Ind. Eng. Chem. Res.*, **29**(7), pp. 1226–1234.
- [261] Hermann, H., Reinhard, R., Klaus, B., and Reinhard, K., 2002, *Biomass CHP Plant Güssing – A Success Story*, Strasbourg, France.
- [262] Marcantonio, V., Bocci, E., and Monarca, D., 2019, “Development of a Chemical Quasi-Equilibrium Model of Biomass Waste Gasification in a Fluidized-Bed Reactor by Using Aspen Plus,” *Energies*, **13**(1).
- [263] Fercher, E., Hofbauer, H., Fleck, T., Rauch, R., and Veronik, G., *TWO YEARS EXPERIENCE WITH THE FICFB-GASIFICATION PROCESS*.
- [264] Hofbauer, H., Rauch, R., Loeffler, G., Kaiser, S., Fercher, E., and Tremmel, H., 2002, “Six Years Experience with the FICFB-Gasification Process,” *Proc. 12th Eur. Conf. Technol. Exhib. Biomass Energy, Ind. Clim. Prot.*, (June 2014), pp. 982–985.
- [265] Pfeifer, C., Rauch, R., and Hofbauer, H., 2004, “In-Bed Catalytic Tar Reduction in a Dual Fluidized Bed Biomass Steam Gasifier,” *Ind. Eng. Chem. Res.*, **43**(7), pp. 1634–1640.
- [266] Doherty, W., Reynolds, A., and Kennedy, D., 2010, “Simulation of a Tubular Solid Oxide Fuel Cell Stack Operating on Biomass Syngas Using Aspen Plus,” pp. 5–11.
- [267] Kautz, M., and Hansen, U., 2007, “The Externally-Fired Gas-Turbine (EFGT-Cycle) for Decentralized Use of Biomass,” *Appl. Energy*, **84**, pp. 795–805.
- [268] Caresana, F., Comodi, G., Pelagalli, L., Renzi, M., and Vagni, S., 2011, “Use of a Test-Bed to Study the Performance of Micro Gas Turbines for Cogeneration Applications,” *Appl. Therm. Eng.*, **31**, pp. 3552–3558.
- [269] Wang, W., Cai, R., and Zhang, N., 2004, “General Characteristics of Single Shaft Microturbine Set at Variable Speed Operation and Its Optimization,” *Appl. Therm. Eng.*, **24**,

pp. 1851–1863.

- [270] Orecchini, F., Bocci, E., and Carlo, A. Di, 2006, “MCFC and Microturbine Power Plant Simulation,” *J. Power Sources*, **160**, pp. 835–841.
- [271] Renzi, M., Patuzzi, F., and Baratieri, M., 2017, “Syngas Feed of Micro Gas Turbines with Steam Injection: Effects on Performance, Combustion and Pollutants Formation,” *Appl. Energy*, **206**, pp. 697–707.
- [272] Clemente, S., Micheli, D., Reini, M., and Tacconi, R., 2013, “Bottoming Organic Rankine Cycle for a Small Scale Gas Turbine: A Comparison of Different Solutions,” *Appl. Energy*, **106**, pp. 355–364.
- [273] Kalina, J., 2011, “Integrated Biomass Gasification Combined Cycle Distributed Generation Plant with Reciprocating Gas Engine and ORC,” *Appl. Therm. Eng.*, **31**, pp. 2829–2840.
- [274] Camporeale, S. M., Pantaleo, A. M., Ciliberti, P. D., and Fortunato, B., 2015, “Cycle Configuration Analysis and Techno-Economic Sensitivity of Biomass Externally Fired Gas Turbine with Bottoming ORC,” *Energy Convers. Manag.*, **105**, pp. 1239–1250.