Biomass gasification process intensification for green hydrogen production: modeling and simulation in Aspen Plus

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“The highest forms of understanding we can achieve are laughter and human compassion.”
— Richard P. Feynman

Resumo

Novas formas de produzir energia, especialmente de origem renovável, estão atualmente a ser amplamente procuradas e pesquisadas. A gaseificação da biomassa é uma das tecnologias em crescimento para a produção de químicos para indústria e combustível gasoso, como syngas, ou gás de síntese, composto maioritariamente por hidrogénio e monóxido de carbono. Neste contexto, um modelo de gaseificação da biomassa foi desenvolvido em Aspen Plus para intensificar a produção de hidrogénio verde.

A primeira parte deste trabalho consistiu em reunir informação sobre o estado de arte atual, desde biomassa, gaseificadores, e a teoria da gaseificação. Depois, um modelo em Aspen Plus foi criado e validado com dados da literatura. A partir deste modelo, dois métodos de intensificação foram implementados usando biomassa de resíduos florestais. O primeiro consistiu na implementação de um reator de "deslocamento água-gás" (water-gas shift) depois do reator de gaseificação. O gaseificador é otimizado para produção de CO, e depois água já existente e adicionada, reagem no reator de "deslocamento água-gás" produzindo hidrogénio.

O segundo método de intensificação consistiu na reintrodução de CO_2 que foi produzido anteriormente.

De seguida, várias análises de sensibilidade foram realizadas: no gaseificador para otimizar a produção de CO; no reator de "deslocamento água-gás" para maximizar a produção de hidrogénio; e no gaseificador, introduzindo CO_2 para analisar a eficiência de usar um caudal reciclado.

Os principais resultados obtidos foram de uma máxima fração molar de CO de 36% no gaseificador, para uma temperatura de 850 °C e caudal de ar de 50 kg/h. O primeiro processo de intensificação, introdução de um reator "deslocamento água-gás", atinge um máximo valor de fração molar de hidrogénio final de 50%, para uma temperatura de reator de 100 °C e caudal de vapor adicional de 43 kg/h. O segundo processo de intensificação, uso de CO_2 reciclado, não se mostrou positivo para qualquer valor de caudal de CO_2 introduzido no gaseificador (1-60 kg/h).

Este trabalho foi capaz de provar a grande vantagem e interesse em introduzir um reator de deslocamento água-gás juntamente com um gaseificador, para a produção de hidrogénio a partir de resíduos florestais. A introdução de caudais de CO_2 reciclado, não foi, no entanto, vantajoso.

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Abstract

New ways of producing energy, especially renewable, are currently very much in demand. Biomass gasification is one of the growing technologies for the production of chemical feedstock and gaseous fuels, such as syngas. In this context, a biomass gasification model was developed in Aspen Plus to intensify green hydrogen production.

The first part of this work consisted of gathering information on the current state of the art in, biomass, gasifiers, and gasification theory. Then, an Aspen Plus model was created and validated with literature data. In this model, two intensification methods were implemented using biomass from forest residues. The first method consisted of incorporating a water-gas shift reactor after the gasification reactor. The gasifier is optimized for CO production, and then the water-gas shift reactor takes that CO, and with the already present and additional steam, the water-gas reaction takes place, producing hydrogen.

The second intensification method consisted of reintroducing CO_2 that had been produced previously.

Next, several sensibility analyses were performed: on the gasifier to maximize CO production; on the water-gas shift reactor to maximize H_2 production; and on the gasifier, introducing CO_2 to verify the recycle stream efficiency.

The main results were that in the gasifier a maximum production of CO occurred at a 36% molar fraction, for a gasifier temperature of 850 °C and an air mass flow of 50 kg/h. The first intensification process, the water-gas shift reactor introduction, operates at optimal conditions of 100 °C and additional steam flow of 43 kg/h for a final hydrogen yield of 50% molar fraction. The second intensification process, CO_2 recycling streams, proved not be positive for any of the CO_2 mass flows introduced in the gasifier (1-60 kg/h).

This work was able to prove the great efficiency and advantage of introducing a water-gas shift reactor alongside a gasifier for hydrogen production from forest residues. The introduction of CO_2 recycle streams, however, did not prove effective.

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1 Introduction

The topic of energy, its source, production, application, and consequences of application, is a current matter in today's society. As the population increases so does the energy demand, and with earth's finite resources, renewable ways of producing energy are the most sought for. The environmental consequences of energy consumption are also of concern because of pollution and global warming. In 2015, the Paris Agreement was adopted by 194 Parties (193 States plus the European Union), in hopes of mitigating the catastrophic results that the unhinged release of greenhouse gases into the atmosphere can create. The goal is to limit the global temperature increase by 2 °C in this century, while pushing efforts to limit the increase to 1.5 °C [1].

Portugal is one of several countries in the world wanting to become carbon neutral by 2050, with the Roadmap to Carbon Neutrality by 2050 (RCN2050) [2].

In this context, a dissertation work was proposed by Professor Eliseu, at the Faculty of Engineering at the University of Porto, Department of Mechanical Engineering, Section of Fluids and Energy, and accepted by the author of this dissertation.

Hydrogen produced sustainably has the potential to be an important energy source in the future, and this dissertation aims to study intensification processes to produce green hydrogen through biomass gasification modeling and simulation using Aspen Plus software.

This dissertation work involved research on the current state of art, from knowledge about biomass, gasifiers and gasification theory, to reading articles about current research done about gasification modelling and H_2 production and optimization. Learning about Aspen Plus software was required and then a model was created and validated through literature data. A new model was implemented as well as the intensification processes and their explanations. These intensification processes are the inclusion of a water gas shift reactor after the gasifier, and the inclusion of CO_2 recycling streams. Finally, parametric studies were done to optimize the process of green hydrogen production and the results were commented on.

In the following four chapters, lays the documentation of the work done. The second chapter consists of the review done of current literature information. The third chapter explains the model created in Aspen Plus and its validation, as well as the explanation of intensification processes. In the fourth chapter the parametric studies are laid out and explained. Finally, in the fifth chapter conclusions are taken from this work and future works envisioned.

2 Biomass Gasification

2.1 Biomass

Biomass is defined as being any organic materials derived from plants or animals, that is currently or was previously living [3]. It differs from fossil fuels for being sustainable and renewable. The interaction of the sun, water, soil, and CO_2 with plants and animals creates biomass on a continuous basis. Carbon dioxide absorbed recently by plants and released later by microorganisms after the plant dies or by biomass combustion renders biomass greenhouse gas (GHG) neutral [3]. This does not happen with fossil fuels.

Humanity has been using biomass since the beginning of civilization, for light and heat. From all the biomass on Earth, only 5% (13.5 billion metric tons) can potentially be converted into energy, but even this value is large enough to account for 26% of the world's energy consumption [3].

Today's developing countries use biomass, such as wood, mainly for cooking and heating. Developed countries not so much, as they use it for more industrial purposes, such as energy conversion or chemical feedstock. The usage of biomass also varies according to its geographical and socioeconomic conditions [3]. Biomass treatment and conversion can be of great benefit to communities, since it can be a solution for wastes produced, such as agricultural wastes and municipal solid wastes, and it can mitigate global warming.

Especially in Portugal, biomass use has great potential. 35% of land use in Portugal is dedicated towards Forests, 32% to Bushland and Pastureland and 24% is dedicated to Agriculture [4]. And since Portugal is constantly affected by wildfires [5], this is an important fact to consider when implementing biomass conversion technologies in the country.

Some common sources of biomass are as follows [3]:

- Agricultural: straw, food grain, and cattle manure;
- Forest: wood or bark, wood waste, sawdust, and trees;
- Biological: biological waste, animal waste, and aquatic species;
- Municipal: food waste, sewage sludge, and waste paper.
- Energy crops: willows, corn, and soybean.

Energy crops are a recent form of biomass, they are plants that are specifically grown for energy conversion [3].

All these forms of biomass can then have their energy released and converted through either of two main processes: biochemical or thermochemical conversions, as shown in Figure 1 [3].

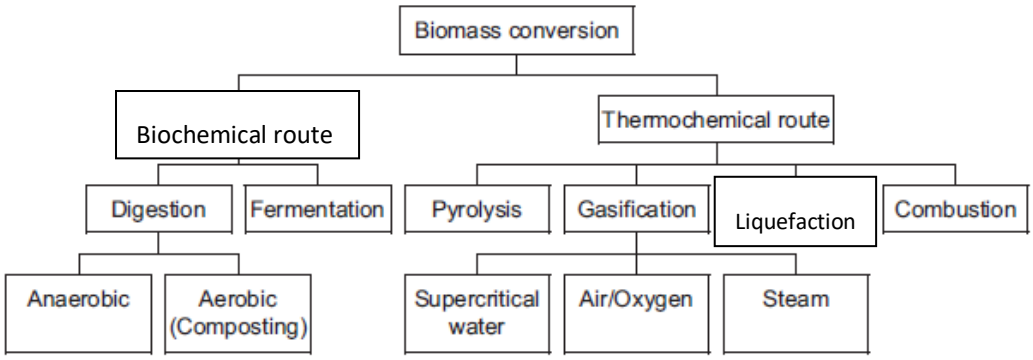


Figure 1 - Different conversion alternatives to obtain gas, liquid and solids fuels or chemical feedstock [3]

Biochemical processes have been used for longer periods of time, and some of their products are methane and ethanol. Thermochemical processes, on the other hand, are rather new, and their products include a wider range of compounds. Thermochemical processes are also more efficient. For example, in Table 1, we can see the comparison of these two processes for the production of ethanol [3].

Table 1 - Comparison of Biochemical and Thermochemical processes for the production of ethanol [3]

	Biochemical route (Sugar fermentation)	**Thermochemical route**
Feedstock	Sugarcane/starch/corn	Cellulosic stock/wood/ MSW
Reactor type	Batch	Continuous
Reaction time	Days	Minutes
Water usage	3.5 - 170 L/L ethanol	< 1 L/L ethanol
By-products	Distiller's dried grain	Syngas/electricity
Yield	400 L/ton	~ 265 - 492 L/ton
Technology maturity	>100 plants in the United States	Pilot plant

2.1.1 Characteristics of biomass

Biomass characteristics are an important factor that helps us understand what technology we might use and what products to expect, as well as the biomass products energy potential. Another way of classifying biomass may be as follows [3]:

- Woody biomass;
- Herbaceous biomass;
- Fruit biomass;
- Mixtures.

For plant biomass (woody, herbaceous and fruit), their composition can be further classified as containing cellulose, hemicellulose and lignin. These three polymers are widely present in most biomass in different quantities [6]. When biomass is gasified, cellulose plays a significant role

in the production of tar. On the other hand, hemicellulose tends to produce more gases and less tar [3].

Another characteristic of biomass is its moisture content. This moisture can be divided into two forms: intrinsic and extrinsic moisture [6]. Extrinsic moisture is the moisture that the biomass contains under the influence of weather effects at the time of its harvest. Therefore, the intrinsic moisture is the biomass moisture content without the same weather effects. In Table 2, the intrinsic moisture of some biomass is shown in its proximate analysis, alongside the volatile matter (VM), fixed carbon (FC) and ash, and the low heating value (LHV) of the biomass [6]. Proximate analysis is explained in Section 2.1.2.

Table 2 - Intrinsic moisture of biomass in proximate analysis [6]

Biomass	Moisture (%)	VM (%)	FC (%)	Ash (%)	LHV (MJ/kg)
Wood	20	82	17	1	18.6
Wheat straw	16	59	21	4	17.3
Barley straw	30	46	18	6	16.1
Lignite	34	29	31	6	26.8
Bituminous coal	11	35	45	9	34

When characterizing biomass, it is helpful to understand a few other concepts, like the atomic ratio. The atomic ratio is a way of classifying biomass, helping us understand its heating value as a fuel, among other things. For example, when the oxygen-to-carbon ratio (O/C) increases, the higher heating value decreases. The same relationship exists for the hydrogen-to-carbon ratio (H/C).

This relation is better explained in the following Figure 2 [3], where a plot is shown, also known as the *van Krevelen diagram*. Because the atomic ratios of a fuel change as its geological age rises, the older the fuel, the more energy it contains [3].

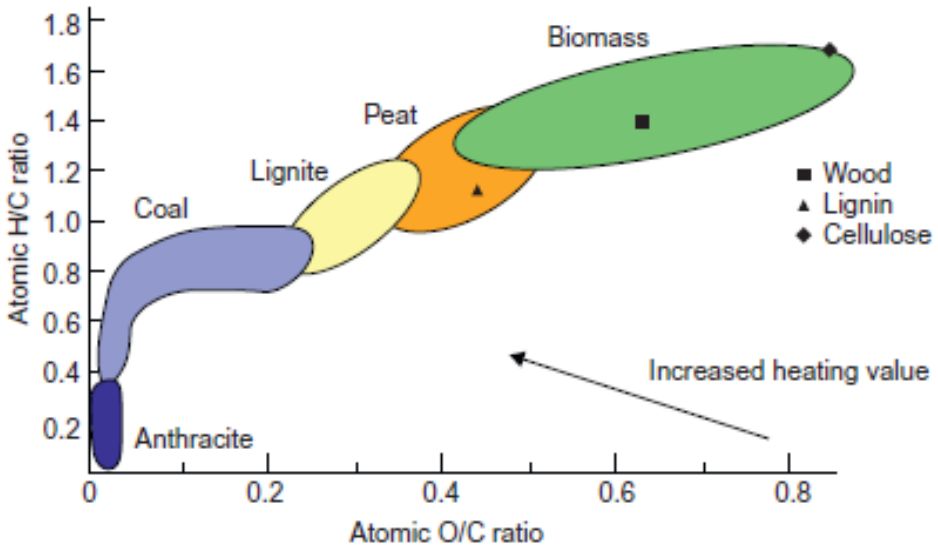


Figure 2 - The van Krevelen diagram [3]

Another diagram that is useful for biomass characterization is the Ternary diagram (Figure 3) [3].
This diagram represents what happens to the biomass composition when a gasification process is applied. In each corner of the triangle, there is 100% of carbon, oxygen and hydrogen. On each side of the triangle, there is a binary mixture. Say that, in the opposite line of the carbon corner, there is a hydrogen and oxygen mixture with no carbon. And inside the triangle, there are ternary mixtures. Then, we can see what happens after different processes occur; for example, the oxygen process moves the gas product towards the oxygen corner [3].

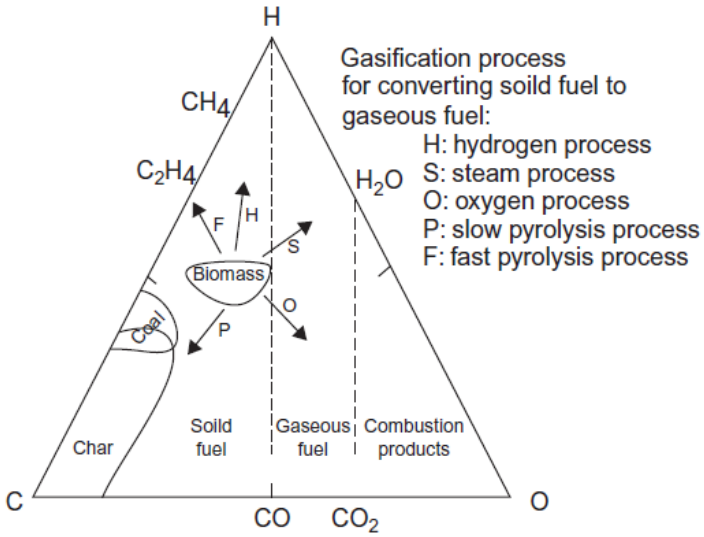


Figure 3 - Ternary diagram of the gasification process [3]

2.1.2 Composition of biomass

Biomass is composed by several complex organic compounds, moisture (M), and small amounts of inorganic impurities, such as, ash. Of the complex organic compounds, there are mainly four: carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). Municipal solid waste (MSW) or animal waste may also have sulfur (S) and chlorine (Cl). When using biomass for thermochemical conversions, there are two ways of describing their compositions: ultimate and proximate analysis [3].

Ultimate analysis

With the exception of moisture, M, and the inorganic components, ASH, the composition of the hydrocarbon fuel is represented in terms of its basic elements [3]:

$$C + H + O + N + S + M + ASH = 100\% \quad (2.1)$$

As we have seen before, not all biomass has these elements, most do not have sulfur (S). The fuel's moisture content, or water content, is represented separately as M. Thus, only the hydrogen and oxygen found in the organic fuel components are considered to be hydrogen and oxygen in the final analysis rather than the hydrogen and oxygen found in moisture [3].

Proximate analysis

According to proximate analysis, biomass is composed of its gross components, such as moisture (M), ash (ASH), volatile matter (VM) and fixed carbon (FC).

Moisture was mentioned before, and it will be further explored here, as it is a very important characteristic of biomass. Some biomass can have up to 90% moisture, and because of this, much of the energy delivered in a gasification plant is for drying and evaporation [3].

Ash is the inorganic solid residue that remains after the fuel has burned all the way through. Its main components are silica, aluminum, iron, and calcium; it may also contain trace amounts of magnesium, titanium, sodium, and potassium. The ash obtained from biomass conversion does not necessarily come from the biomass itself. When collecting, biomass is generally scraped off the forest floor and then undergoes repeated handlings, during which it might pick up a large amount of dirt, stones, and other contaminants. These contaminants are frequently the largest inorganic portion of the biomass feedstock in many plants [3].

Ash has usually a small contribution to biomass composition but may have a big impact on how biomass is used [3].

The condensable and noncondensable vapor that is emitted when a fuel is heated is referred to as its volatile matter. Both the rate of heating and the temperature to which it is heated affect how much there is [3].

To conclude the components of proximate analysis, the fixed carbon is the solid carbon in the biomass that is still present in the char formed during the pyrolysis process after devolatilization. Char is not pure carbon and is not the fixed carbon of the biomass, while being a carbon residue after pyrolysis or devolatilization. It is referred to as pyrolytic char and, in addition to fixed carbon, also includes some volatiles and ash. Char from biomass is highly reactive and quite permeable [3].

FC is a crucial characteristic since, in the majority of gasifiers, the pace of gasification and its yield are determined by the conversion of fixed carbon into gases. The size of the gasifier is decided using this conversion reaction, which is the slowest. Fixed carbon can be determined by [3]:

$$FC = 1 - M - VM - ASH \tag{2.2}$$

2.1.3 Heating values

The higher heating value (HHV) reflects the maximum amount of energy that might possibly be recovered from a specific biomass source because it is the whole energy content released when the fuel is burned in air, including the latent heat contained in the water vapor [6].
The lower heating value (LHV), also known as net calorific value, is the value of HHV minus the heat of vaporization of the water in the combustion product. The following gives the link between HHV and LHV [3]:

$$LHV = HHV - hg\left(\frac{9H}{100} - \frac{M}{100}\right) \tag{2.3}$$

where *hg*, H and M are the latent heat of steam, the hydrogen percentage, and the moisture percentage, respectively. The LHV and HHV units are in kJ/kg [3]. The LHV is a helpful tool to compare fuel potentials in general.

2.2 Gasification theory

Gasification is the process of converting solid, liquid, or gaseous fuels—fossil or non-fossil—into usable gases and chemicals. It needs a reaction medium, which can be either a gas or supercritical water (which should not be confused with regular water under subcritical conditions) [3]. Although gasification and combustion are two thermochemical processes that are very similar to one another, they differ significantly. Gasification stores energy in the chemical bonds of the resultant gas; combustion releases that energy by rupturing those chemical bonds [3].

The result of the gasification is the so-called syngas, – a fuel gas consisting mainly of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), water vapor (H_2O), methane (CH_4), nitrogen (N_2), some hydrocarbons in very low quantities and contaminants, - such as carbon particles, tar, and ash. The reactions takes place in the reactor or also called, gasifier [6]. Whatever their type, a number of steps, that are still the subject of debate among scientists, take place inside the gasifier, as seen in Figure 4 [3]. These steps are drying, pyrolysis, combustion, and gasification.

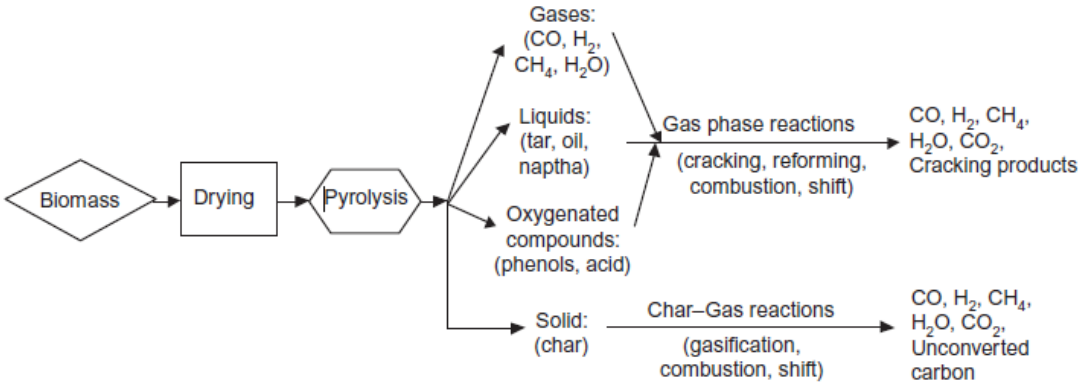


Figure 4 - Sequence of reactions and possible gasification routes [3]

2.2.1 Drying

Before gasification, the biomass moisture content should be between 10% and 15% [7]. The water is evacuated and turned into steam when the temperature rises above 373 K. Fuels do not decompose in any way throughout the drying process [8]. Every kilogram of moisture in the biomass requires at least an additional 2242 kJ of nonrecoverable energy from the gasifier to evaporate water [3]. Thus, some predrying is required to get the biomass as dry as possible before feeding it into the gasifier [3].

2.2.2 Pyrolysis

Pyrolysis (or devolatilization) does not require an outside agent. In pyrolysis, large biomass hydrocarbon molecules are thermally broken down into smaller (condensable and noncondensable) gas molecules without engaging in significant chemical reactions with air, gas, or any other gasifying media. Tar is one of the key byproducts of pyrolysis and is created when the condensable vapor generated during the process is condensed [3].

According to the ternary diagram (Figure 3), more char is produced as a result of a slow pyrolysis process advancing the solid product toward the carbon corner. On the other hand, the rapid pyrolysis process drives the product away from the oxygen corner and toward the C-H axis (Figure 3). By considerably reducing the oxygen, more liquid hydrocarbon is produced.

The thermochemical reaction in Equation 2.4 can describe what happens in pyrolysis [9]:

$$Biomass + Heat \rightarrow H_2 + CO + CO_2 + H_2O + CH_4 + C_nH_m + tar + char \quad (2.4)$$

2.2.3 Combustion

Combustion may also be called oxidation. In addition to oxygen and water vapors, the air introduced in the oxidation zone also contains inert gases like nitrogen and argon. These inert gases are thought to not react with the components of fuel. So, these inert gases can decrease the plant's efficiency [3]. Temperatures between 975 and 1275 K are normal for oxidation [8].

There are two main reactions happening, carbon monoxide being created when solid carbonized fuel and airborne oxygen interact heterogeneously (Eq. 2.5), and steam being created when the fuel's hydrogen combines with the oxygen in the air blast (Eq. 2.6). The supply and release of heat energy during the operations are denoted, respectively, by plus and minus signs [8].

$$C + O_2 \rightarrow CO_2 - 394\ \frac{KJ}{mol} \quad (2.5)$$

$$H_2 + 0.5O_2 \rightarrow H_2O - 242\ \frac{KJ}{mol} \quad (2.6)$$

Other reactions include:

$$CO + 0.5O_2 \rightarrow CO_2 - 284\frac{KJ}{mol} \quad (2.7)$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O - 803\frac{KJ}{mol} \quad (2.8)$$

$$C + 0.5O_2 \leftrightarrow CO - 111\frac{KJ}{mol} \quad (2.9)$$

As we can see from Equations 2.5-2.9, most combustion reactions are exothermic. In a gasifier, a limited amount of exothermic combustion reactions is permitted in order to supply the necessary heat for the gasification reactions as well as that needed for heating, drying, and pyrolysis. Reactions from equations (2.5) and (2.7) are the most used for this purpose [3]. Gasifiers that produce their own heat are referred to as auto-thermal, and those that need heat are referred to as allothermal. Auto-thermal processes are the most typical [7].

2.2.4 Gasification

In the gasification step, also called reduction, the hydrocarbons in the fuel, the steam, carbon dioxide, oxygen, and hydrogen in the reactor, as well as the evolved gases, all undergo chemical reactions. Char gasification is the most significant of these. Below we can see the most important reactions.

$$C + CO_2 \leftrightarrow 2CO + 172\frac{KJ}{mol} \quad (2.10)$$

$$C + H_2O \leftrightarrow CO + H_2 + 131\frac{KJ}{mol} \quad (2.11)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 - 41.2\frac{KJ}{mol} \quad (2.12)$$

$$C + 2H_2 \leftrightarrow CH_4 - 74.8\frac{KJ}{mol} \quad (2.13)$$

These reactions (2.10-2.13), are respectively, the Boudouard reaction, the Water-Gas reaction, the Shift reaction and the Hydrogasification reaction. When total gasification takes place, all the carbon is burned or converted to carbon monoxide, along with some additional mineral matter that is evaporated. Ash and char make up the remainder (unburned carbon), along with the final gas product [8].

In comparable circumstances, combustion processes often occur more quickly than gasification reactions. At a typical gasifier temperature of 900 °C, Table 3 compares the rates of combustion and gasification for a biomass char. The gasification reaction rate is at least an order of magnitude slower than the combustion rate. The combustion of smaller char particles occurs at a significantly faster pace due to pore diffusion resistance [3].

Table 3 - Comparison of char gasification and combustion rates affected by pore diffusion [3]

Particle size (µm)	**Combustion rate (min^{-1})**	**Gasification rate (min^{-1})**	**Combustion rate/ Gasification rate**
6350	0.648	0.042	15.4
841	5.04	0.317	15.9
74	55.9	0.975	57.3

Lastly, in biomass gasification, the use of catalysts is not necessary, but it can be helpful. They may be used for the following motives [3]:

- Removal of tar from the product gas, particularly if the installed equipment or applications downstream cannot tolerate it;
- Reduction in the product gas's methane content, especially when it's intended for use as syngas (CO, H_2 mixture).

Both in situ and postgasification reactions can use catalysts. In the former, the catalyst may be infused into the biomass before gasification. The most commonly used catalysts are dolomite, potassium and sodium carbonate, and nickel [3].

2.2.5 Reactors

With variations within each kind, there are primarily two types of gasifiers: fixed bed and fluidized bed [7].

Fixed bed gasifiers

In fixed bed gasifiers, there is the updraft gasifier and the downdraft gasifier. In an updraft gasifier (Figure 5), fuel is fed from the top, and product gas also exits the gasifier from the top. Via a grid at the bottom of the gasifier, the gasifying agent (air, oxygen, steam, or their combination) is heated and delivered into the device. In Figure 5, we can see the gasifiers zones, where the main reactions take place, and their occurring temperatures [3].

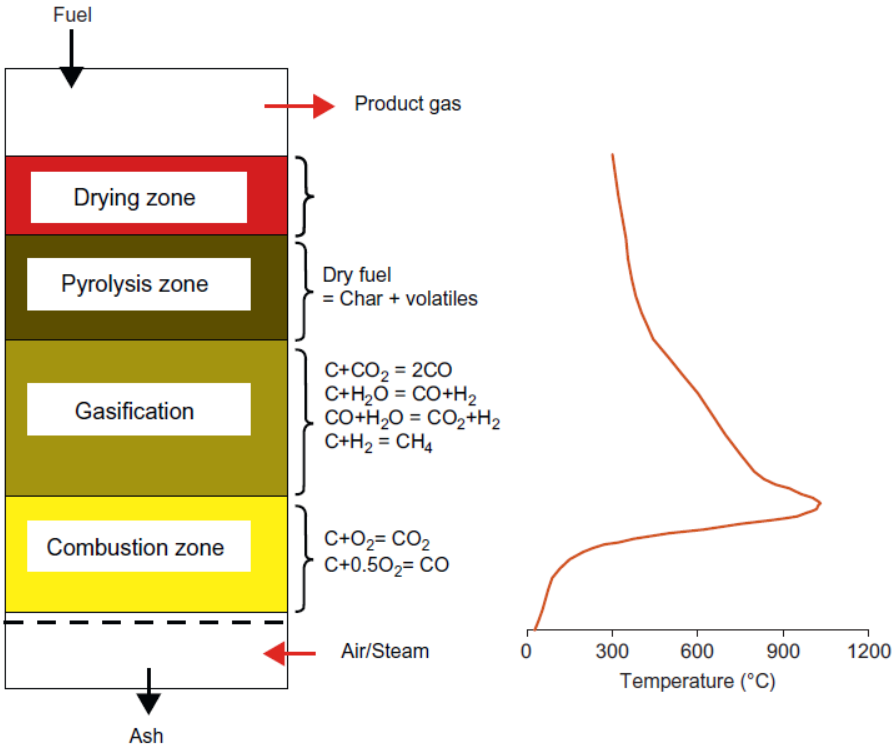


Figure 5 - Gasification in an updraft gasifier [3]

The gas being delivered into the chamber rises through a bed of ash and fuel that is falling. Hot ash and unconverted chars descending from the top of the bed meet the air (the gasifying medium) as it enters the bottom of the bed. The very exothermic combustion reaction, Eq. 2.5, occurs in the presence of too much oxygen because the temperature in the bottom layer is significantly higher than the temperature at which carbon ignites. The solids that are falling and the upward-moving gas are both heated by the energy released. As this reaction happens quickly and consumes most of the oxygen, the reaction from Eq. 2.9 happens next, releasing CO and releasing less than half the amount of heat the previous equation releases [3].

The hot gas from the combustion zone, which is composed of CO, CO_2, and steam (from the feed and the gasifying medium), ascends further into the gasification zone, where char from the upper bed is gasified by Equations 2.10 and 2.12 [3].

Biomass is pyrolyzed in the zone above the gasification zone. The dry biomass that is falling from above is heated by the residual heat of the hot gas rising. After that, the biomass is converted into noncondensable and condensable gases, and char. When the solid char and other solids sink, both gases ascend [3].

In a downdraft gasifier, heat is released when air pumped into the pyrolysis product and biomass supplied from the top descends and reacts (Figure 6). After that, the particles (char and ash) and product gas both descend in the downdraft gasifier. Consequently, the burning of pyrolysis gas provides the thermal energy needed for drying, pyrolysis, and gasification [3].

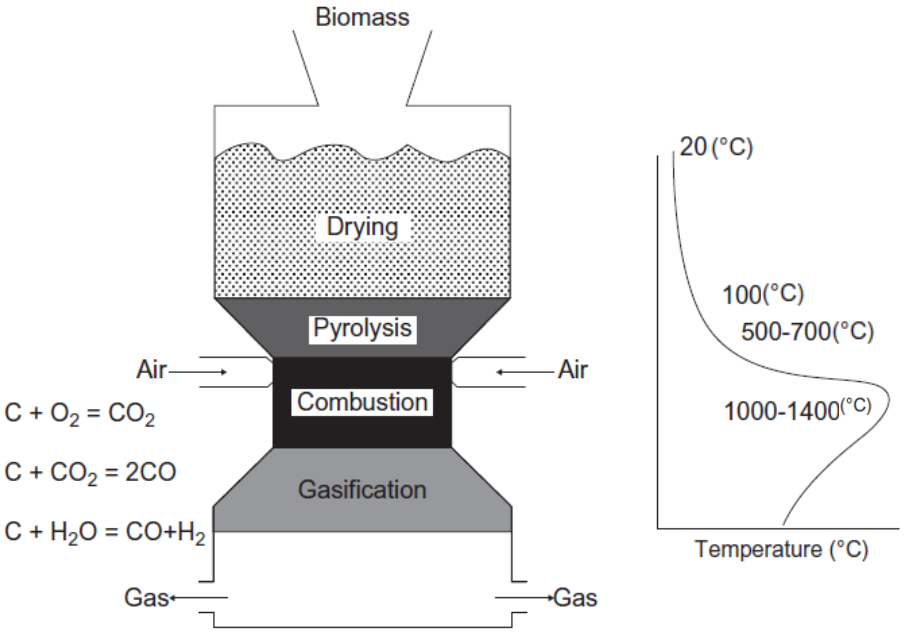


Figure 6 - Gasification in a downdraft gasifier [3]

When pyrolysis occurs, the burning substances move downward. The leftover hot char is subsequently covered by the hot gas, where gasification occurs. Gases with low energy content but no tar are produced as a result of this arrangement [3].

Fluidized bed gasifiers

Fluidized bed gasifiers are divided into two types, bubbling fluidized bed, and circulating fluidized bed. A fluidized bed gasifier, in contrast to other types of reactors, incorporates nonfuel granular materials (bed solids), which serve as a heat transporter and mixer. Fuel put into a bubbling fluidized bed from the top or the sides mixes rather quickly across the fluid bed's whole surface (Figure 7). The fluidizing gas, which also serves as the gasifying medium, is introduced through the reactor's bottom [3].

In a typical fluidized bed gasifier, hot bed solids are used to quickly heat fresh solid fuel particles to the bed temperature, causing them to undergo rapid drying and pyrolysis, which produces char and gases [3].

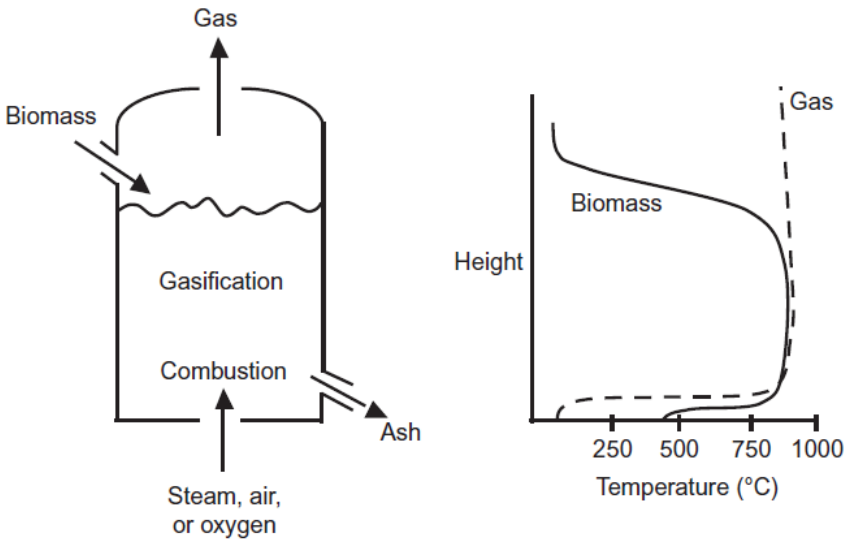


Figure 7 - Bubbling fluidizing bed gasifier [3]

Despite the well-mixed bed materials, the fluidizing gas generally continues to flow in a plug-flow pattern, coming from the bottom and exiting from the top. When oxygen enters the bed's bottom, it quickly exothermically reacts with the char and bed components [3].

When the gas rises, subsequent gasification events occur higher up. The principal channel to the top may be the fluidized bed's bubbles. They contain hardly any solids. Although they aid in mixing, bubbles can also let gas pass through solids without taking part in the gasification processes. In contact with the heated solids, the pyrolysis byproducts transform into noncondensable gases. Tar and char are created if they rise over the bed and into the colder freeboard. Due to the solids' back-mixing, a bubbling fluidized bed cannot achieve total char conversion. A bubbling fluidized bed gasifier can achieve temperature uniformity because of the high degree of solid mixing, but any solids that are removed from the bed will still contain some partially gasified char because of the close mixing of fully and partially gasified fuel particles [3].

In a circulating fluidized bed, materials move through a loop that is distinguished by vigorous mixing and a prolonged solid residence period. The gas-bypassing issue of bubbling fluidized beds is avoided since there are no bubbles [3].

Other gasifiers

Several models, such as twin fluidized beds and entrained beds, have been developed to enhance the quality of the produced gas in addition to the described gasifiers. By encouraging the generation of H_2, the first one seeks to raise the heat value of the produced gas. The second process removes tar and condensable gases from the generated gas by operating at high temperatures between 1200-1500 °C. In fact, it closes in on 100% conversion efficiency. However, there are several issues with the choice of materials to endure the high temperatures and ash liquefaction [8].

2.2.6 Kinetics of gasification

The products of a completed reaction can be determined with the aid of stoichiometric calculations. In a gasifier, not every reaction occurs instantly and entirely, transforming

reactants into products. A large number of the chemical reactions covered in the sections above happen at finite rates and to finite extents.

The equilibrium state of a reaction determines how far it advances. On the other hand, the reaction's kinetic rates govern how quickly the reaction products are produced and if the process is capable of finishing inside the gasifier chamber. With the following reaction we may comprehend chemical equilibrium [3]:

$$nA + mB \rightarrow pC + qD \tag{2.14}$$

where, n, m, p, and q are the stoichiometric coefficients. The concentrations of the reactants A and B are C_A and C_B, respectively. The determination this reaction's rate, r_1, can be seen below [3]:

$$r_1 = k_{for} C_A^n C_B^m \tag{2.15}$$

where k_{for} is the reaction's rate constant.

The reaction can also happen in the other direction. And its rate of reaction, r_2, can be given as [3]:

$$r_2 = k_{back} C_C^p C_D^q \tag{2.16}$$

The concentration of the reactants A and B is high when the reaction starts, whereas the concentration of the products C and D is low. So, the forward reaction rate (r_1) is initially substantially higher than the reverse reaction rate (r_2). The forward reaction speeds up the accumulation of products C and D. The two rates eventually reach a stage when they are equal ($r_1 = r_2$) [3]. The equilibrium stage is then reached, and this can be recognized:

- Neither the concentration of the reactants nor the concentration of the products changes;
- The forward reaction rate and the reverse reaction rate are equivalent;
- The system's Gibbs free energy is at its minimum;
- The system is at its highest level of entropy.

Gibbs free energy

Gibbs free energy, or G, plays a significant role in thermodynamics. Its change can be determined by two ways. The first is by the change in entropy, ΔS, and enthalpy, ΔH, as follows [3]:

$$\Delta G = \Delta H - T\Delta S \tag{2.17}$$

where T is temperature.

The other way to determine the Gibbs free energy is by using Probstein and Hicks' (2006) empirical equations. It uses the heat of formation in the reference state at 1 atm and 298 K, temperature, T, and a number of empirical coefficients, such as a' and b', to describe the Gibbs function and the enthalpy of formation, respectively [3].

$$\Delta G_{f,T}^0 = \Delta h_{298}^0 - a'Tln(T) - b'T^2 - \left(\frac{c'}{2}\right)T^3 - \left(\frac{d'}{3}\right)T^4 + \left(\frac{e'}{2T}\right) + f' + g'T \ \frac{kJ}{mol} \tag{2.18}$$

$$\Delta H_{f,T}^0 = \Delta h_{298}^0 - a'T + b'T^2 + c'T^3 + d'^{T^4} + \left(\frac{e'}{T}\right) + f' \quad kJ/mol \tag{2.19}$$

Nonstoichiometric equilibrium models

Experiments can provide more accurate design data than modeling or simulation, although being more expensive. Yet, experimental data has a significant drawback. The optimal operating condition selected from the experiment is no longer valid if one of the original process variables changes. So, while a gasifier's performance may not be very accurately predicted by simulation or mathematical modeling, it can at least offer general advice on the impact of design, operational, and feedstock characteristics [3].

Thermodynamic equilibrium calculations can be used to examine the effects of fuel and process parameters because they are independent of gasifier design. The greatest attainable yield of a desired product can be predicted by this model, even when chemical or thermodynamic equilibrium may not be attained within the gasifier. It is also unable to foresee the effects of design elements like gasifier height, hydrodynamic or geometric parameters like fluidizing velocity [3].

Prior to 1958, all equilibrium calculations were performed using the governing equations' formulation of the equilibrium constant (stoichiometric model) (Zeleznik and Gordon, 1968). Later, Gibbs free energy minimization (or non-stoichiometric model) computation of equilibrium compositions was recognized as a substitute. The nonstoichiometric equilibrium model is especially appropriate for fuels like biomass, whose precise chemical composition is unknown. The feed's elemental composition, which may be determined from its ultimate analysis, is the sole input required. A specific reaction mechanism is not necessary in nonstoichiometric modeling to solve the problem [3].

When the system's Gibbs free energy is at its lowest, a stable equilibrium condition is attained in a reactive system. To determine the Gibbs free energy, G_{total} for the gasification product comprising N species (i=1, …, N), the equation below is used [3]:

$$G_{total} = \sum_{i=1}^{N} n_i \, \Delta G_{f,i}^{0} + \sum_{i=1}^{N} n_i \, RTln\left(\frac{n_i}{\sum n_i}\right) \quad (2.20)$$

where, $\Delta G_{f,i}^{0}$ is the Gibbs free energy of formation of species *i* at standard pressure of 1 bar.

To reduce G_{total}, equation (2.20) must be calculated for unknown values of n_i while keeping in mind that each element's overall mass balance must be taken into account. For instance, the amount of carbon identified by ultimate analysis must equal the entire amount of carbon in the gas mixture created, regardless of the reaction path, kind, or chemical formula of the fuel [3].

2.3 Intensification processes

As we have seen before, the final composition of the gas product, syngas, can be influenced by a variety of factors, the biomass, gasifier type, and gasifying medium. The solid carbon and heavier hydrocarbons react with the gasifying medium (also known as the "agent") to create low-molecular-weight gases like CO and H_2 [3].

The use of air, oxygen and steam as gasifying agents are the most common used, but now mixtures of these and/with CO_2 are also becoming the focus of academic experiments and reviews.

2.3.1 Air, oxygen, and steam

The type and quantity of the gasifying agent employed has a significant impact on the heating value and composition of the gas produced in a gasifier. Table 4 displays the outcomes of

experiments employing several types of oxidizers (gasifying agents) to gasify wood on different gasifiers [8].

Table 4 - Effect of different oxidizers on final syngas composition [8]

	Composition (% vol. dry basis)					HHV (MJ/m^3)
Oxidizing agent (Gasifier)	H_2	CO	CO_2	CH_4	N_2	
Air (Downdraft)	17	21	13	1	48	5.7
Air (Updraft)	11	24	9	3	53	5.5
O_2 (Downdraft)	32	48	15	2	3	10.4
Air (BFB)	9	14	20	7	50	5.4
Air (CFB)	14.1	18.7	14.7	3.5	47.7	n.d.
Air (BFB)	9.5	18	13.5	4.5	45	n.d.
Steam (CFB)	34.2	27.2	22.7	11.1	4.8	n.d.
Steam (BFB)	52	23	18	7	n.d.	n.d.

The ternary diagram of carbon, hydrogen, and oxygen (Figure 3) illustrates the conversion processes that lead to the synthesis of various products in a gasifier. The conversion path travels in the direction of the oxygen corner if oxygen is used as the gasifying agent. Products from it include CO and CO_2. If air is used in place of oxygen, the nitrogen in it will contaminate the product and reduce its heating value. When steam is used as the gasification agent, the hydrogen corner becomes closer. Hence, the resultant gas has a larger hydrogen to carbon ratio because it has more hydrogen per unit of carbon. Overall, oxygen gasification, followed by steam and air gasification, have the highest heating value [3].

According to [7], we can divide the product gas into three groups, according to their calorific value (CV) and their gasifying agent:

- Low CV (4–6 MJ/Nm^3) - Using air and steam/air;
- Medium CV (12–18 MJ/Nm^3) - Using oxygen and steam;
- High CV (40 MJ/Nm^3) - Using hydrogen and hydrogenation;

Equivalence ratio

In combustion the term Excess of Air (EA) is used. It is the actual amount of air used in a combustion reaction divided by the stoichiometric amount of air. It is the ratio between the actual and stoichiometric air-fuel ratios. EA is generally bigger than 1 for combustion reactions. In a gasifier, or air deficient situations, a similar principle is applied, the Equivalence Ratio (ER). This time, the actual air utilized is way smaller than the stoichiometric one, so the ER value is less than one [3].

$$ER = \frac{actual\ air}{stoichiometric\ air} \tag{2.21}$$

For gasification the ER value should be between 0.2-0.3. If the value is lower than 0.2, there is more char and tar formation because there isn't much gasification and combustion reactions taking place, resulting in a gas with lower heating value. If the ER is bigger than 0.3, more

reactions take place, mainly combustion reactions forming products like CO_2 and H_2O at the expense of wanted gases like H_2 and CO. The heating value will therefore be higher [3].

Steam to biomass ratio

Another useful term concerning gasifying mediums characterization is Steam to Biomass Ratio (SBR). This term is simply the steam mass flow divided by the biomass mass flow.

2.3.2 CO_2

Anthropogenic CO_2 can be consumed in the process of converting a variety of wastes to valuable gaseous fuels, reaching the dual benefits of CO_2-to-fuel and waste-to-wealth. CO_2 gasification offers a potential carbon-negative solution to the two major escalating crises of energy insecurity and global warming. The use of CO_2 by itself or with air/steam as a gasifying agent causes the reaction products to contain more CO. After pyrolysis, the volatiles remaining undergo with CO_2 homogeneous gas phase reactions that include steam reforming, reverse water-gas shift, and dry reforming, as seen below respectively [10].

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO + 206\frac{kJ}{mol} \quad (2.22)$$

$$H_2 + CO_2 \leftrightarrow CO + H_2O + 42\frac{kJ}{mol} \quad (2.23)$$

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO + 247\frac{kJ}{mol} \quad (2.24)$$

As these reactions take place, the gasification reactions, Boudouard, water-gas and the inverse of the hydrogasification reaction, called methane cracking, are intensified [10]. The methane cracking equation can be seen in Equation 2.25.

$$CH_4 \leftrightarrow C + 2H_2 + 74.8\frac{KJ}{mol} \quad (2.25)$$

Article [10] made an extensive review of parameters and properties that maximize CO production in the syngas, and it is summarized below:

- Increasing gasifier temperature, as it favors the Boudouard reaction;
- Increasing gasification pressure/CO_2 partial pressure;
- Lower particle sizes, as it results in higher bulk densities and bigger exterior surface areas per unit volume, which improves the efficiency and uniformity of the heat transfer between the CO_2-reacting particles;
- Pore structure. More porous structures often have greater specific surface areas, which would increase their sensitivity to CO_2 (improved diffusion path);
- Content of intrinsic mineral contents. Alkali and alkaline earth metals (AAEMs), which are naturally occurring in the feedstock, frequently increase the reactivity of the raw feedstock, whereas SiO_2 and Al_2O_3 have an inhibitory influence on reactivity;
- Certain catalysts, help the CO_2 gasification process;
- Co-gasification: certain fuels often manifest increased conversion/reactivity of feedstocks and decreased activation energies, relative to separate feedstocks.

When using CO_2 as the agent, the gasifier temperature decreases, as the Boudouard reaction is endothermic, so in [9], experiments with oxygen enriched air/CO_2 gasification were made in an autothermal downdraft gasifier, and the results were that the CO composition in the syngas increased.

2.3.3 CO_2 adsorption

Besides the use of CO_2 as a gasifying agent, also CO_2 adsorption is a developing technology. Developing an effective purification process is one of the biggest obstacles to producing hydrogen. In conventional hydrogen production facilities, the shifted gas must first be pre-cooled to the required temperature of the CO_2 absorption units, and then it must be reheated after the CO_2 has been removed [11]. Standard practice uses normal temperature pressure swing adsorption (NT-PSA), but as an alternative, the elevated-temperature pressure swing adsorption (ET-PSA) method can be used, which uses in-situ CO_2 adsorption, elevated-temperature CO_2 adsorption, and WGS catalysts, simultaneously (Figure 8). The trade-off between the H_2 recovery ratio (HRR) and the H_2 purity (HP) is also overcome by ET-PSA [11].

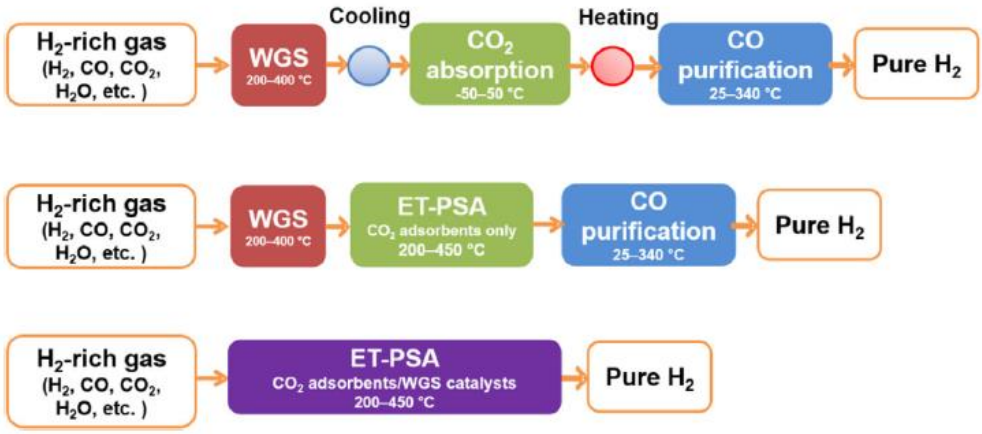


Figure 8 - Diagram showing the block flow for the synthesis of H_2 rich syngas [11]

Adsorption utilizes differences in the strength of contact between various species in the gas phase and the surface of a solid known as a sorbent or adsorbent. When a gas travels through a bed of sorbent, a species that is more strongly adsorbed builds up on the sorbent and is thereby expelled from the gas phase. The gas is cleansed as it passes through the sorbent bed. As the adsorbed component builds up on the sorbent, it eventually reaches saturation and can no longer absorb any more. There is reversible and irreversible adsorption. Most of the time, irreversible adsorption is impractical because the adsorbate is a needed product. For reversible adsorption, the bed must be removed from the process when it achieves or approaches breakthrough so that the sorbent may be renewed and the components that have been adsorbed can be recovered. Increasing temperature or decreasing pressure to get a lower equilibrium concentration of the adsorbed component on the solid surface is the typical method for regeneration of the sorbent [12].

Pressure swing adsorption, or PSA, is the process of regenerating the bed by lowering the applied pressure. Although heat from adsorption and desorption effects must be considered in the design, pressure swing adsorption processes are theoretically isothermal. The utilization of extremely quick cycles lasting only a few minutes is possible since the process is not constrained by heat transfer rates [12].

2.3.4 Water-gas shift reactor

Similar to a gasifier, where biomass goes through a series of reactions with a gasifying agent, there can also be a reactor where only one reaction takes place. In this case, the water-gas shift reaction and its reverse reaction can occur freely in a reactor. The yield of hydrogen can be further increased by carrying out the water-gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 - 41.2\frac{KJ}{mol} \quad (2.26)$$

Above roughly 450 °C, the water-gas shift process quickly reaches equilibrium. In this reaction, higher temperatures encourage the creation of carbon monoxide whereas lower temperatures favor the formation of more hydrogen. When hydrogen is the intended product, a medium- or low-temperature shift catalyst and excessive steam are used to enhance this reaction at lower temperatures [12].

3 Aspen Plus Model

A gasifier's performance may not be very accurately predicted by simulation or mathematical modeling, but it can at least offer general advice on the impact of design, operational, and feedstock characteristics [3].

To simulate our model, Aspen Plus was used. Aspen Plus is an input software with a problem-oriented approach that can be used to more easily calculate physical, chemical, and biological processes. This simulation software is based on mass, energy, and chemical equilibrium relations. It includes a number of integrated unit operations, such as pumps, heat exchangers, separators and reactors [3].

The Aspen Plus model created most proximately replicates a downdraft gasifier.

The following block operations available in the Aspen Plus flowsheet were used in the models:

- Conversion or stoichiometric reactor

A conversion reactor needs a reaction stoichiometry as well as an extent of reaction, which is typically defined as the extent of a limiting reagent's conversion. It can be employed when the reaction kinetics are unknown (which is frequently the case in the early stages of design) or when it is known that the process will continue to full conversion since no reaction kinetics information is required [12].

- Yield shift reactor

By enabling the designer to choose a yield pattern, the yield shift reactor gets around some of the disadvantages of the other reactor concepts, especially when there isn’t a kinetic model. When simulating streams with pseudo components, solids with a particle size distribution, or processes that produce modest amounts of several by-products, yield shift reactors are very helpful [12].

- Gibbs reactor

The Gibbs reactor, subject to the restriction of the feed mass balance, resolves the complete reaction and phase equilibrium of all species in the component list by minimizing the Gibbs free energy. A Gibbs reactor can be configured with limitations like a stipulated conversion of one species or a temperature approach to equilibrium [12].

When simulating a system that is known to reach equilibrium, particularly high-temperature processes involving simple molecules, the Gibbs reactor is quite helpful. It is less helpful when complex molecules are present since they typically have large Gibbs energies of creation, which leads to predictions of very low concentrations of these species unless the model has a very small number of components [12].

- Separator

The separator divides the components of the incoming stream into various exit streams according to the defined flows or split fractions. When the specifics of the separation are unclear, it is employed for component separation processes like distillation and absorption [13].

- Heater

Heaters can simply heat or cool a stream [13].

- Mixer

Mixers combine multiple streams (material, heat or work streams) into one stream [13].

3.1 Model validation

Before working on the main model, a simplified version of the model was constructed in order for it to be validated using literature data (Figure 9). The biomass used was rubber wood from Jayah et al. [14], in Table 5 we can see its ultimate and proximate analysis.

Table 5 - Ultimate and proximate analysis of rubber wood [14]

Ultimate analysis (wt. %, d.b.)		Proximate analysis (wt. %, d.b.)	
N	0.2	**Ash**	0.7
C	50.6	**Volatile matter**	80.1
H	6.5	**Fixed carbon**	19.2
O	42		
Ash	0.7		

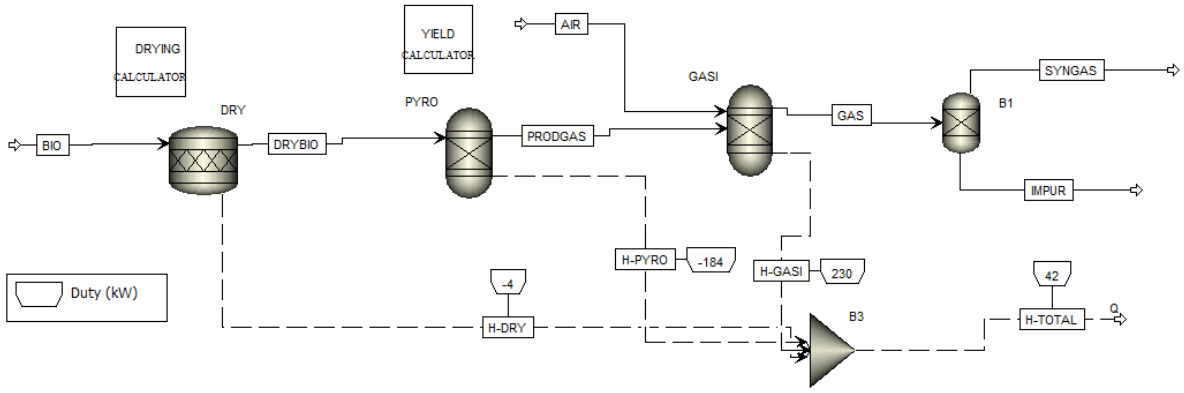


Figure 9 - Flowsheet of Aspen Plus model being validated

The biomass feed was introduced at 25 °C and 1 bar. The whole process will occur at 1 bar. The biomass then follows through a material stream to a unit operation called RStoic, used to simulate the drying of biomass at 100 °C. The biomass and water then proceed to the unit operation RYield, where devolatilization of the biomass happens at 600 °C. The gases of the previous process move to the unit operation RGibbs, that simulates the oxidation and reduction reactions, at 826.85 °C. In this block air also enters with a mass flow of 272.7 kg/h and at 25 °C. The resulting gases go through a separator block called Sep that separates carbon monoxide, carbon dioxide, nitrogen, hydrogen and methane to a single stream. The results in Figure 10 show the comparison with the literature, the experimental results of Jayah et al. [14] and the

numerical data of Jarungthammachote and Dutta [15] using a pure thermodynamic equilibrium model.

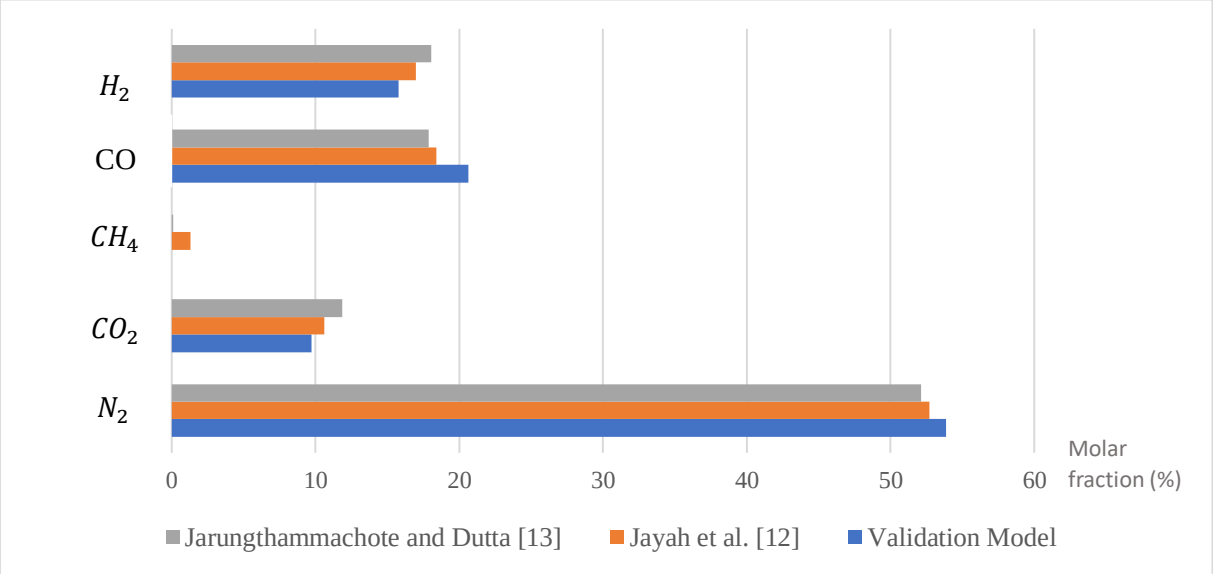


Figure 10 - Comparison between results of the validation model, experimental and numerical model, in molar fraction of the components

The relative error was used to give a better understanding of the results produced. It is given by the Equation 3.1 [16]:

$$Relative\ error\ (\%) = \frac{Obtained\ value - Literature\ value}{Literature\ value} * 100 \quad (3.1)$$

Analyzing the results and relative errors from Table 6, we can observe that the results obtained with the aspen plus model are acceptable. Although the methane value is not in agreement with the value obtained in the experimental result, we can accept this result because the equilibrium model neglects gasification aspects such as system kinetics and fluid dynamics [17].

Table 6 - Relative error of results

	Validation model	Jayah et al. [12]	Error (%)	Jarungthammachote and Dutta [13]	Error (%)
N_2	53.86	52.7	2.2	52.15	3.3
CO_2	9.72	10.6	-8.3	11.84	-17.9
CH_4	0	1.3	-100.0	0.11	-100.0
CO	20.64	18.4	12.2	17.86	15.6
H_2	15.78	17	-7.2	18.04	-12.5

3.2 Aspen Plus model

The first step in constructing the model was to establish the components, which include conventional and nonconventional components. Nonconventional components are the ones like biomass and ash that do not have databanks on Aspen Plus software; conventional components are carbon and hydrogen, for example. Databanks store the physical property parameters of components. For biomass and ash, the model HCOALGEN was used to determine the enthalpy, and for density, the model DCOALGEN was used. These models are for coal and coal-derived

materials, and they require ULTANAL, PROXANAL, and SULFANAL attribute requirements [13].

The property method used was the Redlich-Kwong-Soave cubic equation of state with Boston-Mathias alpha function (RKS-BM) for all thermodynamic properties [13].

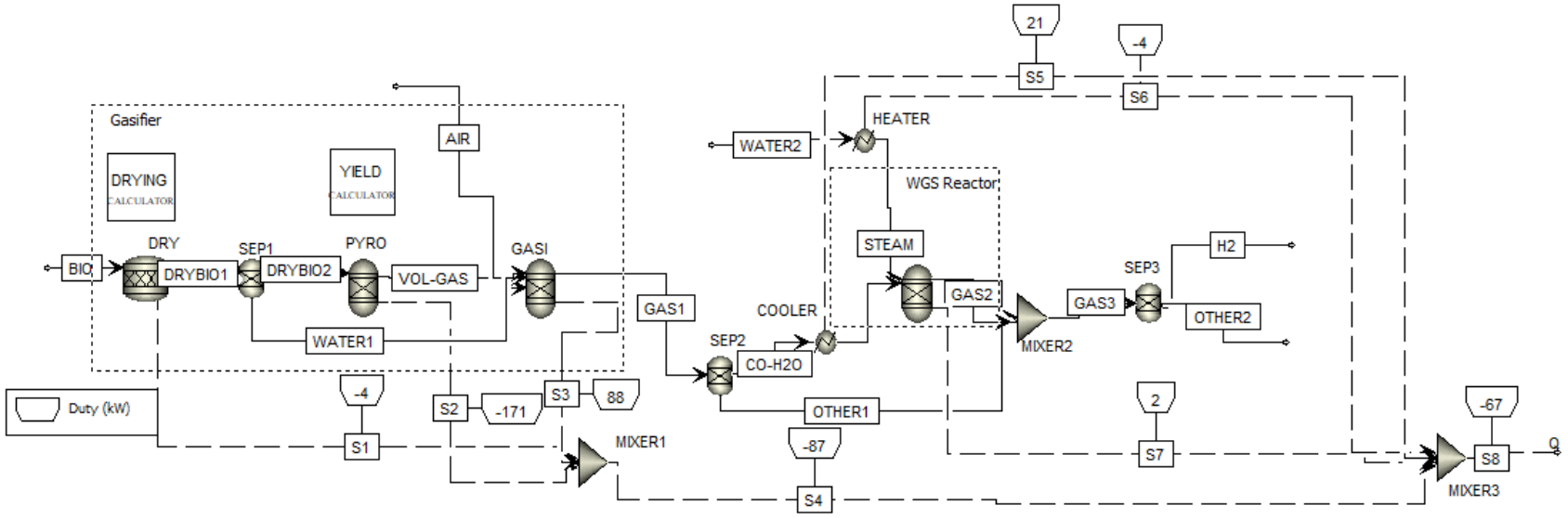
3.2.1 Gasifier

The gasifier is modeled in Aspen Plus consisting of three blocks: RSoitc (drying), RYield (pyrolysis), and RGibbs (oxidation and reduction). The flowsheet of the model can be seen in Figure 11. The first part of this model is fairly similar to the validation model. It consists of 100 kg/h of biomass at 25 °C entering the block operation, RStoic, operating at 100 °C and 1 bar. The pressure will not vary throughout the model. RStoic requires reaction input. We assume the biomass molecular weight is 1 g/mol, and since water's molecular weight is 18 g/mol, its coefficient is 1/18. In this block, a calculator called 'DRYING' was used to help control the removal of water from the biomass. To do this, a Fortran subroutine is employed that calculates the fraction of biomass that is converted into steam. After this, the steam and dried biomass travel through the stream 'DRYBIO1' to SEP1. In this separator, two streams are created; one with steam only ('WATER1') that goes to the block RGibbs, and another stream ('DRYBIO2') that guides the dried biomass to the RYield block.

The following step is the pyrolysis of the biomass. In the block RYield, the biomass is converted into gases (H, C, N, O) and ash at 600 °C. Also in this block, a Fortran subroutine is used by applying a calculator ('YIELD') to control the devolatilization of biomass. The yield composition was derived from the ultimate analysis of biomass. All these new components then travel to the RGibbs.

Arriving in RGibbs, in the stream 'VOL-GAS', the gases meet with air (21% O_2; 79% N_2) at 25 °C, the gasifying agent, and with water from the drying process, ready for oxidation and reduction to take place. This reactor utilizes the minimization of Gibbs free energy to model phase and chemical equilibrium and then calculates the composition of the produced gas. No further input is needed by the gasifier besides its temperature and pressure.

Figure 11 - Flowsheet of model



3.2.2 Water-gas shift reactor

The goal of this work is to intensify H_2 production; however, the previous gasifier was modeled to maximize CO production. The production of H_2 will happen in the WGS (water-gas shift) reactor through the water-gas shift reaction (Equation 2.26).

For this to happen, the produced gas in RGibbs ('GAS1') passes through a separator ('SEP2'), where CO and steam go through a single stream, 'CO-H2O', and the remaining components go through the stream 'OTHER1'. Before entering the WGS reactor, this CO and steam stream pass through a cooler to attain the same temperature as the WGS reactor (which is significantly lower than the gasifier temperature). In this reactor, steam is also introduced by being previously heated in a heater at 100 °C.

This WGS reactor is modeled using a RGibbs block, but in this case a restricted chemical equilibrium is applied where a reaction(s) or a temperature approach for the entire system can be specified (a reaction approach was used in this model).

The reaction introduced was the water-gas shift reaction, along with a temperature approach for this individual reaction. In this reactor, another parameter was specified – the identification of possible products. The products are CO, H_2O, CO_2 and H_2. If this was not done, other products like CH_4 would appear.

Finally, the produced gas in the WGS reactor mixes with the remaining gases from the gasifier in a mixer ('MIXER2'), and then passes through one last separator ('SEP3'). This block creates a stream with only H_2, the desired gas, and another stream with all the other components.

4 Results and Discussion

With the objective of maximizing H_2 production, several sensitivity analyses were performed.

The biomass used for the model in this study was forest residues [18]. The reason for choosing this biomass was Portugal's rich availability, as well as to give an optional outlet to the forest residues that aid in causing wildfires in Portugal almost every year. The biomass's ultimate and proximate analyses can be seen in Table 7. The moisture content is 11.3%.

Table 7 - Ultimate and proximate analysis of forest residues [18]

Ultimate analysis (%)		**Proximate analysis (%)**	
N	2.4	**Ash**	0.2
C	43	**Volatile matter**	79.8
H	5	**Fixed carbon**	20
O	49.6		

The first sensitivity analysis was made in the gasifier to optimize CO production. The manipulated variables were the mass flow of air (50-250 kg/h) and the gasifier temperature (600-1200 °C), to study their effect on the molar fraction of CO at the gasifier exit. The 3D plots of the results can be seen in Figure 12.

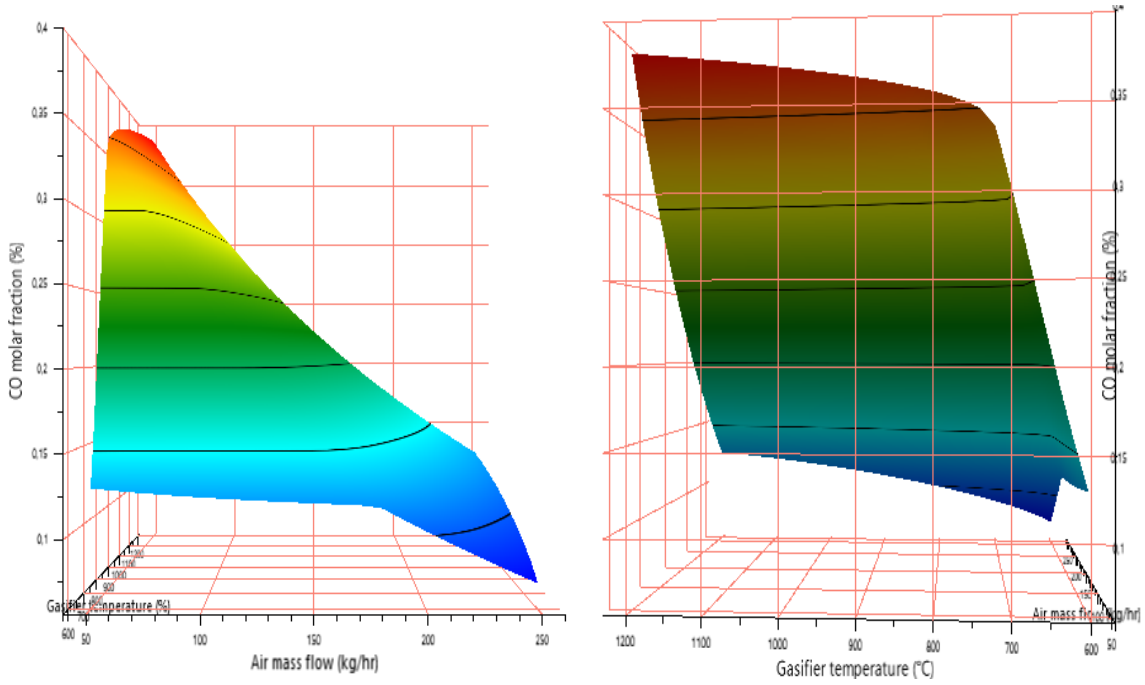


Figure 12 - Results of CO molar fraction varying with air mass flow and gasifier temperature

The less mass of air the gasifier has, the better the production of CO can occur [19]. This may happen because the oxygen is already present in the molecular structure of biomass and is released from the pyrolysis phase together with the structural carbon, forming carbon monoxide and carbon dioxide.

By increasing the presence of oxygen, combustion reactions will take place, consuming pyrolysis gases, including CO [19]. Therefore, increasing the oxygen content is negative for CO production.

A compromised air flow of 50 kg/h was established, which means the equivalence ratio (ER) is 0.129. The gasifier's temperature stalls at around 850 °C, and this was the gasifier's optimal temperature. This temperature is normal for gasification processes [3]. The CO molar fraction value in these conditions is 36.50%.

4.1 Intensification processes

One of the objectives of this work was to study the introduction of process intensifying methods, such as a water-gas shift reactor and CO_2 gasification via a recycle stream. These processes are detailed below.

4.1.1 WGS reactor

As explained in Section 3.2.2, a WGS reactor was introduced after the gasifier, so that CO and steam can react to produce H_2. The sensitivity analysis made in this reactor consisted of varying the steam mass flow (1-100 kg/h) and the reactor temperature (100-600 °C). The 3D plots of the results can be seen in Figure 13.

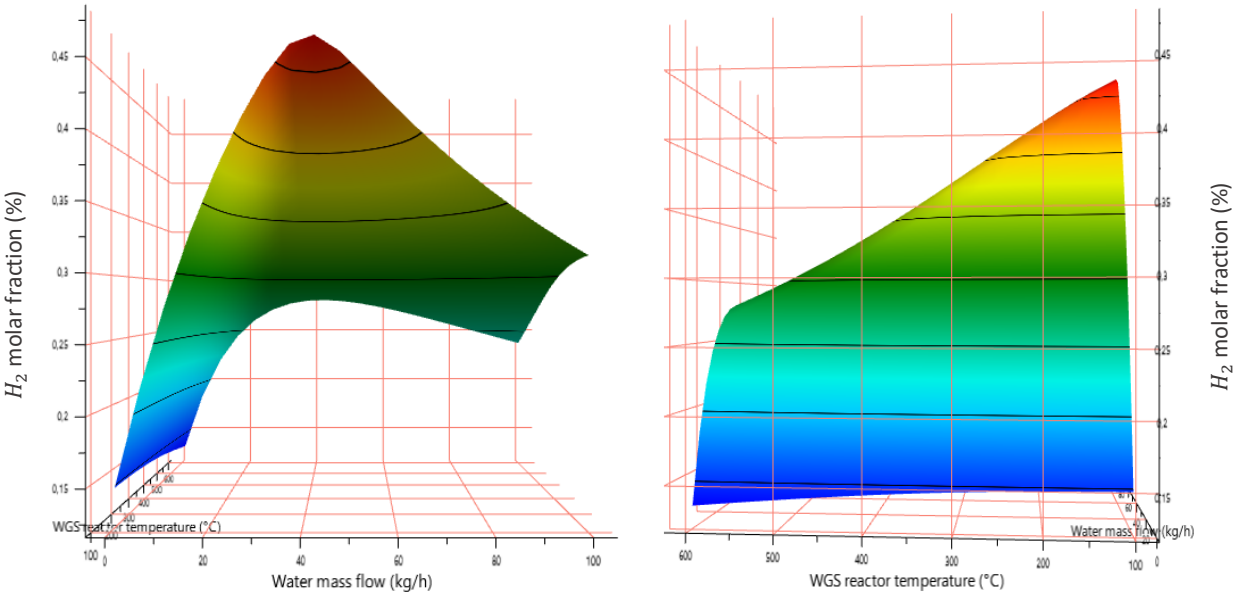


Figure 13 - Results of hydrogen molar fraction varying with steam mass flow and WGS reactor temperature

The ideal steam mass flow that obtains the maximum H_2 molar fraction is approximately 43 kg/h, which corresponds to a steam to biomass ratio (SBR) of 0.43.

The WGS reaction is exothermic (Eq. 2.23), so it is favored at low temperatures (Le Chatelier's principle), as verified in the results. In fact, the equilibrium constant (k) assumes values very close to 1 at low temperatures, which means the reactants (CO+H_2O) are totally converted into the reaction's products (CO_2+H_2) [20].

It does not make sense however to drop the temperature below 100 °C because steam is needed for the reaction to take place. In a real reactor, the WGS reaction happens at higher temperatures (200-400 °C), the reason being the WGS reaction is very slow, so catalyzers are used to accelerate the reaction, which can only operate at higher temperatures. The temperature chosen as optimal for the WGS reactor was 100 °C.

To conclude the analysis, the leftover gases from the gasifier were mixed with the resulting gases from the WGS reactor so a final stream of gas could be evaluated. A selection of gases molar fractions and mass flows can be seen in Table 8. The final stream temperature is around 408 °C.

Table 8 - Mole fraction and mass flow of selected gases from final stream

	Molar fraction (%)	**Mass flow (kg/h)**
H_2	50.64	10.08
CO	1.365	3.773
CO_2	30.78	133.7
CH_4	0.031	0.049
N_2	15.06	41.63

These are very good results for H_2, confirming the efficiency and intensification ability of the WGS reactor.

Heat duty

Aspen Plus software has an option for heat streams that can calculate the amount of heat duty required for a certain block (Figure 11). A general analysis was made through the process concluding that:

- The gasifier (drying + pyrolysis + oxidation and reduction) requires 87 kW of heat;
- The WGS reactor (cooler + heater + WGS reactor) produces 19 kW of heat.

The whole process requires 68 kW of heat to operate. In the gasifier the operation that requires most heat is in the pyrolysis block (111 kW), and in the WGS reactor the main producer of heat is the cooler (21 kW).

4.1.2 Recycle streams of CO_2

The other intensification process studied was CO_2 recycling streams, since there is a large amount of CO_2 at the end of the process. Pandey et al. [9] and Chan et al. [10] demonstrate that CO_2 gasification can be a viable option for CO production as well as an effective way to dispose of this greenhouse gas. To prove the efficiency of the CO_2 recycling stream, first a sensitivity analysis was made in the gasifier by introducing a CO_2 stream as an additional gasifying agent (Figure 14). The mass air flow of 50 kg/h was set as was the gasifier temperature of 850 °C. The mass flow of CO_2 varied between 1-60 kg/h. The results can be seen in Figure 14.

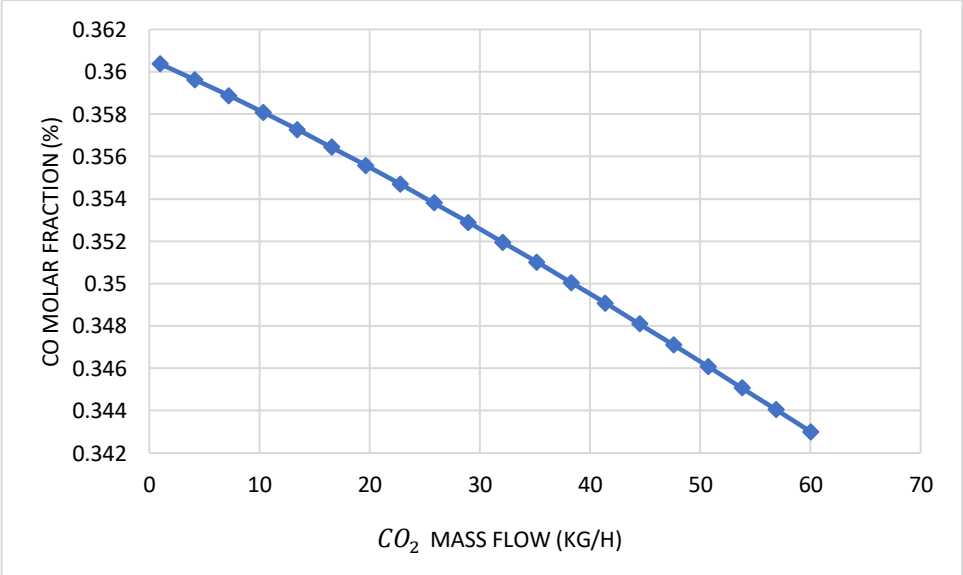
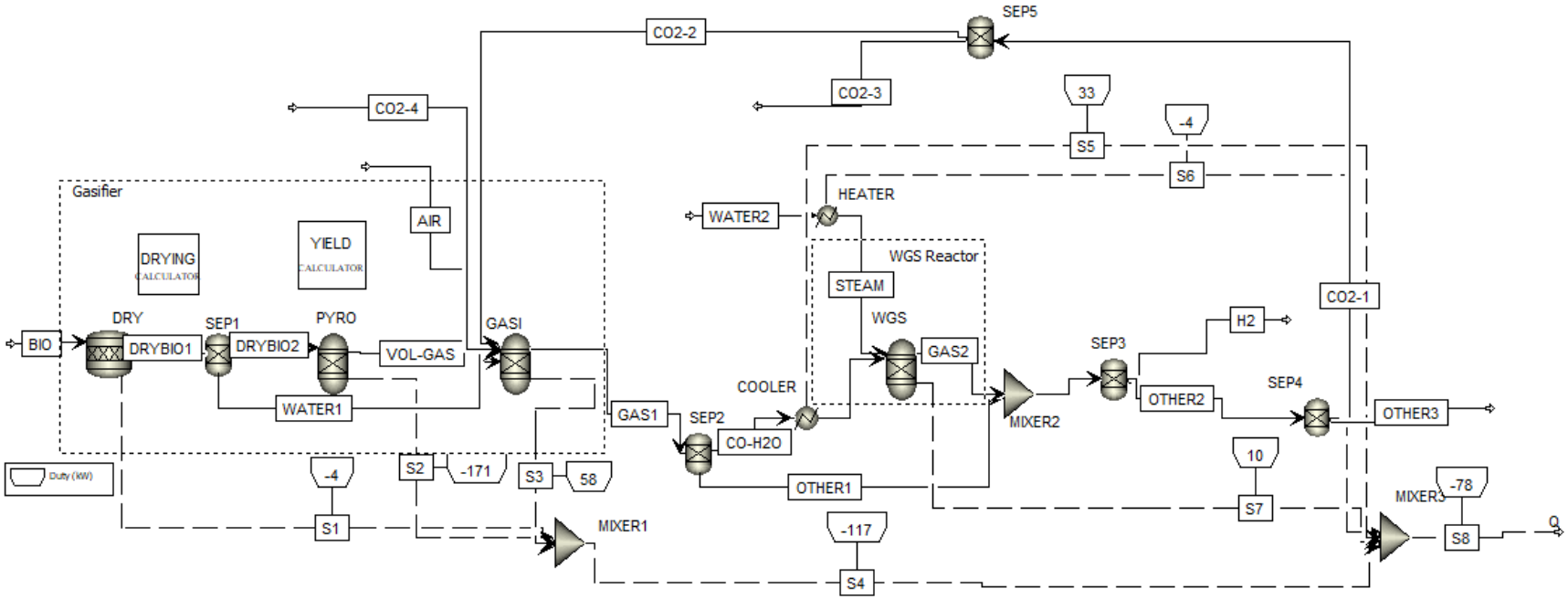


Figure 14 – Results of CO molar fraction varying with carbon dioxide mass flow

By analyzing the results, it can be seen that the introduction of CO_2 has no positive effect on CO production, contrary to what was expected. This may have happened because the conditions are different from the literature and/or, similar to the first sensitivity analysis, the introduction of another gasifying agent, in this case CO_2, does not improve CO production, as other reactions take place.

However, recycle streams were a focus of this work and recycle streams of CO_2 were successfully created. These recycling streams use the CO_2 produced in the process. After the stream 'OTHER2', an additional separator block is applied to create a stream with only CO_2 and another stream with the remaining components. Then, another separator block is put in place to control the flow of CO_2 into the gasifier via mass flow or split fraction (Figure 15).

Figure 15 - Flowsheet with carbon dioxide recycling stream



5 Conclusion and Future Works

5.1 Conclusion

This dissertation work aimed at studying the effects of two intensification processes for green hydrogen production by simulating a gasification model in Aspen Plus using forest residues as biomass.

The state of the art was first researched, followed by Aspen Plus software learning. Then a model was developed and validated successfully using literature data. With this done, the model was subject to the intensification processes and several parametric studies. The results were then discussed.

The results obtained with this Aspen Plus model designed to intensify green H_2 production from forest residues gasification are promising.

In the first parametric analysis, in the gasifier, the best CO production (36% molar fraction) occurs when the air mass flow is 50 kg/h and the gasifier temperature is around 850 °C.

The inclusion of a WGS reactor after the gasifier sees the hydrogen yield achieve a maximum of 50% molar fraction, for a WGS reactor temperature of 100 °C and a steam mass flow of 43 kg/hr.

The addition of CO_2 recycle streams did not, however, have a positive impact on any of the mass flows of CO_2 (1-60 kg/h) injected back into the gasifier.

This work proves the interest in studying and investigating optional alternatives and intensification processes in standard gasification models in order to obtain green hydrogen more effectively.

5.2 Future works

After this simulation model, constructed with Aspen Plus software, it would be interesting to further investigate several ideas. For example, to simulate the same model but using a more complex approach, through a kinetic model, instead of a thermodynamic equilibrium one. This approach allows us to comprehend the gasification process more fully.

The use of other types of available and common biomass, like agricultural residues and municipal solid wastes, could also be explored through this model. Other types of sensitivity analysis could also be performed, particularly, changing the air mass flow along with the CO_2 mass flow in a gasifier optimized for CO production. And another sensitivity analysis could study the effect of introducing CO_2 in a gasifier optimized for H_2 production instead of CO.

A study of the economic viability of this gasifier and WGS reactor combo could be performed. And finally, testing experimentally the simulated process in a real gasifier and WGS reactor.

References

[1] "The Paris Agreement." https://www.un.org/en/climatechange/paris-agreement.

[2] "WHAT IS THE ROADMAP FOR CARBON NEUTRALITY?". https://descarbonizar2050.apambiente.pt/en/roadmap/#:~:text=Portugal%20has%20commited%20internationally%20to,will%20be%20zero%20by%202050.

[3] Basu, Prabir. 2013. *Biomass gasification, pyrolysis, and torrefaction : practical design and theory*. Second edition. ed. still image. Amsterdam ; Boston: Academic Press is and imprint of Elsevier.

[4] Ferreira, S., E. Monteiro, P. Brito, and C. Vilarinho. 2017. "Biomass resources in Portugal: Current status and prospects." *Renewable & Sustainable Energy Reviews* 78: 1221-1235. https://doi.org/10.1016/j.rser.2017.03.140. <Go to ISI>://WOS:000407185900082.

[5] "Burnt area in European countries." https://www.eea.europa.eu/data-and-maps/daviz/burnt-forest-area-in-five-2#tab-chart_4.

[6] McKendry, P. 2002. "Energy production from biomass (part 1): overview of biomass." *Bioresource Technology* 83 (1): 37-46. https://doi.org/Pii S0960-8524(01)00118-3

[7] McKendry, P. 2002. "Energy production from biomass (Part 3): Gasification technologies." *Bioresour Technol* 83 (1): 55-63. https://doi.org/10.1016/s0960-8524(01)00120-1. https://www.ncbi.nlm.nih.gov/pubmed/12058831.

[8] Couto, N., A. Rouboa, V. Silva, E. Monteiro, and K. Bouziane. 2013. "Influence of the biomass gasification processes on the final composition of syngas." *Terragreen 13 International Conference 2013 - Advancements in Renewable Energy and Clean Environment* 36: 596-606. https://doi.org/10.1016/j.egypro.2013.07.068.

[9] Pandey, B., P. N. Sheth, and Y. K. Prajapati. 2022. "Air-CO2 and oxygen-enriched air-CO2 biomass gasification in an autothermal downdraft gasifier: Experimental studies." *Energy Conversion and Management* 270. https://doi.org/ARTN 116216 10.1016/j.enconman.2022.116216.

[10] Chan, Y. H., S. N. F. S. A. Rahman, H. M. Lahuri, and A. Khalid. 2021. "Recent progress on CO-rich syngas production via CO2 gasification of various wastes: A critical review on efficiency, challenges and outlook." *Environmental Pollution* 278. https://doi.org/ARTN 116843

[11] Zhu, X. C., S. Li, Y. X. Shi, and N. S. Cai. 2019. "Recent advances in elevated-temperature pressure swing adsorption for carbon capture and hydrogen production." *Progress in Energy and Combustion Science* 75. https://doi.org/ARTN 100784 10.1016/j.pecs.2019.100784.

[12] Towler, Gavin P., R. K. Sinnott, and Knovel. 2013. *Chemical engineering design : principles, practice, and economics of plant and process design*. 2nd ed. Oxford ; Waltham, Mass: Butterworth-Heinemann.

[13] Aspen Technology, Inc. February 2000. *Aspen Plus® Aspen Plus User Guide*. Vol. Version 10.2. Aspen Technology, Inc.

[14] Jayah, T. H., L. Aye, R. J. Fuller, and D. F. Stewart. 2003. "Computer simulation of a downdraft wood gasifier for tea drying." *Biomass & Bioenergy* 25 (4): 459-469. https://doi.org/10.1016/S0961-9534(03)00037-0.

[15] Jarungthammachote, S., and A. Dutta. 2007. "Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier." *Energy* 32 (9): 1660-1669. https://doi.org/10.1016/j.energy.2007.01.010.

[16] Couto, N., V. Silva, E. Monteiro, S. Teixeira, R. Chacartegui, K. Bouziane, P. S. D. Brito, and A. Rouboa. 2015. "Numerical and experimental analysis of municipal solid wastes gasification process." *Applied Thermal Engineering* 78: 185-195. https://doi.org/10.1016/j.applthermaleng.2014.12.036.

[17] Tavares, R., E. Monteiro, F. Tabet, and A. Rouboa. 2020. "Numerical investigation of optimum operating conditions for syngas and hydrogen production from biomass gasification using Aspen Plus." *Renewable Energy* 146: 1309-1314. https://doi.org/10.1016/j.renene.2019.07.051.

[18] Silva, V., E. Monteiro, N. Couto, P. Brito, and A. Rouboa. 2014. "Analysis of Syngas Quality from Portuguese Biomasses: An Experimental and Numerical Study." *Energy & Fuels* 28 (9): 5766-5777. https://doi.org/10.1021/ef500570t.

[19] Monteiro, E., T. M. Ismail, A. Ramos, M. Abd El-Salam, P. S. D. Brito, and A. Rouboa. 2017. "Assessment of the miscanthus gasification in a semi-industrial gasifier using a CFD model." *Applied Thermal Engineering* 123: 448-457. https://doi.org/10.1016/j.applthermaleng.2017.05.128.

[20] Pereira, Bruno Daniel Silva. 2008. "Uso de reactores de membrana na reacção de 'Water-Gas Shift' para aplicação em células de combustível." Departamento de Engenharia Química, Universidade do Porto.